SWINBURNE UNIVERSITY OF TECHNOLOGY PROJECT REPORT

THE SOLVENT-INDUCED SWELLING BEHAVIOUR OF VICTORIAN BROWN COALS

ΒY

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To my Mum and Dad

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DECLARATION

The work reported in this thesis is, unless otherwise stated, that of the candidate alone and has not been submitted previously, in whole or in part, in respect of any other academic award. The work has been carried out entirely during the period of candidature.

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CHAPTER 1.

BACKGROUND

1.1 INTRODUCTION

Many coal utilisation processes are limited by diffusional parameters such as the transport of reactants into, or reaction products out of, the coal structure⁽¹⁾. For example, the rate of coal liquefaction depends on the diffusion of hydrogen-donor solvent into the coal, and the rate of pyrolysis depends on the diffusion of volatile material from the pore structure. Generally, such penetration of crosslinked macromolecular solids by organic chemicals has been investigated using swelling techniques⁽²⁾.

The "swelling" of coal refers to an increase in the volume occupied by the coal as a result of imbibition of (generally) a liquid. Although the macromolecular network structure does not dissolve, the liquids in question are almost universally termed "solvents".

The extent and nature of coal-solvent interactions are important for a complete understanding of the macromolecular structure of brown coals, and pathways for their conversion to other products. Understanding the nature of hydrogen bonding, and its manipulation by coal pretreatment, may be an important key for understanding and improving coal utilisation processes. One way to investigate hydrogen bonding effects is to study the swelling of brown coal in various solvents. A coal-coal hydrogen bond will be replaced by a coal-solvent bond only if the new coal-solvent bond is thermodynamically favoured. If intramolecular hydrogen bonding in the coal contributes markedly to its structural integrity, then strong coalsolvent bonding should disrupt such a structure and result in coal swelling.

The solvent swelling of coals should be distinguished from solvent extraction even at this early stage, although the two processes are inextricably linked. Although there is no evidence to suggest the possibility of solvent dissolution of the macromolecular coal network at ordinary ambient temperatures⁽³⁾, the bonding between the network and smaller extractable pore species can be broken by solvents having the required properties. Extraction of these small molecules can only proceed if the macromolecular pore system will allow their escape. If the solvent in question is also capable of breaking some of the weaker (e.g. noncovalent) crosslink bonds in the network then the coal will swell and the passage of the extractable species will be made easier. Thus, solvents that yield large amounts of extractable material are most likely to be very good swelling solvents. Conversely, solvents that yield only small amounts of extract are unlikely to swell the coal to any great extent. A clear relationship between degree of swelling and extraction yield has been shown by lino et al.⁽⁴⁾. Swelling itself may be aided by an osmotic pressure build-up due to the high concentration of dissolved extractable species inside the pore system compared to the low concentration in the fresh solvent outside the pore system⁽⁵⁾. If the osmotic pressure builds to an extent where it can overcome intramolecular network forces then swelling will proceed.

With few exceptions^(6, 7), there has been very little fundamental work on the swelling of brown coals to appear in the literature, due to their extreme chemical heterogeneity^(8, 9, 10). Brown coals do, however, offer a unique opportunity to study the mechanisms contributing to the swelling of pore structure, by a separation of electrostatic and organic solvent effects. The polar functionality of the internal brown coal surface can be controlled by (i) variation of the oxygen containing functional groups, achieved through coal selection or prior thermal decomposition, and by (ii) variation of exchangeable metal cations, achieved again through coal selection or prior ion-exchange.

The aims of the present work are to examine and explain the interaction between brown coal and specific solvents, and to probe the bonding mechanisms in very low rank coals (in this case Victorian brown coal).

1.2 <u>COMPARISON OF VICTORIAN BROWN COALS WITH COALS OF</u> <u>HIGHER RANK</u>

Coalification is defined as the gradual increase in carbon content of fossil organic material from peat through lignite to coal and then anthracite. The reaction mechanism is, almost certainly, extremely complicated and it follows that the product coal will also have a complicated, chemically heterogeneous structure. Peat may have a typical composition of 55% C, 5.5% H, and 23% O. The first product of coalification is brown coal (lignite B in the ASTM classification) which has a typical composition of 68% C and 26% O⁽¹¹⁾. A lignite may contain 72% C and 21% O, whilst a high volatile bituminous coal may contain 85% C and 7% O. The composition of anthracite is about 95% C, 3% H and 2% O. It is important to emphasise that not all coals derive from the same precursor materials, so that lignite and anthracite do not necessarily represent different stages of the same coalification process⁽¹²⁾.

The hydrogen content remains fairly constant throughout coalification to the bituminous coals but decreases during the formation of anthracite. The reactions contributing to this loss include aromatisation of cycloalkanes or hydroaromatics, and condensation of isolated ring structures into polycyclic systems⁽¹³⁾. With a carbon content approaching 100% and the formation of large sheets of aromatic rings, increased coalification among the very high rank coals leads to structures that become increasingly like graphite⁽¹³⁾.

Coalification has been identified^(14, 15) to be almost solely due to temperatureinduced metamorphosis. Time alone has been dismissed⁽¹⁴⁾ as an influential factor due to the existence of brown coal deposits (Russian) that were laid down prior to many higher rank deposits. Time only has an effect on coalification when the temperatures are sufficiently high for chemical reactions to occur. With very low temperatures, little happens, even over a long period⁽¹⁵⁾. Whilst the pressure caused by overburden can be held responsible for the porosity and moisture content of the coal, it too has been dismissed as a significant factor in coalification⁽¹⁴⁾. In fact pressure has been identified as retarding coalification because the removal of gas is made more difficult⁽¹⁵⁾, i.e. it forces the reaction equilibrium in the direction of the reactants. Pressure thus promotes "physicostructural" coalification, whilst temperature promotes "chemical" coalification.

Products of the lowest rank have a strongly hydrophilic character and high moisture content. It is not until the bituminous coal stage has been reached that the moisture content becomes low and the coal substance becomes hydrophobic. This is most probably due to the gradual elimination of polar functional groups, especially hydroxyl (–OH) groups, which are markedly reduced in the early stages of coalification⁽¹⁵⁾. Besides hydroxyl groups, carboxyl (–COOH), methoxyl (–OCH₃), and carbonyl (>C=O) groups, as well as ring oxygen, are decomposed and so the carbon content gradually increases⁽¹⁵⁾. In the later stages of coalification, volatile matter, which consists predominantly of the non-aromatic fraction of coal, falls rapidly due to the removal of aliphatic and alicyclic groups and the increasing aromatisation of humic complexes⁽¹⁵⁾.

Porosity, internal surface area and moisture content decrease with increasing rank from brown coal to the medium volatile bituminous coals, where a minimum is reached, and then increase again as the rank increases to anthracite. The increase in these properties from low volatile bituminous coals to anthracite may be due to the progressive removal of the bitumens from the porous coal structure (caused by increasing temperatures)⁽¹⁶⁾.

The fact that the H/C ratio is fairly low, and becomes lower still during (particularly the final stages of) coalification⁽¹⁴⁾ suggests a high, and increasing, degree of aromaticity. Considering that graphite is the final link in the evolution of coal, it is logical to suggest that the aromaticity, and the degree of condensation of the aromatic rings, increase throughout the coalification process. Based on very early solid state C¹³-NMR work, however, Whitehurst⁽¹⁷⁾ disagrees that the mole ratio of H/C is a clear indication of aromatic carbon content. He prefers to regard coal as "...a highly crosslinked amorphous polymer, which consists of a number of stable aggregates connected by relatively weak crosslinks". Stach et al.⁽¹⁵⁾ describe the structure of low rank bituminous coals as comprising randomly dispersed stacks of two or three aromatic layers, with each layer being composed of 5 to 10 aromatic

rings. The stacks are linked together by non-aromatic groups that inhibit the development of close and constant inter-layer spacings. The wide spread of interlayer spacings thus characteristic of low rank coals decreases with increasing rank as the aliphatic groups and oxygen disappear⁽¹⁵⁾.

Victorian brown coals are relatively immature and have not been subjected to high temperatures and pressures for long enough to produce the strong crosslinked structures of a bituminous coal⁽¹⁸⁾. Given the relatively large amounts of oxygen functionalities in brown coals, van Bodegom⁽⁸⁾ proposed that ester bonds will form the predominant linkages between coal molecules; breakage of these ester bonds thus being paramount for the successful solubilisation of the coal⁽⁸⁾.

On the basis of X-ray structural analysis, Hirsch (referenced in van Krevelen⁽¹⁴⁾) developed a model that distinguished between three types of structures; an "open structure" characteristic of low rank coals, a "liquid structure" typical of bituminous coals, and an "anthracitic structure" (see Figure 1).

In the open structure, the lamellae are connected by crosslinks and are randomly orientated, thus constituting a highly porous system. In the liquid structure the lamellae show some orientation and the number of crosslinks has decreased considerably. Pores are practically absent. In the anthracitic structure, the crosslinks have disappeared completely and the degree of orientation of the lamellae has increased significantly.

The solvent swelling behaviour of low rank coals has not received the same attention in the scientific literature as that of the bituminous coals and anthracites due to their extreme chemical heterogeneity^(8, 9, 10), even though coals of lower rank generally respond to the action of solvents to a much greater degree than do those of higher rank⁽¹⁹⁾.



Figure 1. Structural Model of Coal According to Hirsch (referenced in van Krevelen⁽¹⁴⁾. [a = "Open Structure"; b = "Liquid Structure"; c = "Anthracitic Structure"]

1.3 TREATMENT OF COALS AS HIGHLY CROSSLINKED MACROMOLECULAR NETWORKS

Green et al.⁽²⁰⁾ present several compelling reasons as to why coals should be considered as comprising a macromolecular structure. First, coals are insoluble. Although a significant portion of coal is extractable in some solvents, the bulk of most coals will not dissolve, which is indicative of a crosslinked, or highly entangled, macromolecular structure. Secondly, coals swell in the presence of good solvents, and are capable of contracting to their original volume upon removal of the solvent. This behaviour is also characteristic of macromolecular networks. Finally, coals are viscoelastic, i.e. they deform under an applied stress and are able to almost completely recover on removal of the applied stress, indicating extensive crosslinking and/or entanglement.

The two major classifications of macromolecular solids are rubbers and plastics⁽²¹⁾. Rubbery materials are ones that, after being stressed, rapidly recover their original configuration when the stress is released. Plastics on the other hand retain a permanent deformation or orientation when stressed⁽²¹⁾. From the effect of pressure on the optical anisotropy of swollen coal, and from the rate and degree of recovery after release of that pressure, it was found possible by Brenner⁽²¹⁾ to determine whether coal is in a plastic or rubbery state, whether a rubbery state is crosslinked, and how mobile the macromolecular chain segments are. Omethylation (methylation of oxygen functionality) was used to assess the effects of hydrogen bonding on swelling. Bituminous coal (Illinois No. 6), swollen in pyridine, was found to be a crosslinked "rubber" and its macromolecular chain segments had substantial mobility. When the pyridine-extracted coal was dried it reverted to a "plastic". O-methylated coal was also found to be plastic. Since O-methylation has been shown to remove the hydrogen bonding capability of coals⁽²²⁾, this demonstrates that other interactions, in addition to hydrogen bonding, are important in immobilising the macromolecular structure⁽²¹⁾.

If the coal was placed under stress whilst being swollen in pyridine it was deformed. If the coal was dried whilst the pressure was maintained it permanently retained its (pressured) swollen configuration. If dried without any pressure it permanently retained its (unpressured) swollen configuration. The applied pressure caused plastic deformation to occur and the secondary interactions in the coal were sufficiently strong to maintain the new orientation⁽²¹⁾. Pressure alone could permanently change the configuration of the untreated coal, however immersion in pyridine caused complete relaxation.

Bodily et al.⁽²³⁾ used sequential swelling (from poor to good swelling solvents) to illustrate the crosslinked nature of a high volatile bituminous coal. When the coal was first swollen in cyclohexane (a poor swelling solvent), and then, after removal of the preceding solvent, in methanol, acetone, and tetrahydrofuran (THF), the swelling was the same as that of the coal swollen independently in each of the solvents. When the order of solvent treatment was reversed, a dramatic increase in the swelling induced by the weaker solvents was observed. It was concluded that polar crosslinks broken by the better solvents were not entirely reformed upon removal of the solvent, so that the weaker solvents were now able to swell the coal in the absence of some of the constraints previously present in the form of polar crosslinks (i.e. hydrogen bonding).

van Krevelen⁽¹⁴⁾ showed in experiments with model substances that when the number of bridges between monomer units was less than unity, the model substance was completely soluble in solvents such as benzene and pyridine. As soon as the number of linkages between monomer units increased slightly above unity (i.e. crosslinking), complete solubility was no longer possible. As crosslinking became more pronounced the substance became completely insoluble⁽¹⁴⁾. Since coal does not dissolve, even in solvents that are able to swell it to more than twice its original volume⁽²⁴⁾, it must be three-dimensionally crosslinked or consist of such large macromolecules that entanglements cannot be easily separated.

The alternative to a three-dimensional crosslinking of the macromolecules in coal is a situation in which the macromolecules are highly entangled. This model for coal might also be expected to result in the experimentally observed swelling of coals with extraction of only part of the structure. Evidence for the existence of permanent crosslinks between macromolecular chains, rather than purely physical entanglements, includes the fact that coals swollen in good solvents do not continue to swell indefinitely, or to dissolve; instead they reach a limiting size⁽²¹⁾. The fact that low-rank coals swell to a far greater extent than do higher-rank coals may be either a consequence of a lower initial crosslink density or of a greater propensity of the crosslink interactions in low-rank coal to be ruptured by good solvents.

Fuller⁽²⁵⁾ found from sorption studies on Illinois No. 6 coal that coal is a flexible structure with rigidity increasing with an increase in coalification (or rank). Wynne-Jones et al. (referenced in van Krevelen⁽¹⁴⁾) showed a relationship between the yield and molecular weight of solvent extractable species and the temperature of preheating, with a maximum corresponding to the "softening temperature" of the coal. It is not improbable that beyond this point the coal begins to carbonise and thus locks the structure into a less flexible arrangement.

There is a great increase in flexibility when coal is swollen in good solvents and thus the effective crosslink density of the swollen coal is greatly reduced compared to the dry coal. In the dry state, secondary interactions must be creating effective crosslinks and/or the dry coal is in a glassy state⁽²¹⁾.

Larsen and Kovac⁽²⁶⁾, in summarising the literature and using strain-time curves which showed a limit to coal deformation under constant stress (as well as \geq 99% recovery after removal of the stress), argued that bituminous coals must be considered as covalently crosslinked macromolecules. Weak associative forces such as hydrogen bonding and van der Waals forces were cast as making only a small contribution to the macromolecular association. Green et al.⁽²⁰⁾ consider the dimensional changes of a coal during swelling to be due to reorientation of macromolecular chains, with the driving force coming from the free energy of mixing of the solvent and the coal network.

1.3.1 Coals as Polymers

van Krevelen⁽¹⁴⁾ has been credited with being the first to suggest that coal has a polymeric character⁽²⁷⁾. A polymer is a large molecule formed by the repetition of small, simple chemical units⁽²⁸⁾. In some cases the repetition is linear, whilst in other cases the chains are branched or interconnected to form three-dimensional networks.

Polymers can be formed via a condensation or "step" reaction in which two polyfunctional molecules come together to form a larger polyfunctional molecule with the elimination of a small molecule such as water. Addition or "chain" reactions involve reactive free-radicals that attack double-bonds to form further free-radicals. The reaction eventually comes to a halt when two free-radicals combine to annihilate each other. With some exceptions, polymers formed in chain reactions contain only carbon atoms in the main chain (homochain polymers), whereas polymers made in step reactions may have other atoms, originating in the monomer functional groups, as part of the chain (heterochain polymers). In both chain and step polymerisation, the length of the chain is determined purely by random events. In either case the polymeric product contains molecules having many different chain lengths⁽²⁸⁾.

Crosslinked or network structures are formed by side-reactions. Crosslinked polymers are often stable to heat and cannot be made to flow or melt. They are termed *thermosetting*. In contrast, most linear polymers can be made to soften and take up new shapes by the application of heat and pressure. They are said to be *thermoplastic*⁽²⁸⁾. There are many physical and chemical indications that coal is a polymer. The materials from which coal is formed are all polymers (e.g. lignin, cellulose). Coal extract solutions do not crystallise on evaporation of the solvent but instead form colloidal gels and these extracts have been shown by spectrometric techniques to be extremely similar in structure to the original coal. Ouchi and Honda⁽²⁹⁾ have successfully used phenol formaldehyde resins as coal models.

The 3-dimensional network structure of brown coal draws comparison with the structures of crosslinked polymers. Of course, the most readily apparent objection to such a comparison would be the abject failure of researchers to elucidate a structure for brown coal - let alone a repeating unit. Nevertheless, the similarities are striking.

The primary chemical bonds along a polymer chain are entirely satisfied. The only forces between polymer molecules are secondary bond forces of attraction, which are weak relative to primary bond forces. The high molecular weight of polymers allows these forces to build up enough to impart excellent strength, dimensional stability, and other mechanical properties to the substances⁽²⁸⁾. The geometric arrangement of the atoms in a polymer can be either configurations (fixed by the bonding in the molecule) or *conformations* (dependent on the degree of mobility allowed). Plastics and rubbers owe their physical properties to the degree of molecular mobility afforded by their bonding arrangements. As the temperature of a plastic or rubber is lowered, a point known as the glasstransition temperature is reached where the polymer properties change significantly due to virtual elimination of molecular motion. Thermal energy is required for segments of the polymer chain to move relative to other segments, however if the temperature is low enough the required energy is unavailable. Below their glass-transition temperatures, polymers become hard and brittle⁽²⁸⁾.

Coals also show a dramatic change in behaviour as a function of temperature⁽²⁰⁾. Bituminous coals are known to soften and swell (with the evolution of volatile matter) as the temperature is increased, and a range of properties have been shown to undergo rapid change within a narrow temperature range consistent with the changes observed in polymers at their glass-transition temperatures⁽²⁰⁾. Unfortunately, at this stage, the presence or absence of a true glass-transition temperature in coals is still in contention due to the lack of agreement on a structure for coal and, as a result, the many different ways in which the data may be interpreted⁽²⁰⁾.

Coal precursors, humic acids, are soluble in aqueous base. They do not normally have a gel structure (at high pH), or they would not dissolve⁽²⁰⁾. Humic acids are then polymerised to yield the three-dimensionally crosslinked macromolecular gel that is coal (see next Section). Green et al.⁽²⁰⁾ present compelling evidence to show that the coalification process can be modelled on condensation polymerisation.

The following observations have been made on the diffusion of molecules into polymer structures⁽²⁴⁾:

- The diffusion coefficient decreases as molecular size increases.
 Linear molecules diffuse more rapidly than branched molecules of the same size.
- 2. Diffusion increases with greater flexibility of the polymer chains. An increase in the cohesive energy of the polymer reduces diffusion.
- 3. Increasing the degree of crosslinking decreases the diffusion coefficient.

1.3.2 Coals as Colloidal Gels

It must be made clear from the outset of this Section that the term *colloid* is purely a distinction based on size. Colloids have at least one of their dimensions within the range of ~1 nm to 1 μ m, i.e. they are either large molecules or small particles⁽³⁰⁾. The factors that contribute most to the overall nature of a colloid system are⁽³⁰⁾ particle size, particle shape and flexibility, surface (including electrical) properties, particle-particle interactions, and particle-solvent interactions. The same may be said of coals, and the purpose of this report is to concentrate on particle-solvent interactions, with reference to the other factors listed above.

The particles in a colloidal dispersion are sufficiently large for definite surfaces of separation to exist between the particles and the medium in which they are dispersed⁽³⁰⁾. From this definition, Victorian brown coals can be thought of as colloidal dispersions in which the dispersion medium is pore water. Since brown coals are chemically heterogeneous, and the individual coal molecules are likely to vary over a wide range, they would be termed *polydispersed*. Some of the water in brown coal is tightly bound to form a monolayer coverage⁽³¹⁾ whilst the remainder can be considered as being physically trapped (albeit quite weakly) in the three-dimensional macromolecular pore network. Since brown coals are in the early phases of the geochemical stage of coalification, and hence retain many of the properties of the peat from which they are formed, the physical structure, and physico-chemical and mechanical properties of bed-moist brown coals are intermediate between those of a suspension and a solid. They have mechanically trapped and immobilised the water to such an extent that they have a solid appearance and can thus be termed *gels*⁽³²⁾. Coals have a sol/gel ratio (soluble extract/insoluble network) that varies with rank⁽³³⁾.

The fact that distinguishes brown coals as gels rather than moist solids is that the addition of even a small amount of water to bed-moist brown coals results in a pumpable slurry (i.e. at \approx 70% moisture)⁽³⁴⁾. The thixotropic behaviour of brown coal slurries⁽³²⁾ is further evidence of the gel-like structure of brown coal.

Victorian brown coals typically contain about 67% moisture and can be considered as dilute suspensions of solid material ($\approx 30\% \text{ d.b.}$)⁽³²⁾. For higher rank coals the water is simply filling rigid pores, but in brown coal the water is an integral part of the gel structure⁽³²⁾. The removal of the bedmoisture from brown coals results in irreversible loss of the gel structure, i.e. the formation of a xerogel⁽³²⁾. Coal, being a solid colloid, has a porous physical structure which is responsible for many of its properties, i.e. its capacity to adsorb gases and vapours and to swell in vapours and liquids. The coalification process can also be considered as gelification between "hydrogels" (brown coals) and "bitumogels" (bituminous coals)⁽¹⁵⁾.

1.3.3 Coals as Polyelectrolytes

Polymers with ionisable groups along the chain are termed polyelectrolytes, and normally exhibit properties in solution that are quite different from those of non-ionisable structures. When they are soluble in non-ionising solvents, polyelectrolytes behave in completely normal fashion, but in aqueous solution they are ionised. Whenever an uncharged polymer chain is converted, by chemical modification, to a chain carrying a large number of ionised groups the mutual repulsion of fixed charges can lead to chain expansions which are far beyond the range attainable by the transfer of uncharged polymers from bad to good solvents⁽³⁵⁾. With flexible chain polyelectrolytes, the fixed charges can be separated from each other by chain expansion when the system is diluted by the addition of solvent. However, a limit is placed on the attainable separation of the fixed charges by their attachment to the macromolecular

backbone and its elasticity. Chain expansion leads to increased viscosity upon dilution, which is typical of polyelectrolytes⁽³⁶⁾. This behaviour has also been noted for humic acids^{(32).}

The addition of low molecular weight electrolyte to the aqueous solution increases the ionic strength of the solution outside the polymer coil relative to that inside, and also reduces the thickness of the layer of "bound" counter-ions around the chain. Both effects cause the chain to contract⁽²⁸⁾.

When ionised functional groups are attached to macromolecules the forces between charges are very much larger than the dispersion forces or the dipole-dipole interactions between uncharged groups⁽³⁵⁾.

1.4 POLYMER SWELLING THEORY

Dissolution of polymers is a slow process that occurs in two stages⁽²⁸⁾. First, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. At equilibrium, in an excess of solvent, the polymer network will contain a specific volume of solvent which reflects a thermodynamic balance between the reduction in free energy due to mixing and the increase in elastic free energy of the network due to swelling⁽³⁷⁾. If the polymer-polymer intermolecular forces (crosslinking, hydrogen bonding) are strong enough, the polymer will do no more than swell. However if these forces can be overcome by the introduction of strong polymer-solvent interactions, then dissolution can take place.

In the simplest type of mixing, the molecules of component A and B have roughly the same size and shape, and the forces between like and unlike molecules are the same. They may then form an ideal solution (i.e. one in which Raoult's Law is obeyed). Raoult's Law states that the partial pressure of each component in the mixture is proportional to its mole fraction:

$$p_A = p_A^o \left(\frac{N_A}{N_A + N_B} \right) = p_A^o n_A$$

The free energy of dilution of a solution can be given by:

$$\Delta G_A = kT \ln \left(\frac{p_A}{p_A^o}\right) = kT \ln n_A$$

where ΔG_A is the free energy of dilution resulting from the transfer of one molecule of pure liquid A, with vapour pressure p_A° , to a large amount of solution with vapour pressure p_A .

The total free energy of mixing is given by:

$$\Delta G = N_A \Delta G_A + N_B \Delta G_B$$

= $N_A kT \ln n_A + N_B kT \ln n_B$
= $kT (N_A \ln n_A + N_B \ln n_B)$

The conditions for ideal mixing imply that the heat of mixing $\Delta H = 0$:

$$\Delta G = \Delta H - T\Delta S$$

 $kT (N_A \ln n_A + N_B \ln n_B) = 0 - T\Delta S$
 $\Delta S = -k (N_A \ln n_A + N_B \ln n_B)$

Since the mole fraction of both components in a two-component system must be less than 1, both $\ln n_A$ and $\ln n_B$ will always be negative, making ΔS positive for all compositions. ΔG must then be negative for all compositions and hence spontaneous mixing occurs.

Polymer swelling theory allows only for simple van der Waals or London dispersion forces between polymer and solvent, and is inadequate when applied to systems in which there are strong specific interactions such as hydrogen-bonding because of the deviation from completely random mixing that these interactions cause⁽³⁸⁾.

Obviously the size and shape of "dissolved" coal molecules differ from those of solvent molecules which means that the heat of mixing cannot be zero⁽³⁹⁾, i.e. mixing is not ideal. Polymer solutions invariably exhibit large deviations from Raoult's law except at extreme dilutions. At concentrations above a few percent, deviations from ideality are so great that the ideal law is of little value as a predictive tool. Even if mole fraction is replaced with volume fraction (in view of the different sizes of the polymer and solvent molecules), there is not a good correlation with experimental results⁽²⁸⁾.

Deviations from ideality in polymer solutions arise largely from small entropies of mixing. A quantitative theory of the change in conformational entropy produced by the mixing of flexible chain polymers with a solvent of low molecular weight was formulated by $Flory^{(40)}$ and $Huggins^{(41-43)}$, who evaluated the number of different ways in which N₁ solvent molecules with a molar volume V₁ and N₂ polymer chains with a molar volume V₂ could be placed on a 2-dimensional lattice so that each lattice site was occupied by either a solvent molecule or one of the segments of the polymer chain⁽³⁵⁾. The equation for entropy of mixing for polymer solutions, so derived, is analogous to that derived for ideal mixing:

$$\Delta S = -k (N_1 \ln \upsilon_1 + N_2 \ln \upsilon_2)$$

where 1 and 2 denote solvent and polymer and υ_1 and υ_2 are volume fractions:

$$v_1 = \frac{N_1}{N_1 + x N_2}$$
 $v_2 = \frac{x N_2}{N_1 + x N_2}$

The heat of mixing of polymer solutions is analogous to that of ordinary solutions:

$$\Delta H = \chi_1 kT N_1 v_2$$

where χ_1 (the Flory parameter) is a pair-wise parameter quantifying the interaction between the swelling solvent and the coal⁽⁴⁴⁾. The Flory parameter is positive and, thus, unfavourable to mixing.

$$\Delta G = \Delta H - T \Delta S$$

= $\chi_1 kT N_1 \upsilon_2 - T (-k (N_1 \ln \upsilon_1 + N_2 \ln \upsilon_2))$
= $\chi_1 kT N_1 \upsilon_2 + kT N_1 \ln \upsilon_1 + kT N_2 \ln \upsilon_2$
= $kT (N_1 \ln \upsilon_1 + N_2 \ln \upsilon_2 + \chi_1 N_1 \upsilon_2)$
= Flory - Huggins equation

The Flory-Huggins theory has some serious shortcomings. It is based upon, and conserves the important features of, the theories of "regular" solutions of small molecules. Only the term for entropy of mixing has been modified to fit the polymer case. The most important assumption retained is that there is no volume change on mixing.

These difficulties have been overcome in new theories that recognise the dissimilarity in the free volumes of the polymer (which is subject to a significant excluded volume) and the solvent as a result of their great difference in size. The total volume change on mixing a solvent and a polymer is usually negative (due to the attractive forces between the polymer and solvent effectively "condensing" the solvent), and thus is accompanied by a negative ΔS (i.e. ordering of the solvent molecules) and a negative (exothermic) heat, ΔH . The Flory interaction parameter has been modified to account for these negative (conducive to mixing) free volume effects.

Because of the many similarities of coal and polymers, referred to in Section 1.3.1, polymer-swelling theory has often been applied to coal, with varying success^(39, 45, 46). Much of the criticism of the application of polymer theory to coal swelling comes from the attempts to arrive at realistic molecular weights between

crosslinks, and other such quantitative parameters. It should be stated at this point that the purpose of the current study is to yield <u>qualitative</u> information on coal structure from its behaviour when in contact with solvents of varying physical and chemical properties. Polymer theory has been outstanding in its successful application to coals in terms of this qualitative information and has met with significant disapproval only when pushed too far.

If a polymer network is brought into contact with a good solvent, the solvent will be absorbed by the network until the elastic forces of the network exactly balance the swelling pressure. Using the statistical theory of polymer network elasticity and the Flory-Huggins theory of polymer solutions, the following equation can be derived for $M_c^{(26)}$, the average molecular weight per crosslink:

$$M_{c} = \frac{\frac{l}{3}\rho_{2}V_{1}\upsilon_{2}}{-\ln(l-\upsilon_{2})-\upsilon_{2}-\chi \upsilon_{2}^{2}}$$

where ρ_2 is the original density of the polymer, V₁ the molar volume of the solvent, υ_2 the volume fraction of the polymer at equilibrium, and χ the Flory interaction parameter related to the heat of transfer of the solvent from pure solvent to the pure polymer in units of kT. χ must be determined experimentally and M_c is then easy to obtain from equilibrium swelling data.

Sanada and Honda⁽⁴⁷⁾ studied the swelling of pyridine extracted Japanese coals using pyridine as the swelling agent. As Larsen and Kovac point $out^{(26)}$, pyridine is a poor choice of swelling agent due to its incorporation into the $coal^{(48)}$. The Flory-Huggins theory of polymer solutions is dependent on their being no specific reaction between the solvent and the polymer network. Notwithstanding this, Sanada and Honda were still able to arrive at M_c values of reasonable magnitude and which followed the expected trends with rank.

The presence or absence of solubility as solvent properties are varied can yield much information on the polymer structure. The literature is full of examples of how the same can be said of coals.

1.5 THE SOLUBILITY PARAMETER CONCEPT

Solubility occurs when the free energy of mixing of the polymer and solvent (Δ G) is negative. Since the dissolution of a polymer is always accompanied by a large increase in entropy⁽⁴⁹⁾, the relative magnitude and sign of the heat of mixing, Δ H, is the deciding factor in determining the sign of the free energy change.

$$\Delta H = V_m \left[\left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \upsilon_1 \upsilon_2$$
$$\frac{\Delta H}{V_m \upsilon_1 \upsilon_2} = \left[\left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2$$

Where V_m = total volume of the mixture

 ΔE = energy of vapourisation of component 1 or 2

V = molar volume of component 1 or 2

 υ = volume fraction of component 1 or 2 in the mixture.

The expression " Δ E/V" is the energy of vapourisation per cm³ and is known as the cohesive energy density. The cohesive energy of a substance is the energy required to remove a molecule from the liquid or solid to a position far from its neighbours⁽²⁸⁾. The cohesive energy density (or cohesive energy per unit volume) is thus a measure of the intermolecular forces within the liquid or solid structure, and is an excellent measure of a solvent's interaction with itself⁽⁴⁴⁾. The tendency of a molecule to volatilise from its liquid is a function of its total translational energy and therefore of its temperature. The boiling point depends on the relation of the translational energy to the cohesive energy. At higher molecular weights the total cohesive energy per molecule becomes greater than the primary bond energy and the molecules decompose before they volatilise. This point is reached at molecular weights far below those of typical polymers and of coals.

A molecule containing strongly polar groups exerts correspondingly strong attractive forces on its neighbours, thus giving it a higher cohesive energy density. Hence coal, like many polymers, decomposes on heating. The equation above shows that the heat of mixing is proportional to the difference between the square roots of the cohesive energy densities of the two components.

$$\delta = \left(\frac{\Delta E}{V}\right)^{\frac{1}{2}}$$

so that

$$\Delta H = V_m \left(\delta_1 - \delta_2\right)^2 \upsilon_1 \upsilon_2$$

Solution of the polymer is assured by the large positive entropy factor if $(\delta_1 - \delta_2)^2 = 0^{(49)}$. In other words δ_1 must be as close as possible to δ_2 if mixing of polymer and solvent is to proceed. δ has therefore been dubbed the "solubility parameter". According to the solubility parameter concept, a non-crystalline polymer will dissolve in a solvent of similar δ without the necessity of solvation, chemical similarity, association, or specific intermolecular forces. The high entropy change for the polymer is sufficient reason for solution to occur⁽⁴⁹⁾.

The value of the solubility parameter approach is that δ can be calculated for both polymer and solvent. Generally, solubility can be expected if δ_1 - δ_2 is less than 1.7-2.0 (cal/cm³)^{1/2} (3.5-4.1 MPa^{1/2}), but not if significantly larger⁽²⁸⁾. The assumptions made are⁽⁵⁰⁾:

- (i) forces of attraction are due primarily to dispersion forces,
- (ii) molar volumes of the polymer (coal) and of the solvent are not significantly different,
- (iii) no volume change occurs on mixing, and
- (iv) mixing is random.

The solubility parameter of a polymer cannot be determined directly because most polymers cannot be vapourised without decomposing⁽⁴⁹⁾. The same may be said of coal. One way of determining the solubility parameter of crosslinked polymers (or coals) is to immerse the samples in a series of solvents of varying solubility parameter. Being crosslinked, the material will not dissolve but will swell to varying degrees. The amount of swelling will be greatest in the solvent that has the same δ as the polymer. By inference, the soluble uncrosslinked material will also have the same value⁽⁴⁹⁾.

With polymers carrying highly polar, strongly interacting groups (i.e. low rank coal oxygen functional groups), the problem of interpreting solubility behaviour becomes even more difficult⁽³⁵⁾. Schuerch⁽⁵³⁾ studied the solubility of lignin and found that solvents with the same solubility parameter differed widely in their solvent power. These differences were correlated with the hydrogen bonding ability of the solvents. Crowley et al.⁽⁵⁶⁾ found that even a combination of solubility parameter and hydrogen bonding power was insufficient to predict whether or not cellulose nitrate would be soluble in a given solvent. However if dipole moment was added as a third parameter the predictions were improved.

The forces that hold a liquid together are included in the heat of vapourisation regardless of their nature. There are four recognised modes of interaction between molecules. It is these interactions that collectively give rise to the cohesive energy, which is overcome during the evaporation of a liquid to a gas. The first of these modes is the dispersion forces, which are common to all molecules and represent the only mode available to simple saturated hydrocarbons. They arise from the fluctuation of atomic dipoles caused by the presence of positive nuclei with electrons in orbit around them. The second and third modes of interaction (polar forces) arise from permanent dipole-permanent dipole and permanent dipole-induced dipole interactions respectively, and are a characteristic of polar molecules. The fourth mode of interaction is that in which hydrogen bonding is involved⁽⁵¹⁾. If it is assumed that the cohesive energy, ΔE , is comprised of contributions from non-polar (dispersive) interactions (ΔE_d), permanent dipole-permanent dipole and permanent dipole and permanent dipole and permanent dipole (polar)

interactions (ΔE_p), and hydrogen bonding interactions (ΔE_h)⁽⁵²⁾, the following equation may be derived:

$$\Delta E = \Delta E_d + \Delta E_p + \Delta E_h$$

Dividing by the molar volume of a solvent, V, gives:

$$\frac{\Delta E}{V} = \frac{\Delta E_d}{V} + \frac{\Delta E_p}{V} + \frac{\Delta E_h}{V}$$
$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

 δ_d , δ_p , and δ_h are termed "three-dimensional" solubility parameters⁽⁴⁹⁾. δ_p and δ_h may be grouped as "associative" contributions to the solvent solubility parameter (δ_a) according to the following equation⁽⁵¹⁾:

$$\delta_a^2 = \delta_p^2 + \delta_h^2$$

van Bodegom et al.⁽⁸⁾ argue that the solubility of brown coal may depend to a large extent on its polarity, and that of the solvent, being similar, and state that "roughly speaking, the lower the solubility parameter, the less polar the solvent will be". In examining the rank dependence of swelling of coals, Hombach⁽³⁹⁾ found a minimum in coal solubility parameter at around 90% C (daf) and attributed this to the loss of polar functionalities with increasing rank (decrease in solubility parameter) followed by an increase in solubility parameter due to increased aromaticity and crosslinking. Hombach found a good correlation for swelling of previously unextracted coals with solubility parameter of the (mixed) solvents used⁽³⁹⁾. Extensive tabulations of solvent solubility parameters have been published^(49, 52), however much of the data for particular solvents is inconsistent from author to author. This makes it difficult to make firm conclusions about the solubility parameter of the material under examination since the analysis depends on the values used for the solvents employed in swelling experiments.

Figure 2 shows the swelling of linseed-oil film in solvents arranged according to their solubility parameter⁽⁵⁵⁾. A bell-shaped curve is formed, with the range of peak swelling having a span of less than 2 MPa^{$\frac{1}{2}$}. Thus, any solvent with a solubility parameter of 19 to 20 MPa^{$\frac{1}{2}$} could be expected to strongly swell a linseed-oil film. However, close inspection of Figure 2 shows that both methyl ethyl ketone (MEK) and acetone, despite having solubility parameters in the correct range, fail to swell the linseed-oil film to the expected extent. These inconsistencies can be attributed to the differences in hydrogen bonding power of the ketones compared to the chlorinated solvents⁽⁵⁵⁾. The intermolecular forces in linseed-oil are primarily dispersion forces, with practically no hydrogen bonding involved. These forces are almost identical to those in the chloroform, ethylene dichloride, and trichloroethylene, thus encouraging interpenetration and swelling of the linseed-oil film. MEK and acetone, however, are more polar molecules, with moderate hydrogen bonding capability. Despite having total solubility parameters of a similar magnitude to the chlorinated solvents, the difference in component forces, primarily hydrogen bonding, lead to the observed differences in swelling behaviour. MEK and acetone molecules have a greater attraction to each other than to the linseed-oil⁽⁵⁵⁾.

The classical bell-shaped curve relationship has also found between coal swelling and solvent solubility parameter^(23, 46, 50, 56), as shown in Figure 3. Indeed, Reucroft and Patel⁽⁴⁶⁾ found the same relationship (Figure 4) between coal (Kentucky No. 12) internal surface area and adsorbate solubility parameter. These authors concluded that surface area measurements using adsorbates with solubility parameters close to that of coals (e.g. CO₂) are in error due to the sorbate-coal interactions (swelling). A maximum in adsorption/desorption hysteresis was also found for sorbates with solubility parameter closest to the coal⁽⁴⁶⁾.



Figure 2. Swelling of Linseed-Oil Film⁽⁵⁵⁾


Figure 3. Variation of Volumetric Swelling for a Kentucky No. 12 coal with Solvent Solubility Parameter (after Reucroft and Patel⁽⁴⁶⁾)



Figure 4. Variation of Measured Internal Surface Area for a Kentucky No. 12 coal with Adsorbate Solubility Parameter (after Reucroft and Patel⁽⁴⁶⁾)

The conclusions of Reucroft and Patel were criticised by Stacy and Jones⁽⁶⁾ as being experimentally unverified. Swelling was measured at relative pressures of ≈ 0.90 for the liquid solvents and was not measured for gaseous adsorbates. The measurement of coal surface areas using CO₂ and the Dubinin equation is typically performed at relative pressures of up to only 0.03 maximum, and at these pressures Stacy and Jones found the CO₂ induced swelling of a Morwell brown coal to be immeasurably small⁽⁶⁾. Nevertheless, the data of Reucroft and Patel did show a striking relationship between surface areas (measured at low-medium relative pressures) and the solvent induced swelling (at p/p₀ = 0.90) of the Kentucky coal. Figure 5 shows this relationship and suggests that the true surface area of the coal in the absence of swelling effects may be closer to 20 m²/g.

The application of polymer swelling theory to coals may be considered to be inappropriate due to their heterogeneity and the resultant variation in crosslink density. Any attempt to measure the solubility parameter of the coal based on swelling data would thus be an average across the structure studied and places emphasis on sampling techniques. Application of regular solution theory to coal swelling has been moderately successful in some cases^(46, 56, 57), however in other cases^(2, 5, 57) little or no correlation between swelling and solubility parameter has been observed.

Based on the results of all of the above studies, it appears that a solubility parameter approach can "provide systematic information on physical interactions for any material which interacts suitably (dissolves, swells, or absorbs) when contacted with a sufficient number of solvents (energy probes)"⁽⁵²⁾. If reaction occurs, the system cannot be expected to be describable in terms of solubility parameter theory⁽⁵¹⁾. It should also be remembered that solubility parameter theory relates to non-ionic liquid interactions, which have been extended to polymer interactions; water based systems and those systems involving acid-base reactions cannot be evaluated by simple solubility parameter systems alone⁽⁵⁵⁾.



Figure 5. Variation of Measured Internal Surface Area for a Kentucky No. 12 coal with Adsorbate-Induced Swelling (after Reucroft and Patel⁽⁴⁶⁾)

The solubility parameter concept predicts that the closer the solubility parameters of the coal and the solvent the greater will be the swelling. Karim⁽⁵⁸⁾ has estimated the solubility parameter of Latrobe Valley brown coals to be approximately 33 $MPa^{\frac{1}{2}}$, based on extrapolation of a solubility parameter versus carbon content curve⁽⁵⁹⁾ to the 65 - 70% carbon range.

1.6 THE HOST-GUEST MODEL FOR BROWN COAL STRUCTURE

It is difficult to ascertain from the literature just who was responsible for the first model of coal as a two-component system consisting of a macromolecular network and a molecular "filler". However, Green et al.⁽²⁰⁾ bestow the honour on Vahrman⁽⁶⁰⁾, who saw coal as consisting of an insoluble three-dimensional matrix of large molecules and a potentially soluble portion consisting of smaller molecules. The smaller molecules were thought to be inclusions in the pore system. Whilst a large percentage of these molecules were adsorbed in pores of molecular size, some were free inhabitants of larger diameter pores. Their relative ease of extraction was accounted for by the different pore system environments. Palmer and Vahrman⁽⁶¹⁾ found molecules of larger critical dimensions to be extracted (Soxhlet) before smaller molecules apparently retarded by pore restrictions, and concluded that the larger molecules must reside in large, easily accessible pores, whilst smaller extractable species were present in pores offering only restricted access to the extraction solvent.

Green et al.⁽²⁰⁾ questioned whether or not the smaller molecules do reside in the pore system, or whether in fact they are trapped within the coal matrix. This argument would appear to be tenuous, however, because the difference between a *pore system* and a *matrix* must only be a difference in magnification of scale - both representing imperfections in the packing of the macromolecular network. Presumably, the matrix represents internal pores of atomic dimensions. Whilst Vahrman considers the molecular species to be *adsorbed*, Green considers them to be dissolved or *absorbed*. Again, unless there is a difference in the way the molecular species are being held within the network (i.e. hydrogen bonding, electron donor/acceptor interactions), then the argument has little value.

Lynch⁽¹²⁾ found a wide range of experimental evidence to "...encourage the conclusion that brown coals, to a very good first approximation, are "physical" mixtures in varying proportions of a phenolic macromolecular lignin-derived "host" material and a low molecular weight relatively aliphatic "guest" material". The question as to whether the extractable component forms a substantial part of the complete system, or only a minor one, has been debated in a paper by Given et al.⁽⁶²⁾ who arrived at the following conclusions:

- The debate hinges primarily on the interpretation of ¹H nuclear magnetic resonance (NMR) data;
- (ii) There is disagreement in the scientific community as to the suitability of solvent extraction experiments as a means of settling the argument due to the strong possibility that some specific solvents may react chemically with the macromolecular network, thus releasing more than just the small molecular substances that were initially present.

Marzec et al.⁽⁶³⁾ contended that some of the occluded molecules were unable to be freed by organic solvents at normal temperatures based on the fact that the mobile phase, as determined by ¹H pulse NMR, was always significantly higher than the extract yield when the same solvent was applied to both determinations. Given⁽⁶²⁾ raised the possibility that some of the protons in the solvent swollen macromolecular network may be mobile enough to contribute to the NMR signal and thus give an overestimate of the molecular component within the network, however Marzec refuted this suggestion on the basis that observed spin-spin relaxation times were far greater than those calculated for a macromolecule in which all end groups were assumed to rotate⁽⁶²⁾. Nevertheless, Barton and Lynch presented evidence to support Given's argument⁽⁶²⁾.

Central to the issue is the acceptance or non-acceptance of the concept of a coal macromolecular network. If the molecular component residing within this network is bound to the network by polar electron donor/acceptor interactions (see Section 1.7), it must also be highly probable that this type of bonding is responsible for a significant portion of the intra-macromolecular rigidity and conformation⁽⁶²⁾, so that solvents capable of liberating the molecular component are also capable of "loosening" the macromolecular network and thus increasing the mobility of hydrogen associated with the network. Marzec et al. appear to disregard this probability and to contradict themselves in the following:

"...the immobile phase in the original coal consists of macromolecules and molecules which are attached to macromolecules by electron-donor-acceptor interactions; those interactions make the system rigid and inflexible and can be destroyed by some solvents. The more effective the solvent in suppressing those interactions, the higher the ratio of mobile:immobile protons in the coal. It would seem therefore that the technique of ¹H pulse n.m.r. offers a method of determining macromolecular and molecular phases in coal provided that the solvent used detaches all molecules from the macromolecules."⁽⁶³⁾

Following Barton and Lynch's argument⁽⁶²⁾, it would seem impossible for solvents effective in suppressing the electron donor/acceptor interactions responsible for making the "system rigid and inflexible" to discriminate between intra- and intermolecular bonding, so that none of the information gleaned from Marzec et al.'s ¹H pulse NMR experiments is able to differentiate between the two components.

van Bodegom et al.⁽⁸⁾ found that extraction of brown coals with some "specific" (i.e. reactive) solvents under reflux conditions involved the breakage of ester bonds, which were thought to comprise the main linkages between macromolecular coal fragments (based on the relatively large amounts of carboxylic and phenolic functional groups present in brown coals). Extraction with non-specific solvents would then, by inference, involve the dissolution of the soluble component and unhindered passage of this component from the

macromolecular network. Specific solvents capable of rupturing the network allowed greater extraction due to the elimination of structural barriers.

Whilst Marzec⁽⁶²⁾ contends that high extraction yields are unlikely to be due to chemical reaction between the solvent and the macromolecular network for high rank coals, the possibility is unable to be discounted for lignites. Although the literature is full of references to the difficulty of removing reactive solvents from both extract and residue^(48, 64), Schulten and Marzec have found that solvents are released intact from coals by heating from 130 to 250°C (in a time-resolved field ionisation mass spectrometer) and believe that the solvents have not reacted chemically except to break hydrogen bonds⁽⁶²⁾. Marzec concluded that the total content of small extractable molecules clathrated within imperfections in packing of the macromolecular network of low rank coals was 35-45%, and that the difficulty of extracting some of these molecules arises both from the strength of binding to the network and from occlusion⁽⁶²⁾.

It has been observed that the mobile hydrogen content of bituminous coals, in the presence of nucleophilic solvents, is significantly greater than the corresponding extract yield. The difference is much too large to be accounted for by the extracts being \leq 20% richer in hydrogen than the parent coals⁽⁶²⁾.

Barton and Lynch conceded that the ¹H-NMR data for solvent swollen coals are also consistent with models for coal structure other than the host-guest model, most notably one in which coals are composed of molecules having a broad-range continuum of molecular weights⁽⁶²⁾. In a follow-up debate on the existence of a two-component structure for coal⁽⁶⁵⁾, Wilson criticised the host-guest model as being an oversimplification of what must, from its peat-swamp origins, be an extremely heterogeneous mixture. Wilson argues that petrology should not be ignored in the debate on coal structure and that a continuum of molecular and rotational mobilities might be expected on the basis of the many degraded plant remains known to make up coal⁽⁶⁵⁾. Jurkiewicz et al. also recognise that the chemical and physical interpretation of coal structure in terms of ¹H-NMR data is tenuous⁽⁶⁵⁾.

The depolymerisation of the macromolecular network that occurs during the earlier stages of coalification leads to an increase in the concentration of the molecular component with rank⁽⁶⁵⁾. Opposing this, coalification also results in an increase in aromatisation (Section 1.2), which probably reduces the solubility and extractability of the molecular phase. This would seem to account for the maximum in extraction yield versus rank⁽²⁰⁾ at around 86% dry, mineral matter free (dmmf) C.

1.7 THE ELECTRON DONOR-ACCEPTOR APPROACH

Marzec et al.^(3, 66) applied new solvent strength parameters previously developed by Gutmann⁽⁶⁷⁾ to the extraction and swelling of a high volatile bituminous coal in an effort to elucidate the extraction/swelling mechanism. Attempts were made to correlate extraction yields and swelling ratio (swollen volume/unswollen volume) with various solvent strength parameters including electron donor (DN) and acceptor (AN) numbers⁽³⁾, and solubility parameter⁽⁶⁶⁾. The solvents employed by Marzec et al.^(3, 66) are characterised in terms of their DN and AN in Table I.

A trend of increasing extract yield with increasing DN was found, as shown in Figure 6, whilst AN appeared to have only an indirect effect on extract yield, via the relation DN minus AN (Figure 7). For the sake of completeness, the relationship between extraction yield and solvent AN is shown in Figure 8.

Similar relationships were found between swelling and solvent donor/acceptor numbers⁽⁶⁶⁾. Solubility parameter was found not to correlate with solvent extraction yield^(3, 66). Marzec conceded⁽³⁾ that the correlations shown in Figures 6 and 8 are poor because of the dependency of coal extraction on two variables - DN and AN. The results of this work suggested that solvent electron-donor/acceptor properties were primarily responsible for the extraction yields obtained, and the extraction process was thus modelled in terms of donor-acceptor (or polar)⁽⁶²⁾ interactions between the coal and solvent as shown in Figure 9.

Solvent	Abbr.	DN	AN	DN-AN
n-Hexane	Н	0	0	0
Water	W	33.0	54.8	-21.8
Formamide	F	24.0	39.8	-15.8
Acetonitrile	AN	14.1	19.3	-5.2
Nitromethane	NM	2.7	20.5	-17.8
Isopropanol	IP	20.0	33.5	-13.5
Methanol	МОН	19.0	41.3	-22.3
Benzene	В	0.1	8.2	-8.1
Ethanol	EOH	20.5	37.1	-16.6
Dioxane	D	14.8	10.8	4
Acetone	А	17.0	12.5	4.5
Tetrahydrofuran	THF	20.0	8.0	12.0
Diethyl ether	DEE	19.2	3.9	15.3
Pyridine	PY	33.1	14.2	18.9
Dimethyl sulphoxide	DMSO	29.8	19.3	10.5
Dimethyl formamide	DMF	26.6	16.0	10.6
Ethylenediamine	ED	55.0	20.9	34.1
Nitrobenzene	NB	4.4	14.8	-10.4
Ethyl acetate	EA	17.1	-	-
Methyl acetate	MA	16.5	10.7	5.8
Methyl ethyl ketone	MEK	-	-	

Table I.Solvent DN and AN Parameters^(3, 66).



Figure 6. Coal Extract Yields versus Solvent Donor Number (after Marzec et. al.⁽³⁾)



Figure 7. Coal Extract Yields versus Solvent DN-AN (after Marzec et. al.⁽³⁾)



Figure 8. Coal Extract Yields versus Solvent Acceptor Number (after Marzec et. al.⁽³⁾)



Figure 9. Conceptual Model of the Solvent Extraction of Coal (after Marzec et al.⁽³⁾)

Possible electron donor centres in extractable species include pyridine rings, oxygen functional groups and π -excessive heteroatomic rings, whilst electron acceptor centres may include phenolic protons, pyrrole-NH protons and π -deficient heteroatomic rings⁽³⁾. The same chemical species can be found incorporated into the macromolecular network. According to Marzec's model, extraction of pore substances would occur if their bonding to the coal could be disrupted by solvent attack via the following routes;

- (i) attack of solvent donor electrons on network acceptor sites and formation of D_s - A_n bonding,
- (ii) attack of solvent acceptor sites on extractable pore substance donor electrons and formation of D_p -A_s bonding,
- (iii) attack of solvent donor electrons on extractable pore substance acceptor sites and formation of D_s - A_p bonding, and
- (iv) attack of solvent acceptor sites on network donor electrons and formation of D_n -A_s bonding.

According to Gutmann⁽⁶⁷⁾, the donor-acceptor bond energy can be approximated from the donor and acceptor numbers of the participating compounds:

$$\Delta H \approx \frac{DN \, x \, AN}{100}$$

Therefore the formation of new Ds-An bonding via route (i) will only be possible if the value of the product DNs x ANn is higher than DNp x ANn (i.e. the energy of the bond between the solvent and the network must be higher than that between the extractable pore substance and the network) and DNs x ANs (the energy of the intermolecular bonding of the solvent). The requirements for all four routes of bond formation may be summarised as in Table II.
 Table II.
 Required Solvent Electron Donor/Acceptor Numbers for Extraction of Coal⁽³⁾.

Route	Intermolecular solvent bond	New bond	Original coal bond	Requirements for new bond formation
(i)	DN _s x AN _s	< DN _s x AN _n >	DN _p x AN _n	AN _s < AN _n and DN _s > DN _p
(ii)	$\rm DN_s$ x $\rm AN_s$	< DN _p x AN _s >	DN _p x AN _n	AN _s >AN _n and DN _s < DN _p
(iii)	DN _s x AN _s	< DN _s x AN _p >	DN _n x AN _p	AN _s < AN _p and DN _s > DN _n
(iv)	DN _s x AN _s	< DN _n x AN _s >	DN _n x AN _p	AN _s > AN _p and DN _s < DN _n

Thus, solvents with both DN and AN higher than those of the network and the extractable pore substance do not satisfy the requirements of Table II, and extraction cannot occur. The same may be said where the solvent DN and AN values are both less than those of the network and the extractable species.

Solvents that attack via routes (i) and (iii) (i.e. nucleophiles) are characterised by high DN and low AN, whilst electrophilic solvents which attack via routes (ii) and (iv) have low DN and high AN. Solvents that attack via routes (i) and (iv) must have DN and AN values that are larger than those of the extractable species, but smaller than those of the macromolecular network. Conversely, solvents that attack via routes (ii) and (iii) must have DN and AN values that are smaller than those of the extractable species, and larger than those of the macromolecular network. All of these conditions were summarised in a model of coal extraction by Marzec as shown in Figure 10.

Both Group A and B solvents, according to Marzec's classification, are capable of complete extraction of pore substances because they can break both types of coal donor-acceptor bonds. Group F, G, H and I solvents have DN and AN values lying between the extremes found in coal and are therefore capable of breaking only some coal donor-acceptor bonds. Group D and E solvents are not capable of any bond breakage and are thus incapable of extraction.

Marzec's model can be verified by the data shown in Table II, which yields the following classification for the seventeen solvents listed (Table III). The reason for the variation in extract yields for the Group A solvents may be the different swelling abilities of these solvents (see Section 1.1).

The major conclusions from Marzec's work were that donor-acceptor bonds are responsible for binding the macromolecular coal network and the extractable species, and that extraction is principally a substitution reaction in which these donor-acceptor bonds are replaced by bonds involving the solvent molecules.

max. AN _{p,n}	↑ AN	Group B both D _n - A _p and D _p - A _n bonds are broken by electrophilic solvent attack	Group H	Group E solvent DN and AN are too high - no coal donor- acceptor bonds can be broken
		Group G	Group C	Group I
min. AN _{p,n}		Group D solvent DN and AN are too low - no coal donor- acceptor bonds can be broken	Group F	Group A both D _n - A _p and D _p - A _n bonds are broken by nucleophilic solvent attack
	P			$DN \to$
		min. DN _{p,n}		max. DN _{p,n}

Figure 10. Model for Solvent Extraction of Coal⁽³⁾

Group	Solvents	Extract yield (wt. % daf)	DN Range	AN Range
Α	Tetrahydrofuran Diethyl ether Pyridine Dimethyl sulphoxide Dimethyl formamide Ethylenediamine	8.0-22.4	19-55	4-21
D	n-Hexane Benzene Acetonitrile Nitromethane	⊴0.1	0-15	0-21
E	Water Formamide Isopropanol Methanol Ethanol	⊴0.2	19-33	33-55
F	Dioxane Acetone	1-2	15-17	11-13

Table III.Classification of Solvents According to the Extraction ModelProposed by Marzec et al.⁽³⁾.

van Bodegom et al.⁽⁸⁾ also noted the involvement of chemical factors in the dissolution of coals in an explanation of the poor solvent power of ethanol ($\delta = 26 \text{ MPa}^{\frac{1}{2}}$) compared to the strength of ethylenediamine (25.2 MPa^{1/2}) and monoethanolamine (31.7 MPa^{1/2}).

The work detailed above was performed on high rank bituminous coals. No such work has been reported for lower rank coals⁽³²⁾.

1.8 KAMLET-TAFT SOLVATOCHROMIC PARAMETERS

Kamlet et al. have developed a method of classifying solvents in terms of both their solubility parameters and their electron donor/acceptor properties⁽⁶⁸⁾. The treatment in this Section follows a series of papers by Kamlet et al. According to this theory, three "solvatochromic parameters", π^* , α and β , can be used in a single equation capable of predicting various physicochemical properties of solvents in contact with reactants (or "indicators").

The π^* scale is an index of solvent dipolarity/polarisability and measures the ability of the solvent to stabilise a charge or a dipole by virtue of its dielectric properties. The α scale describes the ability of the solvent to donate a proton in a solvent-tosolute hydrogen bond. In other words, it is a measure of the solvent's electron acceptor ability (see Section 1.7). The β scale provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solvent-to-solute hydrogen bond. Multiple linear regression analysis resulted in the following equation:

$$XYZ = XYZ_{o} + s(\pi * + d\delta) + a\alpha + b\beta + h\delta_{H} + e\xi$$

where XYZ is the physicochemical property in question, and XYZ_o is the initial value of the particular property before contact with the solvent.

 δ is a "polarisability correction term" equal to 0.0 for non-chlorinated aliphatic solvents, 0.5 for poly-chlorinated aliphatics, and 1.0 for aromatic solvents. The δ values reflect the fact that, as a general rule, differences in solvent polarisability are significantly greater between these classes of solvents than within the classes⁽⁶⁸⁾. The coefficient of δ , d, is calculated via the equation:

$$d = \frac{2\Delta XYZ}{[s(al) + s(ar)]}$$

where ΔXYZ is the difference between the values calculated through the aliphatic and aromatic regression equations at $\pi^*=0.7$ and s(al) and s(ar) are the slopes of those regression equations⁽⁶⁸⁾.

The δ_h term is the Hildebrand solubility parameter (Section 1.5). The ξ parameter is a measure of "coordinate covalency" equal to -0.20 for P=O bases, 0.0 for C=O, S=O and N=O bases, 0.2 for single-bonded oxygen bases, 0.6 for pyridine bases and 1.00 for sp³-hybridised amine bases. Table IV shows the π^* , α , and β values for all solvents used in swelling measurements in the current study, except for ethylenediamine for which there was no data in the source article.

Kamlet et al.⁽⁶⁸⁾ have shown excellent correlation between predicted (via the equation above) and experimental values for maximum UV/visible absorption frequencies and NMR-spectral shifts etc. The application of Kamlet-Taft solvatochromic parameters to prediction of swelling (i.e. XYZ = final swollen volume, XYZ_0 = initial unswollen volume) will be analysed in Section 3.2.4.

1.9 RECENT ADVANCES

In recent years there has been a shift in thinking on the treatment of coal swelling away from the approaches based on regular solution theory and free of the associated assumptions and limitations. This work has largely been championed by Painter et al.^(33, 38, 69-75). This Section will focus on the important achievements of this group in elucidating the swelling mechanism.

_ <i></i>	
l able IV.	Solvatochromic Parameters ⁽⁰⁰⁾ .

SOLVENT	π*	β	α		
	Aliphatic Hydroca	Irbons			
n-Hexane	-0.08	0.00	0.00		
Cyclohexane	0.00	0.00	0.00		
	Ethers (ξ=0.2	.0)			
Diethyl ether	0.27	0.47	0.00		
Dioxane	0.55	0.37	0.00		
Tetrahydrofuran	0.58	0.55	0.00		
1,2-Dimethoxyethane	0.53	0.41	0.00		
	Ketones (ξ=0.00)				
Methyl ethyl ketone	0.67	0.48	0.06		
Acetone	0.71	0.48	0.08		
	Esters (ξ=0.0	0)			
Ethyl acetate	0.55	0.45	0.00		
Methyl acetate	0.60	0.42	0.00		
Amides (ξ=0.00)					
Dimethyl formamide	0.88	0.69	0.00		
Amines (ξ=1.00)					
Triethylamine	0.14	0.71	0.00		
Sulphoxides (ξ=0.00)					
Dimethyl sulphoxide	1.00	0.76	0.00		

SOLVENT	π*	β	α		
Nitro c	Nitro compounds and Nitriles (ξ not yet known)				
Nitrobenzene	1.01	0.39	0.00		
Nitromethane	0.85		0.22		
Acetonitrile	0.75	0.31	0.19		
	Pyridines	(ξ=0.60)			
Pyridine	0.87	0.64	0.00		
Quinoline	[0.92]	0.64	0.00		
Aromatics					
Benzene	0.59	0.10	0.00		
Haloaliphatics					
Dichloromethane	0.82	0.00	(0.30)		
Alcohols and Water (ξ=0.20)					
2-Propanol	0.48	(0.95)	0.76		
Ethanol	0.54	(0.77)	0.83		
Methanol	0.60	(0.62)	0.93		
Water	1.09	(0.18)	1.17		

Table IV (continued).Solvatochromic Parameters⁽⁶⁸⁾.

Note: Data in parenthesis are less certain. Data in square brackets are determined using equations containing refractive index and bulk dielectric constants.

Painter stresses the key role played by hydrogen bonding in coal structure and points out that the presence of such specific interactions does not permit the use of the Flory-Huggins solution theory^(33, 70). Although, as mentioned earlier, he is not the first to question the validity of polymer theory when applied to coals, he has been the most active in seeking an alternative approach. Phenolic (–OH) groups were identified as being the principle species taking part in hydrogen bonding within coal^(33, 70), although it may be expected that low-rank brown coals may be subject to a larger contribution from carboxylic acid groups. Four general types of hydrogen-bonded structures are expected⁽⁷¹⁾:



Increasing hydrogen-bond strength (approximate)

The fact that hydrogen bonds are present in significant concentrations has a profound influence on the behaviour of the coal and on what theoretical tools can successfully be applied to its structure. Theoretical descriptions of polymeric materials are, of necessity, based on a number of simplifying assumptions - the most critical of which are that chain statistics are Gaussian; all the chain ends are joined to the network; entanglements can be neglected; and that displacement of crosslink points are linear in strain⁽³³⁾. Coal is clearly a long way from meeting these criteria: the chain segments between crosslinks are probably too short and stiff to be anywhere near Gaussian (especially for higher rank coals), and the presence of dangling ends is very likely⁽³³⁾.

The Flory-Huggins theory assumes random mixing. However, significant hydrogen bonding will result in a greater number of interactions than those due to random mixing, the exact number depending on the energy of the interaction (χ). Plotting swelling data for hydrogen bonding materials as a function of solvent solubility parameter is considered by Painter to be meaningless because of these non-random contacts⁽³³⁾.

Recognising that both the enthalpic contribution of hydrogen bonding and the entropic (due to non-random arrangement of hydrogen-bonding functional groups on the coal surface) contribution had to be considered, Painter has modified the Flory-Huggins equation by the addition of a term, ΔG_H , which describes the change in free energy due to the change in pattern of hydrogen bonding when a self-associated material (e.g. coal – through OH groups) is mixed with a species that competes with these hydrogen bonds⁽³³⁾.

The modified Flory-Huggins equation takes the form:

$$\frac{\Delta G}{kT} = N_1 \ln \upsilon_1 + N_2 \ln \upsilon_2 + \chi_1 N_1 \upsilon_2 + \frac{\Delta G_H}{kT}$$

The first two terms to the right of the equation above are always negative and favourable to mixing (Section 1.4) whilst the term containing χ reflects physical dispersion forces and is positive (unfavourable to mixing). The new term, describing the free energy due to the change in the number and type of hydrogen bonds that occur as a function of the composition of the system⁽⁶⁹⁾, is negative⁽⁷²⁾.

When taking into account the energetics associated with specific (hydrogen)bonding, Painter^(70, 73) shows that the minimum in χ occurs with a solvent having a somewhat lower solubility parameter than the coal (determined using molar attraction constants). One of the most instructive pieces of Painter's work involves his construction of phase ("binodal" and "spinodal") diagrams for the coal/solvent system^(38, 69-71, 74), spinodals being given by the second derivative of the modified Flory-Huggins equation with respect to composition:

$$\frac{\partial^2 \left(\frac{\Delta G}{RT}\right)}{\partial v^2} = 0$$

The phase diagrams highlight important factors in both the swelling and extraction of coals. Firstly, below a given temperature (the upper critical solution temperature), dependent on the average molecular weight of the "coal molecule", coal/solvent systems will separate into a (swollen) coal rich phase and a solvent rich phase (i.e. dilute in terms of the concentration of coal extract). Hence in extraction systems (e.g. Soxhlet) where the temperature of the condensed solvent in contact with the coal is lower than the upper critical solution temperature, a great many successive extractions would be needed to free the bulk of the extractable material from the coal⁽⁷²⁾. Secondly, the phase diagrams indicate that if coals were not crosslinked, they would be completely soluble in, for example, pyridine at temperatures above the upper critical solution temperature (and below any lower critical solution temperature)⁽⁷²⁾. The fact that coals do not dissolve in pyridine, but rather swell (even at elevated temperature), is a strong confirmation of network crosslinking. Maximum swelling will only occur if the solvent and the coal can exist in a single phase⁽⁶⁹⁾.

All of the above is most critical to the determination of M_c using swelling measurements because it dictates that swelling be performed at temperatures in excess of any upper critical solution temperature (or below any lower critical solution temperature) in order to obtain meaningful numbers.

Despite his problems with the popular theory, Painter does credit polymer swelling theory with being "...useful as a qualitative and comparative probe of structure"⁽⁷⁵⁾. Larsen et al.⁽⁴⁴⁾ also supports the Flory approach in terms of its simplicity and for its value in comparison between coals. More complex (non-

Gaussian) treatments designed specifically for coal have been found to yield the same trends⁽⁴⁴⁾. Furthermore, Larsen et al. show an excellent relationship between the deviation from the ideal (non hydrogen-bonded) swelling curve and the strength of the hydrogen bonding achieved by the solvent⁽⁴⁴⁾.

1.10 BINARY-SOLVENT SWELLING

Although binary solvent swelling will not be performed in the current work, it is pertinent to review some of the work which has been done in this area and to discuss the implications that the results have for the model of coal-solvent swelling.

Green and Larsen⁽⁷⁶⁾ found selective sorption from binary mixtures and attributed it to hydrogen bonding between oxygen functional groups and the preferentially sorbed solvent. Correlation between degree of swelling and the solubility parameter of the binary-solvent mixture was found in the case of an unextracted coal.

The solubility parameter of a mixture of binary solvents is given by:

$$\delta_m = \upsilon_1 \ \delta_1 + \upsilon_2 \ \delta_2$$

with subscripts m, 1 and 2 representing the mixture, component 1 and component 2 respectively⁽⁵⁰⁾. The complex synergism involved with binary solvents^(4, 75) complicates the use of the solubility parameter approach.

lino et al.⁽⁴⁾ performed binary-solvent swelling/extraction studies on a comprehensive suite of coals ranging in rank from 66 to 94% carbon. A large range of solvents was tested as 1:1 by volume mixtures with carbon disulphide (CS₂). Equilibrium swelling of the coals was attained within 30 minutes for CS₂/N-methyl-2-pyrrolidinone (NMP) but took approximately 10 hours for NMP alone. NMP gave the highest extraction yield when used as a lone solvent, and as a binary mixture with CS₂. CS₂ alone gave very low extraction yields.

For some coals, the synergism observed in swelling with the mixed solvent was spectacular, and for others, very modest. Addition of a small amount (5% by weight) of a third solvent (e.g. tetracyanoethylene) further increases the extraction yield of the mixed solvent by a significant amount⁽⁷⁷⁾.

Painter suggested that NMP may self-associate through very strong dipolar interactions⁽⁶⁹⁾. Now two sets of bonds have to be broken in order to form one coal-solvent bond. This results in Painter's ΔG_H term becoming smaller and mixing becoming less favoured. It was further suggested that the addition of CS₂ to NMP as a binary solvent may "fortuitously" bring the solubility parameter into the right range as well as limiting the self-association of NMP due to the presence of the "polar co-solvent". This assertion is difficult to justify however as CS₂ is not particularly polar⁽⁴⁹⁾ and, even if it was, there is no reason to suggest that association of a single solvent. In addition, it would be unusual for the solubility parameter of the mixture to be in the correct range for such a range of coal ranks.

It is more likely that the results of lino et al. can be explained by virtue of the fact that CS_2 is a kinetically good (small, compact molecule) solvent and NMP is a thermodynamically good ($\delta_1 \approx \delta_2$) solvent for most of the coals in the test suite. Such mixtures are often very powerful polymer solvents^(28, 78). In support of this view, CS_2 alone gave a relatively constant swelling ratio regardless of coal rank whilst NMP alone yielded swelling ratios that increased with rank until about 80 to 85% carbon and thereafter decreased markedly. Ino discounts application of solubility parameters to his extraction data because of the fact that nitrobenzene, ethyl acetate, and dioxane, which have the same δ (MPa^{1/2}) as CS₂ (20.5), are ineffective in the extraction as a mixed solvent with NMP⁽⁴⁾. Burrell⁽⁴⁹⁾ lists the solubility parameter of ethyl acetate as 18.6 MPa^{1/2}, which highlights the difficulty in obtaining consistent data from the literature (see Section 1.5). Nevertheless, an explanation for the low solvent power of nitrobenzene and dioxane when used as mixed solvents with NMP can be found in their molar volumes of 102.6 and 85.5 respectively compared to CS₂ at 60.4. The kinetic advantage of CS₂ is thus

not available to the mixed solvent (with NMP) when larger molecules are employed.

Many coal properties, such as elastic modulus, calculated molecular weight between crosslinks, extraction yield, conversion to liquid products under hydrogenation conditions and fluidity have been shown to be a maximum at around 86% carbon content⁽²⁰⁾. All of these observations are consistent with a minimum in crosslink density as coalification proceeds past the 86% C level, and lino's results show that although NMP is thermodynamically compatible with the coals, swelling is reduced at high carbon contents because of an increase in crosslinking.

That crosslinking increases with rank after the minimum at \approx 86% C is one of two possibilities⁽⁶⁹⁾, the other is that high rank coals (>90% C) are not crosslinked at all, but are simply highly aromatic and very low in functional groups capable of interacting with solvents to any great extent⁽⁶⁹⁾.

lino also showed that the yields from exhaustive extraction of two coals using either NMP or pyridine were significantly lower than would be expected from the solubility in these solvents of the CS_2/NMP extract⁽⁴⁾, indicating that the "exhaustive" extraction was incomplete in both cases (more so for pyridine) - indirect confirmation of Painter's conclusions (Section 1.9), and further evidence that CS_2 facilitates the penetration of the coal structure by NMP in a given timeframe.

1.11 VICTORIAN BROWN COAL BRIQUETTES

Binderless briquetting is a technique widely applicable to low rank coals such as lignites, brown coal and peats, and facilitates the effective utilization of these resources. In the briquetting process, the coal is dried to approximately 12 - 18% moisture content and extrusion pressed to form the briquettes. Many theories on the binding mechanism in briquettes have been proposed^(79, 80), however the role

of hydrogen bonding between oxygen functional groups on the coal surface remains the most popular⁽³¹⁾.

lyengar et al.⁽⁸¹⁾ measured the compressive strengths of briquettes produced using additives of different polarity. Non-polar additives such as benzene and n-heptane resulted in very low strength briquettes. Water yielded stronger briquettes than both methanol and ethanol. Addition of formic and acetic acids resulted in very strong briquettes. Iyengar et al.⁽⁸¹⁾ also showed that briquette strength could be reduced by up to 90% by neutralising polar (phenolic, hydroxyl, carboxyl) functional groups via acetylation of the coal. These experiments confirmed the key role of hydrogen bonding between oxygen functional groups in determining the integrity of "binderless" briquettes⁽³¹⁾.

An industrial problem of great significance is the poor weathering characteristics of briquettes manufactured from Morwell coal⁽⁸²⁾. Freshly stockpiled Morwell briquettes have been found to develop surface crazing that, after a time, results in deep cracks and fracture. This weathering is believed to be caused predominantly by swelling due to the absorption of moisture from the atmosphere⁽¹⁰⁾. Briquettes manufactured from Yallourn coal, however, remain relatively unaffected by weathering when stored in outdoor stockpiles. As a result of the poor weatherability of briquettes produced from Morwell coal, the manufacturer must transport Yallourn coal via a single-purpose railway to the Briquette Factory situated at Morwell. The problem of weathering of briquettes has been estimated to cost the Australian economy several million dollars per annum⁽⁸³⁾.

The interaction of water with brown coal briquettes is thus of special interest in attempts to improve the weathering characteristics of Morwell briquettes. The role attributed to moisture in the briquetting process has been variously described as a lubricant in the press, as a component in a chemical reaction with bitumen, as an adherent film between colloidal particles, as the medium inducing increased surface tension bonding in capillaries, and as the medium creating hydrogen-bond bridges between polar functional groups in the coal⁽³¹⁾.

The swelling properties of Victorian brown coal briquettes, in water, and in organic solvents, will be discussed in Chapter 5.

1.12 SOLVENT PROPERTIES

The degree of solvent swelling of a particular coal is, of course, heavily dependent on the properties of the solvent/s, and is affected by the equilibrium combination of coal-coal and coal-solvent interactions⁽⁷⁶⁾.

Dryden⁽¹⁹⁾ found that a good solvent often contains a nitrogen or oxygen atom possessing an unshared pair of electrons. Other things being equal, nitrogen compounds are better solvents than the corresponding oxygen compounds⁽¹⁹⁾. The well accepted rule "like dissolves like" cannot be discounted here and it becomes obvious that solvents with phenolic and polyaromatic character will be good solvents for low rank coals of like character. Conversely, hydrocarbon solvents would not be expected to be good solvents for low rank coals⁽¹⁷⁾.

The chemical mechanism of coal-solvent interaction has been largely attributed to an acid-base reaction involving hydrogen bonding between the solvent (acting as a Lewis base) and the acid sites in the coal structure⁽⁸⁴⁾. Because brown coals are highly acidic, solvents that are strong bases can be expected to be highly effective if acid-base interactions are important⁽⁸⁾.

van Bodegom et al.⁽⁸⁾ concluded, from their work on solvent extraction of low rank coals at temperatures up to about 200°C, that a good solvent for brown coal should be able to both rupture the ester bonds which supposedly link the coal fragments together, and to dissolve the reaction product(s) of the solvent and the acidic coal fragments. The class of good solvents for brown coals was found to be restricted to strong bases⁽⁸⁾. The question as to whether a solvent that is effective in terms of its ability to extract coal (i.e. a so called good solvent) is automatically a good swelling solvent has been treated in the affirmative in Section 1.1.

Painter et al.⁽⁷¹⁾ found that the types of solvents capable of swelling coal, and the degree of swelling, were inextricably linked to the hydrogen-bonding tendencies of the solvents. Some data on comparative hydrogen-bond strengths (as measured by equilibrium constants and/or heats of reaction) are shown in Tables V and VI.

Solvent polarity is another important property in the consideration of coal-solvent interactions. Polar bonds, where the electron density is altered by the forces of electronegative atoms, have a dipole moment. The size of the dipole moment (μ) is given by:

$$\mu = e x d$$

where **e** is the magnitude of the charge in Coulomb and **d** is the distance between the centres of charge in metres.

Dipole forces constitute the attraction of the positive end of one polar molecule for the negative end of another. As a result of dipole forces, polar molecules are generally held to each other more strongly than non-polar molecules of comparable molecular weight⁽⁸⁶⁾. Solvents with strong dipole moments could be expected to interact more strongly with coal molecules because of their greater solvating power.

The fact that non-polar compounds can solidify is evidence that intermolecular forces exist here also. Since the electrons in an atom are in a constant state of motion, small <u>temporary</u> dipoles will exist at any point in time and these dipoles are capable of inducing <u>temporary</u> dipoles in neighbouring molecules by slightly distorting their charge distribution. The attractive forces between the two temporary dipoles are termed *dispersion forces*. They are present in all molecules and represent a major portion of the intermolecular forces unless very strong dipoles are present. In non-polar solvents only dispersion forces exist⁽²⁸⁾.

Table V.Thermodynamic Data on Donor-Acceptor Hydrogen Bonding.Data collected using IR Spectroscopy (Methanol as Acceptor in a
CCl4 solution)⁽⁸⁵⁾.

Donor Solvent	K _{eq} * moles/litre	∆H (Exothermic reaction) kcal/mole
Pyridine	2.99 ²⁵	3.88
Triethylamine	6.4 ²⁰	3.8
Diethyl ether	1.27 ^{21.7}	3.73
Dimethyl formamide	5.50 ²⁵	3.72
Dioxane	1.50 ²⁵	2.8
Acetone	1.816 ²⁵	2.52
Ethyl acetate	1.40 ²⁵	2.52
Benzene	0.80	
Nitromethane	0.2	

* superscripts denote temperature of measurement

Table VI.Thermodynamic Data on Donor-Acceptor Hydrogen Bonding.Data collected using IR Spectroscopy (Phenol as Acceptor in a CCl4
solution)⁽⁸⁵⁾.

Donor Solvent	K _{eq} * moles/litre	∆H (Exothermic reaction) kcal/mole
Triethylamine	58 ²⁵	9.1
Dimethyl sulphoxide	230.2 ²⁰	8.00
Quinoline	57.4 ²⁰	7.2
Pyridine	42 ²⁵	6.5
Diethyl ether	8.83 ²⁵	5.41
Methyl ethyl ketone	8.83 ²⁵	5.34
Dioxane	3.68 ³⁰	5.00
Acetone	12.31 ²⁰	4.50
Methyl acetate	8.41 ²⁰	4.49
Acetonitrile	4.79 ³⁰	4.3
Ethyl acetate	9.81 ²⁰	4.21
Tetrahydrofuran	13.6 ²⁵	4.0
Benzene	0.28 ²⁵	1.56

* superscripts denote temperature of measurement

CHAPTER 2.

EXPERIMENTAL

2.1 SELECTION AND PREPARATION OF COALS

The coal used in pycnometric swelling measurements was a Loy Yang run-of-mine (ROM) coal from the Flynn 1277 bore (hereafter referred to as LY1277). Pycnometric experiments were also performed on densified samples (see Section 2.3.1) of the LY1277 coal, as well as factory produced Yallourn Township, Morwell, and Loy Yang briquette samples. Briquetted coal was used in preference to raw lump coal because of the relative ease of handling and of measuring the volume of the more compact material, although it is recognised that the reduced macroporosity of the briquetted compared to the unbriquetted coal may reduce the extent of swelling⁽⁸⁷⁾. All samples used in pycnometry experiments were sized to - 8.00, +5.60 mm.

The coal used in the combined gravimetric/volumetric apparatus (Section 2.5) was a Loy Yang ROM sample that had been mined in October 1986 (hereafter referred to as LYROM). This coal was also used in centrifuge experiments (Section 2.4.2), and was subjected to modification via acetylation (Section 2.3.2) and methylation (Section 2.3.3). Prior to gravimetric/volumetric measurements the coal was sized to –2.36 mm, +1.18 mm and particles of wood were removed, by visual inspection, to avoid (as much as possible) the complication of different swelling behaviours between wood and coal. Centrifuge experiments were conducted on –212 μ m, +106 μ m coal fractions due to the requirement for a narrow size range⁽⁸⁸⁾.

In order to compare the swelling behaviour of Yallourn and Morwell briquettes, dry coals from both fields were subjected to ion-exchange (Section 2.3.4). The ion-exchanged coals were briquetted using a laboratory press (Section 2.3.5) and rates of swelling in water were measured. Proximate and ultimate analyses for all samples are given in Table VII.
Content (% d.b.)	LY1277	Yallourn Township briquette	Morwell briquette 13/5/88	Loy Yang briquette 7/5/86	LYROM (October 1986)	Yallourn Dry 3-4 cut	Morwell Dry '83 Bin 63
Moisture (% a.r.)	ND	ND	ND	ND	62.6	ND	ND
Volatile matter	51.1	52.0	49.5	52.6	51.4	50.5	49.8
Ash	1.5	1.6	2.2	1.1	1.3	1.6	1.9
Fixed carbon (by difference)	47.4	46.4	48.3	46.3	47.3	47.9	48.3
С	68.6	65.9	67.6	68.0	67.8	67.4	ND
н	4.7	4.5	4.8	5.0	4.9	4.8	ND
N	0.57	0.55	0.55	0.57	0.54	0.55	ND
S	ND	0.17	0.26	0.27	0.27	0.23	ND
O (by difference)	ND	27.3	24.6	25.1	25.2	25.4	ND

Table VII. Proximate and Ultimate Analyses of Coal and Briquette Samples.

d.b. denotes dry basis a.r. denotes as received

ND denotes not determined

Coals were degassed under flowing N₂ at 60°C prior to all pycnometric and centrifuge swelling experiments. Anderson et al.⁽⁸⁹⁾, recognising that degassing under vacuum at high temperatures could lead to decomposition of coals, found that evacuation of coals (ranging in rank from lignite to anthracite) at 100°C did not cause oxidation and that the temperature, although adequate to remove sorbed water and gases, was not high enough to cause appreciable decomposition of the coals. Berkowitz and Schein⁽⁹⁰⁾ outgassed samples of lignite at between 80 and 90°C prior to swelling experiments, with outgassing considered to be complete when the pressure above the sample had fallen to 10^{-5} mm Hg and showed no tendency to build up when pumping was discontinued. Allardice⁽⁹¹⁾ found that above 60°C, significant quantities of CO₂ were evolved from evacuated coal. Only water could be removed from brown coals at temperatures up to 60°C.

No special precautions such as grinding or storing under $N_2^{(92)}$ were taken. van Bodegom et al.⁽⁸⁾ showed for a suite of low rank coals, including Yallourn and Morwell brown coals, that when sealed in glass jars, failure to take such precautions did not result in significant changes in moisture content, carboxyl group content, or solubility with time.

Criticism may be made of the omission of thorough solvent extraction of coals prior to swelling experiments⁽²⁷⁾ due to the well-documented failure of many classical treatments to cover the possibility of specific coal-solvent interactions. Marzec⁽⁹³⁾ is of the firm belief that the three-dimensional macromolecular network of the two-component (Host-Guest) model should be probed in isolation from the molecular components. However there seems to be little point, especially in regard to the objectives of the present study, in limiting any conclusions to the insoluble portion of coals, which can be changed significantly in physical structure from their parents⁽⁹⁴⁾. It is considered important to study the behaviour of whole coals in contact with solvents so that the behaviour of coals in industrial processes may be better understood. The precedents to this approach are many ^(23, 46, 94). Nelson et al.⁽⁹⁴⁾ believe that both raw and extracted coals should exhibit similar sorption properties because the organic fraction extracted from coal has

been shown to be similar in chemical composition to the insoluble residue. Suffice it to mention that a decrease in swelling will be observed⁽⁵⁰⁾ when studying an exhaustively extracted coal network "residue" compared to an intact coal. This is due mainly to the removal of osmotic forces from within the pore network ordinarily caused by the dissolution of extractable pore species in the solvent (Section 1.1). It must be noted, however, that Green and Larsen⁽⁷⁶⁾ observed *increased* swelling of a Bruceton coal in methanol/N,N-dimethylaniline binary solvent after prior extraction with pyridine. This observation is curious, however the complex synergism involved with binary solvent swelling^(4, 75) may be responsible. Larsen et al.⁽⁴⁴⁾ have studied unextracted bituminous coals and obtained "good quantitative data" using volumetric swelling techniques.

Criticism may also be made of the alteration to the original coal structure caused by drying due to the collapse of the coal-water gel and its associated pore structure. Once again, the current procedure can be defended on the grounds that most industrial processes do, in fact, utilise dried (or partially dried) coals. The experimental results from this study can therefore be directly applied to these processes without the need to allow for differences in porosity between the experimental and real samples. It must be noted, however, that the shrinkage of brown coals, even after air-drying to 12-15% moisture, is both severe and irreversible⁽³²⁾. This can be observed in the hysteresis of desorption/adsorption isotherms of water on brown coal⁽⁹¹⁾.

2.2 SELECTION OF SOLVENTS

A suite of seven solvents was chosen for pycnometry experiments (Section 2.4.1) on the basis of a wide range of solubility parameters, and hence polarities (see Section 1.5). All of these solvents were "Analytical Reagent" grade (except for ethanol which was "Absolute"). Benzene was sodium dried, and triple-distilled water of maximum specific conductivity of 1 x 10⁻⁶ ohm⁻¹cm⁻¹, pH of 5.7, and surface tension of 72.8 mNm⁻¹ at 20°C was used.

A wider selection of solvents was used in the centrifuge method to enable a comparison of the swelling of Victorian brown coal with that of the sub-bituminous coal studied by Szeliga and Marzec⁽⁶⁶⁾. Cyclohexane, dichloromethane, quinoline and triethylamine were added to the test suite due to ready availability both of the solvents themselves, and of solvent data such as solubility parameters, electron donor/acceptor numbers, and Kamlet-Taft solvatochromic parameters. All solvents were "AR" grade except for quinoline ("GPR"), and triethylamine ("LR"). Further purification of solvents by redistillation was considered unnecessary.

All solvents, and their relevant physical properties (not listed in other Tables), are shown in Table VIII. Molecular models are shown in Appendix 1.

2.3 COAL MODIFICATION

2.3.1 Densification

Two densified coal products were prepared for swelling measurements, viz. an ammonia digested LY1277 coal, and an ammonia digested thermally modified (350°C) LY1277 coal. Details of the preparation procedures, developed by Christie⁽⁹⁹⁾, are as follows:

Ammonia digested coal

33% NH₄OH was added to a LY1277 coal/water slurry at a ratio of 1:5 (by weight) and mixed using an IKA-WERKE Ultra-turrax mixer with a fine-grind head for 1 hour. The slurry was dried at room temperature in shallow trays before being crushed to size.

Table VIII.	Solvent Properties.
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Solvent	nt Molecular Weight	Molecular Molecular Size* Weight	Density at 25°C ^(96,97) ** 25°C Viscosity ⁽⁹⁷⁾	Dipole Moment at 20°C ⁽⁹⁸⁾ Dielectric Constant ⁽⁹⁸⁾ **	Vapour Pressure at 20°C ⁽⁹⁸⁾	H-bonding Capacity ⁽⁴⁹⁾	Polarity ⁽⁹⁷⁾	Solubility Parameters ⁽⁴⁹⁾ (MPa ^{1/2})						
	Ū	(Ų)	(g/cm*)	(cm³/mol)	(cp)^^	(x10 ⁻³⁰ C.m)		(hPa)			δο	δ_{d}	δ _p	δ_{h}
Water	18.02	≈ 11	0.9970	18.1	1.002 ²⁰	6.2	80.2 ²⁰	23	Strong	High	47.9	12.3	31.3	34.2
Methanol	32.04	≈ 18	0.7872	40.7	0.597 ²⁰	5.7	32.6 ²⁵	128	Strong	High	29.7	15.2	12.3	22.3
Ethanol	46.07	≈23	0.7873	58.5	1.200 ²⁰	5.7	24.3 ²⁵	59	Strong	High	26.0	15.8	8.8	19.4
Nitromethane	61.04	≈ 22	1.1286	54.1	0.620 ²⁵	10.3	35.9 ³⁰	36	Poor	Low	26.0	15.8	18.8	5.1
Ethylenediamine	60.10	≈ 25	0.8931	67.3	-	-	16.0 ¹⁸	12	Strong	-	25.2	-	-	-
N,N-Dimethyl formamide	73.10	≈ 28	0.9447	77.4	-	12.7	36.7 ²⁰	4	Moderate	Moderate	24.8	17.4	13.7	11.3
Dimethyl sulphoxide	78.13	≈ 26	1.0955	71.3	-	13.0	48.9 ²⁰	0.6	Moderate	Moderate	24.6	18.4	16.4	10.2
n-Propanol	60.10	≈ 27	0.8020	74.9	2.256 ²⁰	5.7	20.1 ²⁵	18.7	Strong	High	24.3	15.9	6.8	17.4
Acetonitrile	41.05	≈21	0.7793	52.7	0.345 ²⁵	11.5	37.5 ²⁰	97	Poor	Low	24.3	15.3	18.0	6.1
Isopropyl alcohol	60.10	≈ 28	0.7827	76.8	2.86 ¹⁵	5.5	18.3 ²⁵	43	Strong	High	23.5	-	-	-
Quinoline	129.16	≈ 37	1.0929 ²⁰	118.2	-	-	9.0 ²⁵	1	Strong	High	22.1	-	-	-
Pyridine	79.10	≈ 29	0.9786	80.8	0.974 ²⁰	7.3	12.3 ²⁵	20	Strong	High	21.9	18.9	8.8	5.9
Dioxane	88.11	≈ 30	1.0286	85.7	-	1.3	2.2 ²⁵	41	Moderate	Moderate	20.5	19.0	1.8	7.4
Nitrobenzene	123.11	≈ 34	1.1985	102.7	2.03 ²⁰	13.3	34.8 ²⁰	0.2	Poor	Low	20.5	17.6	12.3	4.1
Acetone	58.08	≈ 27	0.7856	73.9	0.316 ²⁵	9.0	20.7 ²⁵	233	Moderate	Moderate	20.3	15.5	10.4	7.0

* Calculated⁽⁹⁵⁾

** superscripts = temperature of measurement in °C

Table VIII (continued).	Solvent Properties.
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Solvent	Molecular Weight	Molecular Size*	Density at 25°C ^(96,97) **	nsity at C ^(96,97) ** At 25°C	Viscosity ⁽⁹⁷⁾	Dipole Moment at 20°C ⁽⁹⁸⁾ Dielectric Constant ⁽⁹⁸⁾ **	Vapour Pressure at 20°C ⁽⁹⁸⁾	H-bonding	Polarity ⁽⁹⁷⁾	Solubility Parameters ⁽⁴⁹⁾ (MPa ^{1/2})				
	Weight	(Ų)	(g/cm³)	(cm³/mol)	(cp)**	(x10 ⁻³⁰ C.m)	oonstant	(hPa)	oupdoity		δο	δ_{d}	δ_{p}	δ_{h}
Dichloromethane	84.93	≈ 25	1.3182	64.4	0.449 ¹⁵	5.3	9.1 ²⁰	453	Poor	Low	19.8	18.2	6.3	6.1
Methyl acetate	74.08	≈ 28	0.9273	79.9	0.381 ²⁰	5.7	6.6 ²⁵	220	Moderate	Moderate	19.6	-	-	-
Methyl ethyl ketone	72.11	≈ 31	0.7994	90.2	-	9.0	18.5 ²⁰	105	Moderate	Moderate	19.0	15.9	9.0	5.1
Benzene	78.11	≈ 31	0.8729	89.5	0.652 ²⁰	0	2.3 ²⁰	101	Poor	Low	18.8	18.3	1.0	2.0
Tetrahydrofuran	72.11	≈ 29	0.8800	81.9	-	5.4	7.4 ²⁰	200	Moderate	Moderate	18.6	16.8	5.7	8.0
Ethyl acetate	88.10	≈ 33	0.8942	98.5	0.455 ²⁰	5.9	6.0 ²⁵	97	Moderate	Moderate	18.6	15.2	5.3	9.2
Ethylene glycol dimethyl ether	90.12	≈ 34	0.8628 ²⁰	104.5	-	-	-	64	Moderate	-	17.6	-	-	-
Cyclohexane	84.16	≈ 35	0.7731	108.9	1.02 ¹⁷	0	2.0 ²⁰	104	Poor	Low	16.8	16.7	0	0
Diethyl ether	74.12	≈ 34	0.7080	104.7	0.2332 ²⁰	4.2	4.3 ²⁰	587	Moderate	Moderate	15.1	14.4	2.9	5.1
Triethylamine	101.19	≈ 41	0.7245	139.7	-	-	-	70	Strong	-	15.1	-	-	-
n-Hexane	86.18	≈ 40	0.6563	131.3	0.326 ²⁰	-	1.8 ²⁰	160	Poor	Low	14.9	14.8	0	0

* Calculated⁽⁹⁵⁾

** superscripts = temperature of measurement in °C

Thermally modified NH₃-digested coal

Ammonia digested coal (-20, +6 mm) was thermally modified under flowing nitrogen in a temperature controlled oven according to the following temperature profile: heat to 65°C and maintain for 11 hours; heat to 150°C in 15 minutes; heat to 200°C in 20 minutes; heat to 300°C in 45 minutes; heat to 350°C in 30 minutes and maintain for 1½ hours before cooling. This temperature regime was developed to yield a strong, non-friable product⁽⁹⁹⁾.

2.3.2 Acetylation

LYROM coal was O-acetylated following the procedure of Blom et al.^(2, 100); approximately 70 g of dry coal was added to a 1400 cm³ mixture of acetic anhydride and pyridine (1:2 by volume) and fine ground in-situ using an IKA-WERKE Ultra-turrax mixer with a fine-grind head for 5 minutes. This grinding treatment has been shown elsewhere⁽¹⁰¹⁾ to reduce the size of dry brown coal to less than 212 μ m. The mixture was refluxed with stirring under N₂ for 24 hours. The resultant slurry was cooled and then added to 3.5 litres of distilled water, before being filtered through a Whatman Nº 541 (qualitative) filter paper. The O-acetylated coal was washed with warm (<60°C) distilled water until the filtrate pH was slightly acidic (pH ≈ 6.5), dried overnight at 60°C under vacuum, and sealed in plastic bags prior to analysis.

In order to separate the effects of the pyridine from those of the acetylating agent (on the swelling behaviour of the coal), the above procedure was repeated without the addition of acetic anhydride.

2.3.3 Methylation

LYROM coal was O-methylated following the procedure of Liotta et al.⁽²²⁾; approximately 70 g of dry coal was added to 1060 cm³ of THF (700 cm³), 1 M aqueous tetrabutyl ammonium hydroxide (240 cm³), and iodomethane (120 cm³) and fine ground in-situ using an IKA-WERKE Ultra-turrax mixer with a fine-grind head for 5 minutes. The mixture was stirred overnight under N₂, filtered using a large Whatman (cellulose) Soxhlet extraction thimble, and washed with 5 litres of hot (>90°C) water.

The thimble was then placed in a Soxhlet extractor and the methylated coal was washed with hot distilled water under N_2 for 3 days. The thimble containing the coal was dried overnight at 60°C under vacuum and sealed in plastic bags prior to analysis.

In order to separate the effects of the THF from those of the tetrabutyl ammonium hydroxide (TBAH) and of the methylating agent (on the swelling behaviour of the coal), the above procedure was repeated without the addition of TBAH and iodomethane, and again without the latter.

2.3.4 Ion-Exchange

In order to isolate the effects on swelling of the major inorganic ions in the Yallourn and Morwell briquettes the respective dry coal feeds were separately acid-washed and ion exchanged with Na⁺, Ca²⁺, Mg²⁺, and Fe³⁺ (all as the chlorides).

The coal was thoroughly wetted prior to exchange, on the recommendation of Marshall⁽¹⁰²⁾, by overnight contact with distilled water using 20 litre plastic pails on a drum roller. The coal was then slurry transferred into glass columns with glass wool plugs inserted at the outlets and separating funnels secured at the inlets via rubber stoppers.

Stock solutions of HCl, NaCl, CaCl₂, MgCl₂, and FeCl₃ were prepared and the concentration of each was determined; HCl by titration against a "Volucon" KOH solution, and the other cations by atomic absorption spectroscopy (AAS) under conditions recommended in the Varian handbook⁽¹⁰³⁾.

The coal in the glass columns was then subjected to approximately 5 bedvolumes of each cation solution via the separating funnels so that the flow of cations through the bed was controlled by the head of solution above the column (Figure 11). This procedure ensured that residence (equilibration) times were approximately equal for all solutions. 0.2 M solutions were used for the monovalent cations, 0.1 M solutions for the divalent, and .066M for the trivalent cations. Breakthrough was confirmed by determination (as above) of the cation concentration of the effluents. The coal was then washed with 5 bed-volumes of distilled water to remove unexchanged cations and the chloride anion. Effective washing was verified in the case of the acid exchanged column by testing the pH of the column effluent immediately following ion-exchange (pH = 1), and again following water washing (pH = 4.5). Effective washing of the other exchanged coals was assumed.

The ion-exchanged coals were air dried for one week by spreading out in approximately 2 cm thick layers and turning the coal over daily using a suitable spatula. Subsamples of the coals were taken for exchangeable cation analysis, the results of which are shown in Table IX. The coals were then briquetted using the laboratory press described in section 2.3.5.



Figure 11. Apparatus for Ion-Exchange of Coals

Dry Briquette	Ion-Exchanged	Acid-Extractable Cation Content (% d.b.)						
Feedstock	Species	Na	Са	Mg	Fe	AI		
	Nil	0.07	0.05	0.12	0.20	0.03		
	H⁺	0.03	0.01	0.01	0.12	0.01		
Yallourn	Na⁺	0.37	0.03	0.02	0.27	0.02		
Tanourn	Ca ²⁺	0.02	0.39	0.02	0.24	0.02		
	Mg ²⁺	0.02	0.03	0.25	0.26	0.02		
	Fe ³⁺	0.02	0.01	0.02	0.88	0.02		
	Nil	0.10	0.69	0.35	0.28	0.01		
	H⁺	0.02	0.01	0.01	0.05	<0.01		
Morwell	Na⁺	0.80	0.44	0.05	0.26	0.01		
Morwen	Ca ²⁺	0.03	1.10	0.01	0.25	<0.01		
	Mg ²⁺	0.03	0.16	0.74	0.26	<0.01		
	Fe ³⁺	0.02	0.01	0.01	0.75	<0.01		

 Table IX.
 Acid-Extractable Cation Contents of Ion-Exchanged Coals.

2.3.5 Briquetting

Briquettes were produced in the laboratory using an Enerpac Press with a ram diameter of 73.25 mm. 15 g of air-dried coal was pressed in a die of 30 mm diameter at a gauge pressure of 220 bars (corresponding to 130 MPa on the briquette) for 10 seconds. A small amount of distilled water was sprayed onto the walls of the die before each pressing in order to lubricate the removal of the briquettes from the die. Briquettes were stored in loosely sealed plastic bags prior to analysis in order to facilitate a slow equilibration with the laboratory atmosphere. Swelling rates in water were measured at intervals of days/weeks in order to study the effects of ageing on weathering characteristics.

2.4 SWELLING MEASUREMENTS

Swelling is often measured by the weight increase of the sample, or by the amount of solvent lost from a calibrated reservoir⁽⁸⁸⁾. However the high porosity of most coals, and especially Victorian brown coals, means that they are able to absorb a significant amount of solvent without expanding by the corresponding volume⁽⁹⁴⁾. It is unsatisfactory simply to allow for the porosity of coals as determined by, for instance, helium and particle densities because the accessible pore volume varies considerably with the nature of the solvent and may be greater or less than that accessible to helium⁽⁹⁴⁾.

In order to overcome these difficulties, volumetric swelling may be measured <u>directly</u> by pycnometry using a glass vessel comprising a stem-shaped lid with capillary opening. By filling the pycnometer with a solvent of known density (at constant temperature) and fitting the lid so that excess solvent is expelled from the top of the capillary tube, the pycnometer volume (body and lid) can be accurately determined. By placing a sample inside the pycnometer prior to the introduction of solvent, the volume of solvent required to completely fill the pycnometer is reduced by an amount exactly equal to the volume occupied by the sample. Uptake of the solvent into the pore structure of the sample during

the analysis is avoided by prior equilibration (swelling and pore filling) of the sample in a separate sample of the solvent. Note that pycnometric swelling experiments can thus only be used for the measurement of equilibrium swelling values (as opposed to the measurement of rates of swelling).

The centrifuge method proposed by Hombach⁽³⁹⁾ may also be used for the <u>direct</u> measurement of volumetric swelling with some success⁽⁸⁸⁾. The sample is packed in a cylindrical glass tube and centrifuged. The height of the coal in the tube (h_1) is measured and solvent is then added and mixed with the sample. After some time the sample is centrifuged again and the height of the swollen coal in the tube (h_2) is measured. The volume swelling ratio (**Q**) is calculated as the swollen volume over the unswollen volume (h_2/h_1).

The centrifuge method may be expected to suffer from some inaccuracy due to differences in packing density between swollen and unswollen coals. Measurement of the height of a packed bed will be effected by the volume of interparticle voids. However, by ensuring that samples are finely ground prior to analysis, this technique has been demonstrated to yield reproducible results which are in agreement with those obtained using other techniques⁽⁸⁸⁾. The centrifuge method may be used to measure rates of swelling by recording h_2 at intervals until a constant height has been reached (equilibrium swelling).

2.4.1 Pycnometry

A clean, dry pycnometer was weighed and filled with distilled water at the laboratory temperature of 23°C, after which it was reweighed and the weight of added water determined. The volume of the pycnometer was calculated from the density of water at 23°C (0.9975415 g/cm³⁽⁹⁷⁾).

The density of each of the other six solvents to be used in pycnometry experiments was then determined by filling the pycnometer with each solvent in turn and determining the weight of solvent added (Table X).

Solvent	Density at 23°C
Water	0.9975 ⁽⁹⁷⁾
Methanol	0.7897
Ethanol	0.7911
Pyridine	0.9803
Acetone	0.7865
Benzene	0.8744
n-Hexane	0.6550

 Table X.
 Densities of Solvents Determined Pycnometrically.

Coals and coal products (-8.00, +5.60 mm) were dried overnight under a flowing stream of N_2 at 60°C. The coals were then evacuated for about 15 minutes using a rotary vacuum pump and solvent was introduced under vacuum (see Figure 12), after which evacuation was discontinued. This method of solvent introduction was chosen to prevent air, which may otherwise be trapped in the pore network, from excluding full and immediate solvent penetration⁽¹⁰⁴⁾. In initial experiments where solvent was added to the dried coals without prior evacuation, air bubbles were observed on the coal particles for some considerable time (extending to days in some cases). The coals were left in contact with solvent for 4 weeks, in which time equilibrium was deemed to have been attained.

Some coal was removed from the solvent and quickly damped on paper to remove excess solvent (based on the method of $Dryden^{(105)}$). It was then introduced to the dry pycnometer and its weight determined by subtracting the initial weight of the pycnometer ($MC_s + MS_i$ = mass of swollen coal + mass of imbibed solvent). Simultaneously, a separate sample of the solvent-laden coal was weighed and vacuum dried at 110°C in order to determine the quantity of imbibed solvent (both in %wt./wt. and in cm³/g). The assumption was made that the density of the imbibed solvent was equal to the solvent's bulk density⁽⁹⁴⁾. The weight of solvent laden coal in the pycnometer could then be converted to a dry weight (MC_d) and the volume of imbibed solvent (VS_i) could be determined.

The relevant solvent was quickly reintroduced to the coal in the pycnometer and the pycnometer was reweighed. The volume of the added solvent (VS_a) was calculated from its weight and density. The volume occupied by the swollen coal and imbibed solvent ($VC_s + VS_i$) was then calculated by difference from the pycnometer volume and expressed as the volume occupied (cm³) per dry unit weight ([$VC_s + VS_i$]/ MC_d = specific volume of swollen coal). The "skeletal" volume of the swollen coal



Figure 12. Apparatus for the Introduction of Solvent to the Sample Under Vacuum⁽¹⁰⁶⁾.

 (VC_s) , independent of the imbibed solvent, was calculated (again by difference) and divided by the dry weight of the coal. The inverse of this value (i.e. MC_d/VC_s) is effectively the density of the material in the given solvent.

2.4.2 Centrifuge Method

An attempt was made to measure swelling rates (see also, Section 2.4.3) using the centrifuge method as proposed for American sub-bituminous coals by Otake and Suuberg⁽¹⁰⁷⁾. Factory produced briquettes (Section 2.1) were ground to -212, +106 μ m and dried under N₂ at 60°C overnight. The dried briquette samples were added to centrifuge tubes and centrifuged at 2000 rpm for 3 minutes. The level of the coal in the centrifuge tubes (h₁) was measured using a travelling microscope.

Approximately 10 cm³ of prewarmed (23°C) solvent was added to each tube and the tubes were placed into a shaking water-bath at 23°C. The tubes were removed from the bath at intervals, centrifuged as above, and the height of the coal (h_2) was again measured. The volume swelling ratio (**Q**) was calculated as the swollen volume over the unswollen volume (h_2/h_1).

Unfortunately, this method was found to be inappropriate for lower rank coals because the rate of swelling was so fast that at least 90% of the total swelling was achieved inside the first time interval. This phenomenon has also been observed for a range of low rank coals from around the world by Jones et al.⁽⁸⁷⁾, who found the equilibrium swelling value to be reached within one hour of introduction of solvent to the coal.

In another set of experiments, LYROM coal and its O-methylated and Oacetylated derivatives (along with samples which had been treated with pyridine, THF and THF/TBAH - see Sections 2.3.2 and 2.3.3) were subjected to the same method in order to determine equilibrium swelling ratio only. In these experiments, no special precautions were taken to control the temperature (laboratory temperature 21±2°C). Coal to solvent ratio was kept approximately the same in all cases as it has been shown to have a significant effect on measured swelling ratios, although mostly at low coal/solvent ratios⁽¹⁰⁸⁾. Centrifuging was performed at 3,500 rpm for 3 minutes. Coal heights were measured by gently placing a lightweight hollow glass probe of known length on top of the centrifuged coal and measuring the height of the probe with a ruler. The probe had a flat sealed base and its top came to a sharp point to aid the accurate reading of its height. This method of measuring the coal height was made necessary due to the dark coloured extract solutions, which obscured visual detection of the coal. Although the method was necessarily crude, it allowed rapid comparison of equilibrium swelling of a number of coals in a large suite of solvents.

2.4.3 Swelling Rates

An adaptation of the Wykenham-Farrance consolidation test, commonly used in soil mechanics and similar to those used by Yost and Creasy⁽⁷⁾, Aida and Squires⁽¹⁰⁴⁾, and Woskoboenko⁽¹⁰⁹⁾, was used for measuring swelling rates. Two sets of apparatus were constructed:

A glass syringe (50 cm³), incorporating a ground glass plunger of 2.75 cm diameter, was modified to include a coarse glass frit at one end through which solvent was contacted with the sample. This apparatus was suitable only for crushed briquette samples (-8.50, +6.00 mm) and could also be completely evacuated to allow measurement of swelling rates without the complication⁽¹⁰⁴⁾ of displacement of air in the pores of the briquette by the solvent.

 A large glass cylinder, again incorporating a coarse glass frit at its bottom was fitted with a close fitting PTFE plunger of 7.46 cm diameter. This apparatus was suitable for whole briquettes however prior evacuation of the sample was not possible.

A digital displacement meter and processor (Mitutoyo) were used to measure the rise of the plunger in both cases. Ballotini spheres (Potter Industries Pty. Ltd., Grade Specification 22, -600, +425 μ m) were used as the supporting medium.

2.5 <u>COMBINED GRAVIMETRIC / VOLUMETRIC SWELLING</u> <u>MEASUREMENTS</u>

The apparatus used for adsorption/desorption measurements was similar to that used by Reucroft and Patel⁽⁴⁶⁾. A Cahn 1000 Vacuum Recording Electrobalance was used to monitor the mass of the sample which was suspended from the balance arm on a platinum platform previously tared using a calibration weight. A change in mass of the coal due to sorption was recorded as an electrical signal from the balance and was displayed on a Philips PM8251A chart recorder. The pressure was recorded via two MKS Baratron pressure gauges (Type 222B, 0-1000 Torr; Type 127A, 0-100 Torr) on an MKS Baratron PDR-C-2 digital display. Swelling was also able to be measured at each equilibrium pressure by incorporating an apparatus similar to that used by Stacy and Jones⁽⁶⁾ into the apparatus described above. An identical mass of the coal to that on the balance pan was suspended in a platinum wire cage so that it could be submerged in mercury at intervals in order to determine its change in volume. In this case the mercury displaced by the sample was not collected and weighed but instead its volume in a capillary sight-tube was recorded using a travelling microscope.

The samples were outgassed under vacuum by controlling the temperature of a heating tape around the sample hang-down tube to 60°C. Vacuum was applied via a mercury diffusion pump backed by a two-stage rotary pump. Joins in the

system were sealed using "black-wax" compound which was applied using a heatgun to soften the wax after it was found impossible to eradicate leaks when using the viton "O" rings supplied with the balance. The "black-wax" had a negligible vapour pressure. When the coal attained a constant weight it was cooled to room temperature under vacuum, and solvent vapour was introduced to the sample. The system was allowed to reach equilibrium, as determined by a constant pressure. Constant pressure was used as the criterion to indicate equilibrium conditions since it is more sensitive to variations in equilibrium conditions than is the sample weight⁽⁹¹⁾. A small amount of solvent adsorbed onto or desorbed from the sample will cause a significant change in system pressure due to the small volume of the sorption apparatus⁽⁹¹⁾.

The entire apparatus was enclosed in a constant temperature chamber, which was constructed from Perspex and insulated on the outside by sheets of high-density polystyrene foam. Inside the chamber was a bank of four 60 Watt lamps in series (i.e. a 240 Watt heater) that was controlled by a Eurotherm temperature controller linked to a K-type thermocouple inserted within the chamber. The temperature gradient throughout the chamber was kept to a minimum by virtue of a circulating fan mounted in the side of the chamber. The temperature in the laboratory environment was maintained at 22°C, and the temperature inside the chamber at 25.0±0.2°C.

Subsequent points were obtained either by increasing or reducing the pressure of the solvent, depending on whether an adsorption or a desorption process was being measured, and recording the change in mass and volume of the sample due to the amount of solvent adsorbed/desorbed. The apparatus was re-evacuated (using the rotary vacuum pump only) between each equilibrium point in order to ensure complete removal of any mercury vapour in the system.

2.5.1 Proton NMR Spectroscopy

Proton NMR analysis consists of detection of free-induction decay (FID) signals for coal samples swollen with deuterated solvents; the deuterated solvents being invisible to proton NMR⁽⁶²⁾.

The FID signals are resolved into two components and the initial amplitudes for these components are calculated. One type forms the Gaussian part of FID and is characterised by a short spin-spin relaxation time (9-12 μ s for coals of 65-81 wt.% dry, ash free (daf) C content, only slightly increased to 11-14 μ s in the presence of an efficient solvent, pyridine-d₅⁽⁶²⁾). The other type gives the exponential part of the FID signal and is characterised by a relaxation time longer than that of the Gaussian part by a factor of 15-30 for coal samples swollen with pyridine- $d_5^{(62)}$. Slow and fast-relaxing (or decaying) protons occur in two different types of environments, which are significantly different with respect to freedom of reorientation or rotational mobility. The fast-decaying proton population occurs in that part of the organic substance of coal that has very limited freedom for reorientation, no matter whether in an original coal sample or in the sample swollen with pyridine; therefore this population is attributed to the macromolecular network. The other population has much higher mobility and is attributed to relatively small coal molecules⁽⁶²⁾.

A manifold containing 14 individual samples of the coal in glass ampoules, suitable for insertion in the NMR probe, was attached to the combined gravimetric/volumetric apparatus. The coal, on the balance pan and in the ampoules, was exposed to deuterated water (99.9% deuterium; Cambridge Isotope Laboratories, Massachusetts, USA) in the same manner as described in Section 2.5. At each equilibrium pressure a single ampoule was removed from the manifold and simultaneously sealed against the atmosphere by melting the stem of the ampoule with an oxygen/acetylene flame. The ampoules were delivered to CSIRO Division of Coal and Energy Technology for NMR analysis.

2.6 SOLVENT EXTRACTION

Approximately 2 gram quantities of each dry briquette sample were immersed in ethanol, methanol, acetone and pyridine according to the method described in Section 2.4.1. After 4 weeks the extracts were recovered by filtering the solvents through a Whatman filter paper and the solvent was removed by rotary evaporation.

The amount of extract recovered, expressed as a percentage of the dry weight of briquette used, is shown in Table XI. It is interesting to note that the extent of extraction is the same for all solvents, in the order LY>Morwell>Yallourn. Pyridine extraction was 3 times that of the other solvents, due to the highly specific (reactive) nature of its interaction with the coals.

2.7 INFRARED SPECTROSCOPY

Samples of Yallourn, Morwell and Loy Yang briquettes from the pycnometric experiments (Section 2.4.1) were dried at 60°C under vacuum and prepared as KBr disks at a sample to KBr ratio of 2 mg:250 mg. The disks were dried under vacuum in a desiccator containing P_2O_5 , prior to analysis using a Perkin-Elmer 752 infrared spectrophotometer, in order to monitor any irreversible bond-modification caused by the swelling solvents via comparison with untreated briquette samples.

Acetone, ethanol, methanol and pyridine extracts of the three types of briquette were also treated in the above fashion in order to compare the structural features of the extracts with those of the initial coals.

Infrared spectra of the coals and collected extracts are included as Appendix 2.

Briquette	Solvent	Mass briquette (g)	Mass extract (mg)	Extraction (% wt./wt.)	
Yallourn		2.3109	66.9	2.89	
Morwell	Acetone	2.0490	70.9	3.46	
Loy Yang		2.0755	102.7	4.95	
Yallourn		2.2695	62.6	2.76	
Morwell	Ethanol	2.1628	69.0	3.19	
Loy Yang		2.1602	95.1	4.40	
Yallourn		2.2964	62.1	2.70	
Morwell	Methano	2.1227	61.6	2.90	
Loy Yang	-	2.1707	63.5	2.93	
Yallourn		2.0031	187.1	9.34	
Morwell	Pyridine	2.0293	218.9	10.79	
Loy Yang		2.0700	306.3	14.80	

Table XI.Extraction of Factory Produced Briquette Samples in Various Solvents.

2.8 **DENSITIES**

True (helium) densities were determined using a Micromeritics 1305 Multivolume Pycnometer. Samples were vacuum oven-dried at 60°C prior to density determinations.

<u>CHAPTER 3.</u>

SWELLING OF RUN-OF-MINE COALS

3.1 INTRODUCTION

Larsen et al.⁽²⁴⁾ describe the uptake of solvent molecules by coal as falling into two categories viz. diffusion through pores (imperfections in the packing of lamellae), and diffusion into the solid material. When two atoms in the coal structure are in contact with one another, and must separate to allow a diffusing molecule through, then the process is termed diffusion into the solid. When the diffusing molecule can move between the two atoms, without causing them to separate, then the process is termed diffusion through the pores. A third type of diffusion occurs when the diffusing molecule is larger than the separation between the atoms in the coal; so that they must move further apart to allow the diffusing molecule through. Although Larsen does not classify this type of diffusion, it would seem most properly to belong to the second type, i.e. diffusion through pores, albeit restricted (activated diffusion). The distinction between the two proposed modes of diffusion thus becomes less distinct; the case where atoms in the coal are touching prior to diffusion may be thought of as diffusion through pores, where the separation required is a maximum.

Indeed it may well be a misnomer to describe a crosslinked solid material as nonporous, because the measured porosity (or lack of it) can only be a function of the size of the molecular probe being employed. The analogy of a thick sponge provides a reasonable example of the different types of diffusion (Figure 13(a) shows a 2-dimensional view with cylindrical pores for simplicity). Whereas it is easy to rationalise the initial uptake of water by the sponge as being due to filling of the pores at the surface (filled areas), migration of the water throughout the entire thickness of the sponge is most often thought to involve <u>ab</u>sorption into the sponge material (shaded area). On the contrary, it is more likely that the water finds its way through a complicated network of interconnected pores which are too small to observe at anything greater than the molecular level (Figure 13(b)). Like polymer networks, the sponge will swell to accommodate the advancing water molecules and equilibrium will be attained when the pore system is completely full such that the elastic forces in the sponge "network" cannot tolerate further swelling.



Figure 13a. 2-Dimensional Representation of Coal Pore System with Outer Pores Filled and Inner Pores Inaccessible.



Figure 13b. 2-Dimensional Representation of Coal Pore System Showing Inter-Connecting Capillaries.

Consideration of Hirsch's models for coal structure (Figure 1) suggests that diffusion through the solid material can occur via diffusion between aromatic rings in the lamellae. Lamellae are bound together by hydrogen bonds, van der Waals forces, and occasional covalent bonding (such as bridging via etheric oxygen⁽¹¹⁰⁾) and if these forces are weak enough to be overcome by a diffusing molecule then the space between the aromatic rings can be considered to be pores. Diffusion through the centres of aromatic rings is possible, but could only be expected to account for a minor fraction of overall uptake. Although some solvents (e.g. pyridine) are capable of reacting with coals to break existing bonds and "open up" the structure for further uptake and swelling, other non-reactive solvents will reach equilibrium uptake as soon as the accessible pores are full.

Nelson et al.⁽⁹⁴⁾ attributed the extent of solvent induced swelling to three factors:

- (i) the affinity of the coal network structure for the solvent,
- (ii) the average size of network chains (or molecular weight) between crosslinks, and
- (iii) the flexibility of the network.

Of course specific solvents capable of rupturing crosslinking further complicate the issue by causing unexpectedly high network "flexibility". Low swelling values for some solvents in contact with coal may be caused by the restriction of solvent imbibition by one or more of the above factors⁽⁹⁴⁾.

The average molecular weight between crosslinks is not considered in the present work, and its measurement is an indefinite art^(27,69). Suffice it to say that the open pore structure of Victorian brown coals, as opposed to higher rank coals, lends itself to the imbibition of solvent molecules, so that steric factors are usually at a minimum. Densification of these coals via ammonia digestion (Section 2.3.1) or briquetting (Section 2.3.5) may, however, lead to a more closed structure. Swelling of these modified coals will be discussed in Chapter 4.

3.2 RESULTS AND DISCUSSION

Pycnometric swelling data for LY1277 are given in Table XII (see also Appendix 3). Figure 14 shows a plot of swollen volume versus solvent uptake and indicates that the initial volume of the LY1277 coal at zero solvent uptake, and hence zero swelling, is 0.6520 cm³/g. Great care should be taken in the interpretation of this result. It has been arrived at by extrapolating data based on swollen volumes, which include the volume occupied by the coal and the volume occupied by the imbibed solvent. It is tempting to take the inverse of this figure (1.534) as the apparent density of the coal. At zero uptake the volume of the imbibed solvent is, of course, zero, however it may be false to assume that the volume of the empty (original) porosity is identical to that of the solvent conceptually removed from it. Swelling, which as can be seen from Table XII is pronounced, is accompanied by enhanced solvent uptake. That quantity of imbibed solvent which is excess of the original pore volume must occupy "new" porosity, access to which is gained by swelling of the coal. It is most probable that the line of best fit shown in Figure 14 owes its steepness to the increasing amount of newly opened porosity accessed by solvents showing higher uptakes. Therefore, in the absence of the proposed phenomenon of pore opening, the line of best fit would intersect the abscissa in Figure 14 at a value much closer to 1.0. This would more closely reflect the apparent density of the dry coal sample⁽³²⁾.

The correlation coefficient for the line of best fit in Figure 14 is 0.999, indicating a remarkably constant relationship between uptake and swelling. This is somewhat surprising because it indicates that chemical specificity is relatively unimportant to swelling. Although chemical effects are presumably responsible for the increased uptake of some solvents (i.e. the most polar ones) compared to others, the relationship between uptake and swelling remains constant. Thus the extent of swelling is solvent specific, but the mechanism appears not to be.

	LY1277							
Solvent	Solven	Swollen volume						
	% wt./wt. (d.b.)	(cm ³ /g d.b.)	(cm³/g d.b.)					
Water	117.83	1.181	1.886					
Methanol	136.19	1.725	2.350					
Ethanol	161.62	2.043	2.735					
Pyridine	295.53	3.015	3.728					
Acetone	117.13	1.489	2.159					
Benzene	74.08	0.847	1.505					
n-Hexane	37.42	0.571	1.241					

 Table XII.
 Pycnometric Swelling Data for Loy Yang ROM Coal.



Figure 14. Swollen Volume versus Solvent Uptake for LY1277.

The fact that the gradient of the line of best fit is unequal to, and slightly greater than, 1 could be taken to indicate that the coal structure is over-relaxing a little to accommodate the absorbed solvent, i.e. absorption of 1 cm³ of solvent yields swelling of 1.0154 cm³. However, in view of the previous discussion, and given the porosity of the coal (approximately 44% d.b.⁽³²⁾) which could be expected to accommodate a quantity of capillary solvent <u>before</u> swelling occurred (see further discussion in Section 3.4), the gradient of the line of best fit in Figure 14 may merely be a good approximation to 1. Walker et al.⁽¹¹¹⁾ also found coal swelling in a pycnometer to exactly equal the volume of solvent imbibed by the coal.

The density of Loy Yang coal in each solvent (Table XIII) was calculated according to the following formula:

$$\rho_{c,dry} = \frac{w_{c,dry}}{\left[\upsilon_p - \frac{\left(w_t - w_p - w_{c,dry}\right)}{\rho_s} \right]}$$

where	$ ho_{c,dry}$	= density of the dry coal (g/cm ³)
	Wc,dry	= weight of the dry coal (g)
	Up	= volume of the pycnometer (cm ³)
	Wt	= total weight of pycnometer + coal + solvent (g)
	Wp	= weight of the pycnometer (g)
	$ ho_s$	= density of the solvent (g/cm^3)

The density of coal in water is undoubtedly affected by the presence or absence of polar groups in the coal. This accounts for the fact that low-rank coals, with their high oxygen content, generally have a relatively high density in water compared to high rank coals⁽¹¹¹⁾, which are strongly hydrophobic. However in this case the coal had been dried at 60° C under N₂, and was thus partially hydrophobic, explaining the lower density for this sample in water.

Solvent	Density of Coal (g/cm ³)
Water	1.419
Methanol	1.599
Ethanol	1.446
Pyridine	1.403
Acetone	1.494
Benzene	1.519
n-Hexane	1.494

Table XIII.Densities of LY1277 Coal in Various Solvents.

Note: Helium density = 1.394 g/cm³

The density of Loy Yang coal in methanol was the highest in the series of solvents tested. Franklin found that the densities of coals in water, and particularly in methanol, often exceed the corresponding helium density⁽⁸⁹⁾. It was suspected that either the coal or the methanol must decrease in volume and, since coal is known to swell on immersion in methanol, it was assumed that the methanol contracts⁽⁸⁹⁾. Dryden⁽¹⁰⁵⁾ found that when a liquid is adsorbed or imbibed by a porous solid, causing swelling or expansion of the solid phase, the total volume of the system is diminished. In relating the swelling of particles to the amount of liquid imbibed the value of this contraction must be known⁽¹⁰⁵⁾. Adsorbed methanol was found by Maggs to occupy 17% less volume than does free methanol⁽¹¹²⁾. In the current pycnometric studies it has been assumed that the density of imbibed solvent is identical to that of the bulk solvent (see

Section 2.4.1). This approach has been supported by Nelson et al.⁽⁹⁴⁾ and, much earlier, by Anderson et al.⁽⁸⁹⁾, who surmised that methanol may enter pores inaccessible to helium, or that it may form a complex with the coal which occupies less volume than the sum of the separate solid and liquid volumes.

The fact that all of the measured densities are greater for the organic solvents shown in Table XIII than for helium (1.394 g/cm³) is indicative of the greater penetrative powers of the solvent molecules. Since helium is a smaller "solvent" molecule than any of the other solvents used in the present study, any solvent penetration of coal which is greater than that which occurs with helium (high penetration \equiv high density) must be due to specific interactions (i.e. reaction) or to swelling. A very good measure of swelling can thus be given by the difference in accessibility of the solvent (measured by displacement techniques such as pycnometry) and that of helium⁽⁹⁴⁾. Nelson et al.⁽⁹⁴⁾ found very good correlation between the swelling of a range of coals and the differences between their accessibility to the solvent (methanol) and to helium.

Table XIV shows swelling ratios, Q = swollen volume/unswollen volume, for LY1277 calculated by dividing swollen volumes (Table XII) by the unswollen volume (0.6520 cm³/g) determined via Figure 14. Some solvents, most particularly pyridine and ethanol, have produced spectacular swelling of the dried

Table XIV.	Swelling	Ratios for	LY1277	Coal.
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Solvent	Q
Water	2.89
Methanol	3.60
Ethanol	4.19
Pyridine	5.72
Acetone	3.31
Benzene	2.31
n-Hexane	1.90

coal particles. The extent of swelling is more remarkable when it is considered that the swollen coal particles remained intact, i.e. they did not dissolve, although the extent of extraction (as indicated visually by the colour of the bulk solvents in contact with the coals) correlated extremely well with the measured Q values.

The densities shown earlier, in Table XIII, demonstrate that the solvents are unable to penetrate the LY1277 coal to the same extent. As discussed earlier, methanol appears to have the strongest penetrative powers, and densities measured in benzene, acetone and n-hexane were all relatively high. It is interesting then that swelling ratios in the latter three solvents were relatively low, whilst pyridine, which appeared to have low penetration (see Table XIII), was clearly the strongest swelling agent. Where solvent molecules of different molecular size are capable of penetrating a coal to the same extent, the molecules of greatest molecular size would be expected to induce the greatest swelling as the macromolecular network "relaxes" to accommodate the solvent molecules. However the clue to the strong swelling power of pyridine cannot be found in its molar volume (Table VIII), which is similar to that of benzene and acetone, and much smaller than that of n-hexane. Benzene has good access to the coal porosity (as evidenced by the data in Table XIII) but produces relatively low swelling. Whilst n-hexane has similar penetrative powers to acetone, the latter is a significantly more effective swelling agent, despite its lower molar volume. Clearly, the reason for enhanced uptake and swelling of some solvents compared to others lies in the chemical interactions between solvent and coal, rather than physical size effects alone.

Many researchers have excluded pyridine from swelling measurements because of the apparently specific nature of its interaction with coals (see Section 1.4). However it would appear, even with the limited number of solvents studied thus far, that the point of diminishing returns would soon be reached if some of the data was excluded on the suspicion of specific interaction with coal. There is strong evidence of such interaction with several of the solvents used. Obviously, interpretation of data in the presence of chemically specific interactions is tenuous unless more solvents, representing a
greater breadth of chemical properties, are added to the test suite. Since the pycnometric technique is relatively tedious when testing large numbers of solvents, the centrifuge technique (Section 2.4.2) was employed.

Aida and Squires⁽¹⁰⁴⁾ found that the centrifuge method was unable to detect the early stages of solvent swelling of Illinois No. 6 coal due to problems of solvent access to air-filled pores (see discussion in Section 2.4.1). These researchers developed a new method of measuring swelling using the apparatus shown schematically in Figure 15. A modified version of this apparatus was used in the current work to measure swelling rates (see Section 2.4.3). The new method was claimed to yield an advantage over the original centrifuge method in that the integrity of the coal bed was maintained throughout the swelling measurement⁽¹⁰⁴⁾. In support of this claim the authors noted the acute sensitivity of the new method to mechanical shock, and that any shock usually resulted in an instant drop in the reading (of bed expansion). It is more likely that the foregoing observation illustrates the measurement of creation or expansion of voids between particles and that the response to mechanical shock is the result of a realignment of the particles. Indeed, Aida and Squires explain different relative swelling ratios between the centrifuge and the new method as being due to the "involvement of non-swelling volume increases" such as particle-particle repulsions. They contend that the new method overcomes these forces via the pressure of the piston on the coal bed, however this explanation is at odds with the observation of sensitivity to mechanical shock. Centrifugation at high speed would be much more likely to overcome the problem of expansion of the void volume than the mere weight of the plunger. The centrifuge technique has been shown to yield the same results as those from gravimetric techniques⁽⁸⁸⁾.

Swelling data obtained using the centrifuge technique is given in Table XV for LYROM (October 1986) coal. Here also, swelling ratios are significantly lower than for the same solvents measured pycnometrically. However, the relativities are more or less preserved, and the technique has allowed fast comparison of swelling behaviour in a large range of solvents. Swelling behaviour is discussed in terms of the chemical properties of the solvents in the following Sections.



Figure 15. Apparatus for Measuring Liquid Phase Solvent Swelling of Coal⁽¹⁰⁴⁾.

Solvent	Q
Water	1.38
Methanol	1.56
Ethanol	1.65
Nitromethane	1.40
Ethylenediamine	1.91
Dimethyl formamide	2.72
Dimethyl sulphoxide	2.52
Acetonitrile	1.45
Isopropyl alcohol	1.65
Quinoline	1.25
Pyridine	2.48
Dioxane	2.05
Nitrobenzene	1.49
Acetone	1.71
Dichloromethane	1.22
Methyl acetate	1.43
Methyl ethyl ketone	1.63
Benzene	1.16
Tetrahydrofuran	2.09
Ethyl acetate	1.35
Ethylene glycol dimethyl ether	1.77
Cyclohexane	1.00
Diethyl ether	1.45
Triethylamine	1.14
n-Hexane	1.04

Table XV.Swelling Ratios for LYROM (October 1986).

3.2.1 Swelling vs. Solubility Parameter

A plot of swelling ratio versus solvent solubility parameter (see Table VIII) for both data sets (pycnometric and centrifuge swelling data) is shown in Figure 16. The classical bell-shaped curve discussed in Section 1.5 is apparent when considering only the seven solvents included in both methods of swelling determination (solid symbols). However, no trend is readily apparent when more solvents are studied, as shown by the hollow symbols. At best, both sets of data predict a similar maximum in the coal swelling at approximately 20-25 MPa^{1/2}. This prediction is significantly different from that of Karim⁽⁵⁸⁾ (33 MPa^{1/2}), however there is a paucity of commonly available solvents having solubility parameters around 33 MPa^{1/2} and, in view of the data presented in Figure 16, it would be unwise to place too much faith in the ability of the solubility parameter concept alone to predict the degree of coal swelling. Solvents having very similar solubility parameters exhibit a wide range of swelling abilities.

It is concluded that the solubility parameter estimated by Karim for Latrobe Valley brown coals⁽⁵⁸⁾ is unlikely and, in any event, reliance on this figure in the selection of suitable swelling solvents for brown coals would unfairly discriminate against several strong swelling agents having solubility parameters in the range 20-30 MPa^{1/2}.

Bodily et al.⁽¹¹³⁾ observed two maxima in a similar plot of swelling versus solubility parameter for a high rank coal; corresponding to pyridine and THF. The high swelling observed in pyridine was attributed to replacement of intra-molecular polar bonding in the coal molecule with hydrogen-bonds between the solvent and the coal, whilst that in THF (a less polar solvent) was attributed to the mechanisms predicted by the solubility parameter approach, i.e. swelling within the constraints of the hydrogen bonding in the coal without causing appreciable breakage of the crosslinks⁽¹¹³⁾. This hypothesis was rejected by Painter et al.⁽³³⁾ who pointed out that both pyridine and THF contain a lone-pair of electrons



• Pycnometric determination (LY1277)

 Centrifuge determination (LYROM October 1986) solid symbols indicate the same solvents as for pycnometric determination

Figure 16. Variation of Volumetric Swelling with Solvent Solubility Parameter.

and, as such, are *both* capable of hydrogen bonding with the coal network. The separation of the two solvents on the x-axis by virtue of their different solubility parameters was thus meaningless in terms of their propensity to swell the coal⁽³³⁾. Painter et al.⁽³³⁾ instead, expressed confidence in the approach of Marzec et al.⁽³⁾ (i.e. the electron-donor acceptor approach – Section 1.7), although a new measure of solvent hydrogen-bonding ability was introduced in preference to the "... physically... obscure..." donor and acceptor numbers of Gutmann. Painter et al. were able to show a good correlation between literature coal swelling data and the spectral shift in (FTIR) OH-stretching modes caused by hydrogen bonding between solvents and phenol⁽³³⁾.

As detailed in Chapter 1, the theory of Flory and Huggins, from which the solubility parameter concept was derived, expressly excluded specific interactions between solvent and polymer (or coal). Painter et al.⁽³³⁾ highlight the problems associated with using the Flory-Huggins theory in the presence of strong interactions such as hydrogen bonding. Larsen and Shawver⁽²⁾ avoided the difficulties caused by specific interactions by employing only non-polar solvents, however even with relatively non-polar bituminous coals, swelling was not large using these non-specific solvents. The swelling interaction between non-polar solvents and highly polar lower rank coals could thus be expected to be minimal (because like dissolves like; see Section 1.12). Indeed, a plot of solvent solubility parameter versus swelling ratio for a Texas lignite⁽²⁾ yielded a scatter-graph (rather than a bell-shaped curve) and it was concluded that regular solution theory failed to describe the interaction of solvents with coal of this rank⁽²⁾.

The higher rank coals to which the solubility parameter approach has been applied in the literature are higher in covalent bonding, lower in functional group content, and lower in hydrogen bonding than lower rank coals. Thus the list of solvents capable of specific interaction with higher rank coals is much smaller than that for Victorian brown coal. This would appear to cast doubt on the use of all but 7 solvents employed in this study, viz. the "poor" hydrogen bonding solvents (see Table VIII); nitromethane, acetonitrile, nitrobenzene, dichloromethane, benzene, cyclohexane and n-hexane. If the data points for these solvents are isolated, as shown in Figure 17, the bell-shaped curve is again apparent (with maximum swelling occurring at approximately 22 MPa^{1/2}). However, the utility of the solubility parameter approach to Victorian brown coal has to be seriously questioned when so few of a large suite of solvents qualify for inclusion in the analysis.

Figures 18 to 21 show attempts to correlate the observed swelling with one or other of the three-dimensional solubility parameters (see Section 1.5 and Table VIII). Maximum swelling was observed at a δ_d of 17-19 MPa^{1/2}, δ_{D} of 9-15 MPa^{1/2}, δ_{h} of 6-12 MPa^{1/2}, and δ_{a} of 10-20 MPa^{1/2}. With optimum values already determined for δ_0 (20-25 MPa^{1/2}), a good swelling solvent for Loy Yang brown coal might then be expected to have a total solubility parameter of \approx 22.5 MPa^{$\frac{1}{2}$}, and three-dimensional solubility parameters (δ_d , δ_p , δ_h , and δ_a) of approximately 18, 12, 9 and 15 MPa^{1/2} respectively. A dependence of swelling on hydrogen-bonding and other weak associative forces is consistent with an understanding that hydrogenbonding plays a key role in the structural integrity of low rank coals. The dispersive component of the solvent solubility parameter would appear to be the least critical to brown coal swelling, however its magnitude is governed by those of the other components. Table VIII shows that N,Ndimethyl formamide comes closest of the solvents studied here to satisfying the solubility parameter criteria listed above and, indeed, this solvent produced the largest swelling ratio for LYROM coal.

The lack of other solvents in this study having similar total, and threedimensional, solubility parameters to N,N-dimethyl formamide means that caution must be exercised in making any strong conclusions on the ability of the solubility parameter approach to accurately predict coal swelling. Nevertheless, use of both total and three-dimensional solubility parameters, rather than total solubility parameter alone, does appear to



Figure 17.Volumetric Swelling versus Solubility Parameter for Solvents with
Poor Hydrogen Bonding Capacity.



- Pycnometric determination (LY1277)
- Centrifuge determination (LYROM October 1986) solid symbols indicate the same solvents as for pycnometric determination
- Figure 18.Volumetric Swelling versus the Dispersive Component of Solvent
Solubility Parameter.



• Pycnometric determination (LY1277)

Figure 19.Volumetric Swelling versus the Polar Component of Solvent
Solubility Parameter.

Centrifuge determination (LYROM October 1986) solid symbols indicate the same solvents as for pycnometric determination



- Pycnometric determination (LY1277)
- Centrifuge determination (LYROM October 1986) solid symbols indicate the same solvents as for pycnometric determination
- Figure 20.Volumetric Swelling versus the Hydrogen Bonding Component of
Solvent Solubility Parameter.



- Pycnometric determination (LY1277)
- Centrifuge determination (LYROM October 1986) solid symbols indicate the same solvents as for pycnometric determination
- Figure 21.Volumetric Swelling versus the Associative Component of Solvent
Solubility Parameter.

provide some promise as a tool to predicting and understanding swelling behaviour.

3.2.2 <u>Swelling vs. Solvent Electron-Donor and Electron-Acceptor</u> <u>Numbers</u>

Solvent DN and AN data have been given in Chapter 1 (Table I). Figures 22 to 24 show swelling ratio versus DN, AN, and DN-AN respectively. A reasonable correlation is shown between Q and DN in Figure 22, with both the pycnometric and the centrifuge swelling data appearing to follow a similar trend to that observed by Marzec et al.^(3, 66). However the failure of water to swell the coal appreciably despite having a similar donor number to pyridine raises doubts about the significance of the correlation. Unfortunately, ethylenediamine is the only solvent in the test suite with an electron donor number of greater than 33 so it is difficult to ascertain whether the slight peak evident in the centrifuge data at a DN of approximately 27 is real. Surprisingly, in view of Marzec's results (Section 1.7), a relationship is shown between solvent AN and Q (Figure 23) for both sets of data (see below). The relationship between DN-AN and Q is slightly different to that shown in Figure 7, and is perhaps more likely, with Q showing a minimum at DN-AN = 0 (Figure 24) and rising either side of this point. Figure 10 illustrates that large differences between solvent DN and AN will result in a large amount of coal extract, and high extraction should also lead to large swelling values⁽⁶⁶⁾.

The bell shape curve of the Q versus AN plot (Figure 23) is remarkably similar to that of the plot of Q versus solvent solubility parameter shown in Figure 3. Indeed, a plot of solubility parameter versus AN shows a good correlation as shown in Figure 25. The correlation coefficient (r^2) of the straight line through data points for the non-alcohols in Figure 25 is 0.984. It is noteworthy that all three alcohols in the solvent suite form a separate straight line, which is lower with respect to δ and almost parallel with the main line, having a correlation coefficient of 0.996.



Figure 22. Variation of Swelling Ratio with Solvent Electron Donor Number.



Figure 23. Variation of Swelling Ratio with Solvent Electron Acceptor Number.





Figure 24. Coal Swelling Ratio versus Solvent DN-AN.



Figure 25. Solvent Solubility Parameter versus Electron Acceptor Number.

Given that a solvent with a high electron acceptor number would ordinarily be expected to contain an electron-deficient site, and that solubility parameter is a reasonable measure of solvent polarity⁽⁸⁾ (or the ability of a chemical group to withdraw electrons and create an electron-deficient site within the solvent) the relationship between δ and AN is not so surprising. The reason for the distinctive behaviour of the alcohols, whilst interesting, remains outside the scope of the present work. It is, however, worth considering the implications of electron acceptor numbers being directly proportional to solubility parameters, especially in light of the theories proposed by Marzec et al. (Section 1.7).

It has been shown in Figure 10 that the solvent electron acceptor number requirements for extraction of coal are such that low AN_s favours nucleophilic attack on the coal provided that DN_s is high, and high AN_s favours electrophilic attack on the coal provided DN_s is low. The definitions of high and low AN_s (33 and 21 respectively) appear to have been made rather arbitrarily, based only on the properties of the solvents being studied⁽³⁾. There were no examples of solvents having high AN_s and low $DN_s^{(3)}$. Figure 23 suggests that the optimum AN_s for swelling Loy Yang brown coals is centred around a value of approximately 15-20, and that swelling is reduced considerably when AN_s varies either side of this optimum. Solvents with very low AN_s (<15) and high DN_s might therefore be expected to produce only mild swelling of Loy Yang coals, which is in contrast to the model proposed in Figure 10. Unfortunately there are not enough solvents in the test suite with low AN_s /high DN_s to test this conclusively.

In contrast to the solubility parameter approach (which suffers from the uncertainty caused by specific interaction between coal and solvent), the electron donor/acceptor approach is *about* specific interactions and these trends show promise for the prediction of solvent swelling of brown coal.

3.2.3 <u>A Combined Solubility Parameter / Electron Donor-Acceptor</u> <u>Approach to Predicting Swelling</u>

The solubility parameter approach is useful only in the absence of strong polymer-solvent interactions (where \triangle S would become negative), and a number of modifications have been proposed to account for these cases. Hydrogen bonding⁽⁴⁹⁾ and dielectric constant⁽⁵⁴⁾ are often used as additional parameters to δ , however Billmeyer⁽²⁸⁾ points out that the point of diminishing returns is soon reached. In light of the correlation shown between solvent electron acceptor number and solubility parameter in Figure 25, a combined solubility parameter / electron donor-acceptor number approach to predicting swelling warrants some consideration. The possible advantage in using a combined approach is that variations from the "rule" may become less significant if diluted by consideration of other relevant solvent parameters.

It has been demonstrated that the swelling of Loy Yang coals in the present suite of solvents is a maximum when:

- (i) the total solubility parameter of the solvent is around 20-25 MPa^{$\frac{1}{2}$} (Figure 16), or when the absolute value of (δ -22.5) is closest to zero,
- (ii) the polar component of the solubility parameter of the solvent is around 9-15 MPa^{$\frac{1}{2}$} (Figure 19), or when the absolute value of (δ_{p} -12) is closest to zero,
- (iii) the hydrogen-bonding component of the solubility parameter of the solvent is around 6-12 MPa^{$\frac{1}{2}$} (Figure 20), or when the absolute value of (δ_h -9) is closest to zero,
- (iv) the electron acceptor number of the solvent is around 15-20
 (Figure 23), or the absolute value of (AN-17.5) is closest to zero, and

 (v) the difference between electron donor and electron acceptor numbers of the solvent (or the absolute value of DN-AN) is a maximum (Figure 24).

It follows then that swelling should be a maximum when the relation:

$$|DN - AN| - |(\delta_0 - 22.5)| - |(\delta_h - 9)| - |(\delta_p - 12)| - |(AN - 17.5)|$$
 is a maximum.

Figure 26 shows a plot of Q against the proposed relationship and a reasonable trend is evident, although use of this approach to predict swelling remains somewhat limited due to the scatter shown in the plot. Some solvents are able to swell the coals to more or less extent than would be expected from the discussion above. For example, water, which has both high donor and high acceptor numbers, and a solubility parameter of double the expected optimum, is able to swell LYROM coal to the same extent as nitromethane, which has a significantly higher acceptor number than its donor number, and a solubility parameter much closer to that predicted for the coal. Water has a strong hydrogen bonding capacity whilst nitromethane has low polarity and is unable to participate in strong hydrogen bonding.

3.2.4 Swelling vs. Kamlet-Taft Solvatochromic Parameters

The origin of the Kamlet-Taft approach, and values for solvatochromic parameters, are given in Section 1.8 and Table IV respectively. The Kamlet-Taft equation can be expressed as:

$$Q = Q_0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H + e\xi$$

where Q = predicted swelling ratio Q_0 = swelling ratio at time = 0, i.e. 1



- Pycnometric determination (LY1277)
- Centrifuge determination (LYROM October 1986) solid symbols indicate the same solvents as for pycnometric determination
- Figure 26.Prediction of Volumetric Swelling Ratio by a Combined SolubilityParameter / Electron Donor-Acceptor Approach.

Swelling data collected using the centrifuge technique were fitted (by iteration) to the solvatochromic parameters in Table IV for 17 solvents. Solvents for which ξ was unknown⁽⁶⁸⁾ were unable to be fitted, and those for which ξ was not given⁽⁶⁸⁾ were not included due to uncertainty on how to perform the iteration (i.e. whether to set ξ for these solvents to zero, or to exclude the final term from the Kamlet-Taft equation – different approaches yield slightly different results). The plot of measured versus predicted swelling ratio is shown in Figure 27 and shows a rough correlation only (r² = 0.50). Solvents more than 10% away from the line representing a perfect prediction are identified in order to illustrate that the "outlying" solvents fit the chemical groupings shown in Table IV.

The Kamlet-Taft approach is mathematically complex, and a little difficult to interpret. The extent of volumetric swelling predicted by the Kamlet-Taft equation is only a fair approximation to measured values and the merit of this approach appears to be questionable for the coal/solvent interactions studied thus far. The relative magnitudes of the calculated coefficients in the Kamlet-Taft equation (s, a, b, h, and e) are, however, of interest, because they provide a measure of the relative sensitivity of Q to the different solvent property scales⁽⁶⁸⁾. Iterative fitting of measured swelling with the Kamlet-Taft solvatochromic parameters yielded coefficient values of 1.74, -0.15, 0.70, -0.03, and 0.02 respectively (note that pyridine and quinoline were excluded from the calculation of coefficients, since they are the only solvents in the test suite with nonzero polarisability correction terms, and exclusion of this term, and the d coefficient, simplifies interpretation of the s coefficient). The solvent's ability to stabilise a charge by virtue of its dielectric properties (π^* scale) appears to be most important to coal swelling, whilst the ability of the solvent to donate an electron pair (as indicated by the β scale) also appears to be relatively important. Surprisingly, the solvent's electron acceptor ability (α scale) appears to slightly inhibit coal swelling. The h and e coefficients all but eliminate the effects of solvent solubility parameter and coordinate covalency on coal swelling.



Figure 27.Prediction of Volumetric Swelling Ratio using Kamlet-Taft
Solvatochromic Parameters.

Although the influence of solvent electron acceptor number and solubility parameter on coal swelling would appear, from Kamlet-Taft analysis, to be negative and minimal respectively, in apparent contradiction of the bell-shaped curve relationships found in Figures 16 and 23, it should be noted that the type of relationship observed (i.e. a distinct maximum in swelling at certain values of AN or solubility parameter, falling significantly either side of this maximum) is difficult to handle in a linear relationship such as the Kamlet-Taft equation. Solvent parameters with which coal swelling shows a linear increase, such as DN (Figure 22), are much more appropriate inclusions in a linear fitting exercise and a strong dependence of coal swelling on solvent DN is indicated by the Kamlet-Taft approach.

3.3 NATURE OF SOLVENT-INDUCED CHANGES TO COAL STRUCTURE

As mentioned in Section 2.1, factory produced briquette samples were used in some of the pycnometric swelling studies because of the relative ease of handling and of measuring the volume of the more compact material compared to run-of-mine coals. Swelling of briquetted coals *per se* is discussed in detail in Chapter 5. In this Section, the nature of solvent-induced coal structural changes is studied via an analysis of infrared spectra from the previously swollen briquette samples and of the collected extracts. All spectra are shown in Appendix 2 and assignment of frequencies to structural configurations is after Verheyen and Perry⁽¹¹⁴⁾.

The infrared spectra of collected coal extracts show the striking similarity of structure between extracts from all of the solvents and the parent coals. All major structural characteristics in the coal are represented in the extracts. Only the relativity of some structural features is changed between the extracts and the parent coals. Hydrogen bonded –OH stretching, centred at 3,430 cm⁻¹, has been reduced in the extracts, and aliphatic C-H stretching from -CH₃ and -CH₂- groups, seen at around 2,900 cm⁻¹, becomes relatively dominant. The relative strength of absorption by C=O stretching, due to carbonyl and carboxyl groups, at 1,710 cm⁻¹, compared to C⁻⁻⁻C stretching of aromatic and polyaromatic structures, at 1,630 cm⁻¹, is also altered. Whilst the latter is markedly dominant in all three parent coals, the former becomes an equal, if not greater, contributor to absorption in all extracts, with the exception of the Yallourn acetone extract. The doublet peaks centred at around 1,260 and 1,200 cm⁻¹ respectively in the parent coals, attributed to etheric oxygen, are also reduced in the extracts. These minor differences between the structural configuration of extracts and the parent coals are consistent with the extractable material being very similar to the coal in structure but with a higher ratio of aliphatic to aromatic carbon. The observed reduction in hydrogen bonded -OH stretching may be due to more complete removal of hydrogen bonded water in the rotary evaporated extracts than in the vacuum dried parent material. As etheric oxygen may be responsible for a portion of the covalent bonding in the parent coals⁽¹¹⁰⁾ it is not surprising that the smaller, more aliphatic material held within the coal network by ionic interactions is lower in these ether linkages.

The infrared spectra of pyridine extracts are similar for all three coals. They are also a little more detailed due to resolution of more structural groups than in the parent coals. The broad peak in the 3,400 cm⁻¹ region is flattened, and a previously unresolved peak occurs at 3,125 cm⁻¹ due to retention of pyridine⁽¹¹⁵⁾ by the extracted material. The small peak at 1,445 cm⁻¹ in the parent coal spectra, attributed to deformation vibrations in $-O-CH_3$ and $-CH_2$ - linkages, becomes significantly more prominent in the pyridine extracts. A small peak, that remains unresolved within a shoulder in the spectra of the parent coals, appears at 1,020 cm⁻¹ in the pyridine extracts. This is thought to indicate aliphatic ether linkages and it is noteworthy that the less specific solvents were unable to extract this type of material. Weak and poorly resolved peaks in the spectra of the parent coals at 835 and 625 cm⁻¹, attributed to C-H bending in aromatic and olefinic structures, is resolved into small distinct peaks.

The difference spectra shown in Appendix 2 show structural differences between the solvent swollen coals and the original coals as positive and negative peaks. Where a difference spectrum shows small peaks identical in shape and location to that of the original coal, it can be concluded that the weighting applied to the latter was slightly underestimated due to small variations in the quantities of coal material in each KBr disk. If the difference spectrum is a mirror image of that of the original coal (i.e. with valleys instead of peaks), the weighting applied to the solvent swollen coal may have been underestimated. It can be further concluded in these cases that solvent swelling has had no irreversible effect on the structure of the coal, as is the case for all solvents except pyridine. It should be remembered here that the majority of extractable material has been removed from the solvent swollen coal. The pyridine difference spectra are not direct, or mirror, images of the original coal spectra. They show that pyridine swollen coals have a reduced concentration of hydrogen bonded –OH stretching (3,430 cm⁻¹), reduced aliphatic C–H stretching (2,900 cm⁻¹), reduced C=O stretching due to carbonyl and carboxyl groups (1,710 cm⁻¹), and increased aromatic bending at 680 to 750 cm⁻¹. Pyridine is thus shown to destroy the original hydrogen bonding in the coal, perhaps by replacing intramolecular hydrogen bonds with similar bonds between the coal and the solvent, and to remove a significant portion of the aliphatic material from the coal.

3.4 <u>COMBINED GRAVIMETRIC / VOLUMETRIC SWELLING</u> <u>MEASUREMENTS</u>

Prolonged difficulties in commissioning the electromicrobalance due to problems with maintaining vacuum, together with experimental difficulties associated with coal dust fouling the mercury used to measure its volume, resulted in only two experiments being performed on the combined gravimetric/volumetric swelling apparatus. This result was extremely disappointing due both to the amount of time invested in this particular phase of the work, and to the promise that a technique such as this has for elucidation of a swelling mechanism. Gravimetric/volumetric measurements were made using water vapour and deuterated water vapour (see Section 3.4.1) as the adsorbate/swelling agents. The adsorption isotherm for water uptake on LYROM coal, determined gravimetrically, is shown in Figure 28. Allardice⁽⁹¹⁾ describes the different types of water found in run-of-mine brown coal in terms of a desorption isotherm. The adsorption process can be characterised by reversing the order of this description as follows:

As the pressure is increased, a monolayer of water is formed on the coal surface, resulting in the convex region of the isotherm at relative vapour pressures of up to approximately 0.2. The relatively straight-line region in the middle section of the isotherm is attributed to formation of an adsorbed multilayer. Next the water that condenses in the capillary structure of the coal is adsorbed giving the concave section of the isotherm at medium to high relative vapour pressures⁽⁹¹⁾. The monolayer capacity of the LYROM coal was determined by BET analysis⁽⁹⁵⁾ of the isotherm in Figure 28 to be 54.4 mg/g (correlation coefficient, r^2 =0.993). This value compares very well with the 56 mg/g determined by Allardice⁽⁹¹⁾ for Yallourn brown coal.

At each of the adsorption points shown in Figure 28, the volume of the coal sample was determined by enveloping the sample in liquid mercury (see Section 2.5). A plot of both volumetric uptake of water vapour (calculated from gravimetric data), and volumetric swelling of the coal, against p/p_o is shown in Figure 29.

Despite the scatter in the swelling data, it appears to be reasonably clear that the increase in volume of the LYROM coal with increasing partial pressure of water is almost identical to (or possibly slightly lower than) the volume of water adsorbed, up to p/p_0 of approximately 0.4. Thereafter, the degree of swelling begins to outpace uptake to the extent that, near saturation, the coal has swollen by over 0.05 cm³ more than the volume of water adsorbed. It is interesting to compare this observation with that made from pycnometric swelling of LY1277 coal (see Table XII and Figure 14) where total swelling also exceeded water uptake by over



Figure 28.Gravimetric Determination of the Adsorption Isotherm for WaterVapour on LYROM Coal.



Figure 29. Water Vapour Uptake and Volumetric Swelling of LYROM Coal.

0.05 cm³. Again, there is an indication that the coal structure is over-relaxing a little to accommodate the absorbed solvent. Nelson et al.⁽⁹⁴⁾ contend that solvent uptake due to physical adsorption and pore filling will not result in coal swelling. This appears to be a reasonable proposition, given that the high internal porosity of most coals should theoretically be able to accommodate a quantity of capillary solvent without causing swelling (see Section 3.2). However if that were the case, volumetric selling would be expected to lag behind uptake at higher partial pressures. Figure 29 shows the reverse to be true.

3.4.1 Proton NMR Spectroscopy

The gravimetric/volumetric measurements discussed in the previous Section were repeated using deuterated water vapour as the adsorbate/swelling agent. NMR measurements were completed on all of the samples equilibrated with D₂O at the various adsorption/desorption pressures. As illustrated in Figure 30, the variation with pressure of some of the NMR parameters, which reflect the extent of hydrogen mobility, shows a hysteresis effect. However this is believed⁽¹¹⁶⁾ to be an artefact arising from the removal of H₂O (produced by exchange with the coal) as well as D_2O during desorption. Therefore, at a given pressure, the H₂O/D₂O concentration ratio is lower on desorption than on adsorption. Because of the complication of deuterium exchanging with coal hydrogen, the NMR results do not provide conclusive information. In retrospect, the use of non-deuterated solvents would have provided for less confusion in interpretation of the NMR signals. Provided that the masses of solvent and coal are known at each pressure, it is a simple process to correct the NMR signal for the contribution of the solvent. Unfortunately, continued difficulties with the combined gravimetric / volumetric measurements (see previous Section) meant that further work in this area was not possible.

Also shown in Figure 30 is the volumetric swelling recorded during the adsorption and desorption of D_2O . A marked hysteresis is evident in the volumetric swelling data. The coal swells as increasing amounts of (deuterated) water are adsorbed. However, as the water is removed, the coal fails to shrink to its original volume. This hysteresis survives until close to zero relative pressure has been reached on the desorption curve.

Low-pressure hysteresis was also observed in gravimetric adsorption measurements by Allardice and Evans⁽¹¹⁷⁾ and was attributed to shrinkage/swelling effects. The explanation proceeded as follows:

"As adsorption proceeds, the brown coal swells, exposing more surface for adsorption. On desorption however this process is not reversed.

The water molecules will be desorbed in order of increasing bond strength, the weakly sorbed water being desorbed first. The water molecules which are strongly adsorbed at active sites all over the internal surface will be the last desorbed, and will delay the collapse or shrinking of the capillary structure to very low coverages. This mechanism would result in a hysteresis loop persisting well into the monolayer region."

In earlier work, Allardice had discussed the origin of hysteresis in terms of shrinkage/swelling of the coal during drying/rewetting and described adsorption as occurring at active sites on the surface with associated swelling exposing more active sites. Shrinkage of the structure during desorption was thought to be delayed by strongly adsorbed molecules acting as "props" between the pore walls⁽⁹¹⁾.





- Total mobile hydrogen (desorption)
- ▲ Most mobile hydrogen fraction (adsorption)
- Most mobile hydrogen fraction (desorption)
- delta Volume (Adsorption)
- □ delta Volume (Desorption)
- **Figure 30.** Variation of Hydrogen Mobility and Swelling of LYROM Coal with Uptake of (Deuterated) Water Vapour.

<u>CHAPTER 4.</u>

SWELLING OF MODIFIED COALS

4.1 INTRODUCTION

The discussion of swelling behaviour shown by ROM coals in Chapter 3 has centred on the coal being a highly crosslinked macromolecular structure containing smaller extractable species within its open pore network. Low rank coals have a high degree of oxygen functionality so that polar interactions associated with hydroxyl, phenolic, carbonyl and carboxylic groups are a feature of their molecular structure⁽¹²⁾. To further probe the coal structure using solvent swelling techniques it would be instructive to modify the coal structure by thermal, physical and chemical treatments and to observe the effects of these changes in structure on swelling behaviour.

The densification process employed here (see Section 2.3.1) is essentially the same as the "solar dried coal slurry" (SDCS) process developed by the SECV as a possible dry fuel substitute for briquettes⁽³²⁾. In the SDCS process ROM brown coal is slurry ground to very fine particle size (d_{50} <10 µm) in order to form a homogeneous paste, and then slowly air-dried to form a hard densified product (due to the elimination of macropores during grinding). In some cases alkali additives are used to chemically digest the coal and to help in binding the coal molecules. SDCS processing increases the physical but not the chemical rank of the coal⁽³²⁾. Woskoboenko et al.⁽¹¹⁸⁾ have concluded that the pore sizes in SDCS densified coal are largely determined by the size of the interstices between the constituent particles. Dissolved humic material is believed to be responsible for some pore filling⁽³²⁾. Hodges et al.⁽¹¹⁹⁾ have shown that the binding in ammonia digested SDCS coal is mainly ionic bridging between functional groups via cations, and van der Waals and hydrogen bonding. Infrared spectroscopy failed to reveal any signs of covalent bonding. Thermal modification of the ammonia-densified coal was employed as a means of "locking" the structure and forming a strong non-friable product⁽⁹⁹⁾.

The acetylation and methylation procedures employed here (see Sections 2.3.2 and 2.3.3) are known to remove internal hydrogen bonding in the coal by derivatisation of the hydroxyl functional groups^(22, 120). Acetylation may be inferior

to methylation in this regard, due to the use of pyridine under reflux conditions in the former. Since pyridine is known to be capable of structural rearrangement in coals, especially at elevated temperatures, the acetylation reaction may not be limited purely to capping of polar functional groups. Pyridine is used to swell the coal since acetylation is a mass-transfer limited reaction^(22, 120). Acetylation of coal is also incapable of permanent derivatisation of carboxylic acid groups in the coal since anhydride structures are easily hydrolysed⁽¹²⁰⁾. O-methylation, on the other hand, converts hydroxyl and carboxyl groups to the corresponding methyl ether and methyl ester, respectively, under reaction conditions so mild and so specific to these two acidic groups, that essentially no other chemical transformation takes place⁽²²⁾. Tetrabutyl ammonium hydroxide is used as a catalyst in the methylation of the oxygen functional groups, and has the added advantage of swelling the coal to aid mass-transfer (although mass-transfer is not rate-limiting for this reaction⁽¹²¹⁾.

Larsen and Shawver⁽²⁾ found O-acetylation and O-methylation to decrease the observed solubility parameter of a sub-bituminous coal from 19.4 to 18.6-18.8 MPa^{1/2}, consistent with a decrease in polarity caused by derivatisation of the oxygen functional groups (see Section 1.5). Kini et al.⁽¹²²⁾ have shown that acetylation of low rank coals yields lower values for heat of wetting in methanol, which is also consistent with a lower concentration of oxygen functional groups on the surface of the coal. Nair et al.⁽¹²³⁾ observed an increase in solubility of acetylated coal due to a decrease in non-covalent polar interaction (hydrogenbonding) between mobile and macromolecular phases of the coal structure. Nishioka⁽¹⁰⁸⁾ found O-alkylation to enhance swelling of lower rank coals in which ionic interactions were thought to be responsible for the stability of the network structure.

In this Chapter, the solvent swelling of thermally, physically, and chemically modified brown coals is investigated in terms of the solvent properties discussed in Chapter 3. A comparison of swelling for the modified coals with that of the untreated coals should help to further elucidate those structural features which govern the solvent swelling behaviour of Victorian brown coals.

4.2 RESULTS AND DISCUSSION

4.2.1 Chemical Densification and Thermal Modification

Pycnometric swelling data for ammonia digested LY1277 (ADLY) and ammonia digested thermally modified LY1277 (ADTMLY) are given in Table XVI (see also Appendix 4). Figures 31 and 32 show plots of swollen volume versus solvent uptake and indicate that the initial volumes of the ADLY and ADTMLY products at zero solvent uptake, and hence zero swelling, are 0.6585 and 0.7062 cm3/g respectively. As discussed in Section 3.2, care should be exercised in interpreting these values, however they are useful as measures of unswollen volume in later calculation of swelling ratios. They also provide a clear indication that the porosity of the ADLY has increased upon thermal treatment, consistent with the data of Christie⁽⁹⁹⁾. The correlation coefficient of the line of best fit in Figure 32 is not as convincing as those for the ROM coal (Chapter 3) or for the ADLY (Figure 31), however it represents a statistically significant correlation and the gradients of all of the lines of best fit remain approximately equal to 1.

The densities of the two samples in each solvent were calculated as shown in Section 3.2 and are shown in Table XVII. Measured densities for the modified coals are compared with unmodified LY1277 in Figure 33. ADLY may be expected to show less solvent penetration than the other samples due to its lower porosity. However, in reality, solvent accessibility appears to be insensitive to a reduction in pore volume, and chemical effects appear to be dominant. The density of the ADLY sample in water was high because, in fact, this sample readily disintegrated in water. The humic acid material believed to be responsible for the binding of coal molecules in alkali-digested coals (Section 4.1) is highly water-soluble. Filtration was necessary to retrieve the solid material from the water prior to pycnometry. Thermal treatment of the ADLY "locks" the structure of the coal against attack by water and
	LY1	I277 (NH₃ dige	ested)	LY1277		
Solvent	Calva		Sweller	Colvent unteke		
	Solvei	nt uptake	volume (cm ³ /g)	Solvent uptake		Swollen
	% wt./wt.	cm ³ /g (d.b.)		% wt./wt.	cm ³ /g (d.b.)	volume (cm³/g)
Water	93.47	0.937	1.611	11.05	0.111	0.867
Methanol	43.09	0.546	1.238	26.60	0.337	0.908
Ethanol	47.61	0.601	1.360	25.78	0.326	1.159
Pyridine	126.75	1.293	2.004	85.09	0.868	1.599
Acetone	11.57	0.147	0.859	32.87	0.418	1.107
Benzene	14.24	0.163	0.834	3.07	0.035	0.812
n-Hexane	14.25	0.218	0.787	3.07	0.047	0.658

Table XVI.Pycnometric Swelling Data for Modified LY1277 Coals.



Figure 31. Swollen Volume versus Solvent Uptake for NH₃-Digested LY1277.



Figure 32. Swollen Volume versus Solvent Uptake for NH₃-Digested/Thermally Modified LY1277.

Solvent	Density (g/cm ³)			
Convent	ADLY	ADTMLY		
Water	1.484	1.322		
Methanol	1.445	1.752		
Ethanol	1.319	1.200		
Pyridine	1.407	1.368		
Acetone	1.404	1.450		
Benzene	1.489	1.287		
n-Hexane	1.757	1.638		

 Table XVII.
 Densities of Modified LY1277 Coals in Various Solvents.

Note: Helium densities = 1.385, and 1.335 g/cm³ respectively.



□LY1277 ■ADLY ■ADTMLY

Figure 33. Comparison of Measured Densities between LY1277 and Modified LY1277 Coals.

the density of ADTMLY in water is lower than that of the non-thermally modified product despite the larger porosity of the former. Hydrophobic effects may also play an important role in differentiating between the ability of water to penetrate the different materials. Methanol is unique, amongst the seven solvents in the test suite, in its ability to penetrate the structure of ADTMLY to a greater extent than for either the original coal or the non-thermally modified coal. The reason for this is unclear. Table VIII shows that methanol is highly polar and has a strong hydrogenbonding capability, as do water and ethanol. The total and the threedimensional solubility parameters of methanol and ethanol are not greatly dissimilar. Table I shows similar electron DN/AN properties for methanol and ethanol. The only significant differences between methanol and ethanol are the much higher vapour pressure and the much lower viscosity of the former. Differences in solvent vapour pressure would not be expected to result in differences in behaviour in complete immersion experiments. It may be possible that the lower viscosity of methanol enables greater penetration of a constricted pore structure (all other things remaining equal), however this does not explain the greater affinity for the thermally modified product.

Table XVIII shows swelling ratios for the modified LY1277 samples, calculated by dividing swollen volumes (Table XVI) by the unswollen volumes derived from Figures 31 and 32. Swelling ratios for LY1277 and for ADLY and ADTMLY are compared in Figure 34. Some interesting observations are readily apparent:

Although the densities shown in Table XVII and Figure 33 illustrate a widely varying order of penetration for each solvent depending, it would seem, on chemical effects, the swelling ratios show:

 very much reduced swelling ratios for the densified coals compared to untreated LY1277

Cabuant	Q			
Solvent	ADLY	ADTMLY		
Water	2.45	1.23		
Methanol	1.88	1.29		
Ethanol	2.07	1.64		
Pyridine	3.04	2.26		
Acetone	1.30	1.57		
Benzene	1.27	1.15		
n-Hexane	1.19	0.93		

 Table XVIII.
 Swelling Ratios for Modified LY1277 Coals.



□LY1277 ■ADLY ■ADTMLY

Figure 34. Comparison of Swelling Ratios between LY1277 and Modified LY1277 Coals.

 (ii) lower swelling ratios for the thermally modified coal than for the ammonia digested coal without thermal modification.

The higher than expected swelling of the ADLY in water has been explained above, whilst the anomalous behaviour of acetone results more from a failure of acetone to swell the ADLY to the extent expected, than from an exaggerated swelling of the ADTMLY. It would seem that the ability of acetone to swell the ADLY is reduced by a combination of only moderate hydrogen-bonding capacity, together with a relatively high molar volume (i.e. a chemical and a steric barrier to swelling). Swelling ratios of less than unity, such as that for the ADTMLY in n-hexane, appear to indicate that the coal/solvent system occupies less volume than did the original coal (i.e. coal shrinkage). However, this is unlikely, especially in the case of such a non-specific solvent as n-hexane. A more reasonable explanation for the apparent decrease in coal volume may be that the solvents provide lubrication between coal particles under the influence of the applied centrifugal force. The particles may then realign in a configuration with slightly less void volume. This is only evident when negligible coal swelling occurs. Hence, the positive swelling ratios measured for other coal/solvent combinations using the centrifuge technique may be slightly underestimated.

Generally, the observed comparison of swelling ratios in Figure 34 is consistent with the ADLY having a higher density and more rigid structure than the LY1277⁽¹²⁴⁾. Thermal treatment of the ADLY results in even greater structural rigidity and an increased resistance to swelling.

Table XIX shows the differences between swelling of the untreated and modified LY1277 coals. The solvents can be grouped according to the magnitude of the reduction in swelling caused by alkali digestion and thermal modification. Leaving the ADLY/water swelling to one side due to the solubility discussed above, benzene and n-hexane suffered an 80% reduction in the amount by which they are able to swell LY1277

Solvent	∆V (Swollen Volume – Unswollen Volume) cm³/g					
Convent	LY1277	ADLY	% reduction	ADTMLY	% reduction	
Water	1.23	0.95	22.76	0.16	86.99	
Methanol	1.70	0.58	65.88	0.20	88.24	
Ethanol	2.08	0.70	66.35	0.45	78.37	
Pyridine	3.08	1.35	56.17	0.89	71.10	
Acetone	1.51	0.20	86.75	0.40	73.51	
Benzene	0.85	0.18	78.82	0.11	87.06	
n-Hexane	0.59	0.13	77.97	-0.05	108.47	

 Table XIX.
 Swelling of LY1277 and Modified LY1277 Coals.

after alkali-digestion. The two alcohols suffered a 65% reduction, and pyridine a 55% reduction. The magnitude of the reduction in swelling of the coal in pyridine after alkali digestion is surprising given pyridine's ability to strongly disrupt hydrogen bonding and the importance of this type of bonding to the integrity of alkali digested coals⁽³²⁾. Conversely, the reduction in the ability of n-hexane and benzene to swell the coal after alkali digestion is not surprising. Neither of these two solvents is capable of disruption of hydrogen bonding (see Table VIII). To a rough approximation, the 80% reduction in swelling for these non-specific solvents gives a measure of the extent of interparticle hydrogen bonding in the alkali digested coal.

4.2.2 Chemical Alteration of Surface Functionality

Swelling data obtained using the centrifuge technique for chemically modified LYROM derivatives are given in Table XX. The measured swelling ratios are compared with those obtained for the parent coal (Table XIV) in Figures 35 and 36. Figure 35 shows that solvents can be grouped according to their relative abilities to swell the parent and the acetylated coals (see Table XXI). With few exceptions, notably the amines (ethylenediamine and triethylamine), all strong and moderate hydrogen bonding solvents (see Table VIII) had their swelling power significantly reduced by acetylation of the LYROM coal (only minor reductions in swelling were observed for methyl acetate and methyl ethyl ketone). Nitromethane and acetonitrile, both poor hydrogen bonding solvents with reasonably high solubility parameters, saw little change in swelling power due to acetylation of the coal, whilst the poor hydrogen bonding solvents with lower solubility parameters were able to swell acetylated LYROM to a greater extent than the parent coal. Measured swelling ratios for cyclo- and n-hexane were too low in all cases to give confidence in the relative comparison between swelling of LYROM and its acetylated derivative.

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	Q				
Solvent	Pyridine	yridine		THF/TBAH	
	Extracted	Acelylated	Extracted	Extracted	Methylated
Water	DNW	1.04	1.05	1.05	DNW
Methanol	1.42	1.30	1.37	1.42	1.18
Ethanol	1.41	1.41	1.53	1.15	1.15
Nitromethane	1.35	1.40	1.17	1.09	1.23
Ethylenediamine	1.93	1.85	1.78	1.55	1.90
Dimethyl formamide	2.37	1.89	2.46	1.93	2.18
Dimethyl sulphoxide	2.48	2.06	2.48	1.97	2.24
Acetonitrile	1.36	1.37	1.28	1.23	1.24
Isopropyl alcohol	1.51	1.37	1.55	1.49	1.22
Quinoline	1.27	1.11	1.16	1.34	2.15
Pyridine	2.24	1.80	2.28	1.97	2.12
Dioxane	1.85	1.63	1.79	1.27	1.64
Nitrobenzene	1.32	1.57	1.22	1.18	1.56
Acetone	1.45	1.45	1.46	1.24	1.38
Dichloromethane	1.24	1.37	1.04	ND*	1.36
Methyl acetate	1.42	1.39	1.29	1.14	1.35
Methyl ethyl ketone	1.59	1.49	1.59	1.37	1.39
Benzene	1.13	1.27	1.04	1.08	1.18
Tetrahydrofuran	1.90	1.61	1.85	1.41	1.75
Ethyl acetate	1.34	1.34	1.22	1.13	1.30
Ethylene glycol dimethyl ether	1.75	1.51	1.57	1.16	1.47
Cyclohexane	1.04	1.00	0.96	0.96	0.97
Diethyl ether	1.24	1.31	1.22	1.13	1.17
Triethylamine	1.21	1.34	1.27	1.05	1.07
n-Hexane	1.04	0.96	0.96	0.95	1.03

Table XX.Swelling Ratios for Chemically Modified LYROM Coals.

DNW denotes "did not wet"; ND denotes "not determined" (THF/TBAH extracted LYROM floated on the CH2Cl2)



Figure 35. Comparison of Swelling Ratios between LYROM and its Chemically Modified Derivatives.



Figure 36. Comparison of Swelling Ratios between LYROM and its Chemically Modified Derivatives.

 Table XXI.
 Relative Swelling Power of Solvents for Untreated and Acetylated

 LYROM.

Q(LYROM) > Q(Acetylated)	Q(LYROM) ≈ Q(Acetylated)	Q(LYROM) < Q(Acetylated)
Water	Nitromethane	Nitrobenzene
Methanol	Ethylenediamine	Dichloromethane
Ethanol	Acetonitrile	Benzene
Dimethyl formamide	Ethyl acetate	Triethylamine
Dimethyl sulphoxide	Cyclohexane	
Isopropyl alcohol	n-Hexane	
Quinoline		
Pyridine		
Dioxane		
Acetone		
Methyl acetate		
Methyl ethyl ketone		
THF		
1,2 - Dimethoxyethane		
Diethyl ether		

The enhanced swelling of the acetylated coal in non-polar solvents is as expected due to the reduction of polar crosslinking in the coal and an increase in the relative importance of dispersive forces in the coal solvent system^(2, 125). The reduced swelling of the acetylated coal in the more polar solvents is also to be expected because the very basis of the specific interactions between these solvents and the untreated coal (i.e. hydrogen bonded crosslinks) has been removed.

Figure 36 shows the solvents grouped according to their relative abilities to swell the parent and the methylated coals (see Table XXII). It is apparent that methylation has had a slightly smaller effect on solvent swelling than acetylation due to the presence of some poor hydrogen bonding solvents (nitromethane and acetonitrile) in the left hand column of Table XXII. Again, the differentiating factor for these two solvents may be their higher solubility parameters. Along with the two acetates, which are moderate hydrogen bonding solvents, the poor hydrogen bonding solvents exhibit similar swelling powers for the parent and for the methylated coals. Here too, the behaviour of the amines appears to be anomalous, with little difference between their swelling of the methylated and of the parent coals. It is interesting to note here the strong enhancement of swelling in quinoline after methylation. Quinoline is a strong hydrogen bonding solvent (Table VIII) with a moderately high solubility parameter, and might be expected to behave like the other strong hydrogen bonding solvents. Quinoline also has a very high molar volume (118 cm³/mole), and the enhanced swelling of the methylated coal may be an artefact of the lack of swelling of the untreated coal due to steric constraints.

As with the acetylated coal, O-methylated coal swells less than its parent in highly polar solvents due to a reduction in the secondary crosslinking so susceptible to attack by these solvents. The relative indifference of the non-polar solvents to methylation of the coal may indicate some residual oxygen functionality, possibly as a result of the omission of an acidification step (to protonate cation-exchange groups) in the methylation procedure.
 Table XXII.
 Relative Swelling Power of Solvents for Untreated and Methylated

 LYROM.

Q(LYROM) > Q(Methylated)	Q(LYROM) ≈ Q(Methylated)	Q(LYROM) < Q(Methylated)
Methanol	Ethylenediamine	Quinoline
Ethanol	Nitrobenzene	
Nitromethane	Dichloromethane	
Dimethyl formamide	Methyl acetate	
Dimethyl sulphoxide	Benzene	
Acetonitrile	Ethyl acetate	
Isopropyl alcohol	Cyclohexane	
Pyridine	Triethylamine	
Dioxane	n-Hexane	
Acetone		
Methyl ethyl ketone		
THF		
1,2 - Dimethoxyethane		
Diethyl ether		

The seemingly anomalous behaviour of the amines may be attributable to an overestimation of their hydrogen bonding capacity, especially in the case of triethylamine (a tertiary amine). Since tertiary amines are without an N– H bond, the opportunity for them to participate in hydrogen bonding is limited in comparison with primary and secondary amines (ethylenediamine is a primary amine). Hydrogen bonding can still occur via the lone pair electrons associated with the nitrogen in triethylamine, however the primary and secondary amines can also hydrogen bond via the electron-starved hydrogen atoms. Hence, ethylenediamine has the ability to form hydrogen bonds with itself, which may also diminish its capacity to engage in solvent to coal interactions. The influence of solvent solubility parameter on swelling of the modified coals is discussed in the following Section.

It is interesting to compare the swelling behaviour of the solvent extracted intermediaries in Table XX and Figures 35 and 36 with that of the derivatised coals. Pyridine extraction is known to destroy secondary crosslinking in coals⁽¹²⁵⁾ and is often insisted upon before any classical treatment of coal swelling according to regular solution theory^(2, 93). It would therefore be expected that pyridine extraction alone could account for the observed changes in swelling for polar and non-polar solvents attributed to the acetylation reaction above. Figure 35 shows that, for many of the more polar solvents, acetylation of oxygen functionality has had a greater effect on the reduction in swelling when compared to pyridine extraction alone. For only a few of the polar solvents, notably ethanol and acetone, pyridine extraction gave an identical reduction in swelling to acetylation. The non-polar solvents, nitrobenzene, dichloromethane and benzene, which would be expected to swell coals in which the hydrogen-bonding capability had been removed to a greater extent, swelled the acetylated coal more than the pyridine extracted coal. This is confirmation that whilst pyridine may destroy the secondary crosslinking in the coal, it does not remove or cap the surface oxygen functionality, which can contribute to specific

interaction with highly polar solvents and limit interaction with non-polar solvents. Acetylation does succeed in neutralising these modes of interaction, so that dispersive forces gain prominence and swelling in non-polar solvents increases.

Figure 36 shows that for all of the non-polar solvents (see Table VIII), with the exception of acetonitrile, swelling is substantially reduced after extraction with THF and/or TBAH, but returns to approximately the same level as the parent coal after methylation. The moderate polarity solvents all show substantial reductions in swelling after extraction of the coal with THF and/or TBAH, followed by a slight increase in swelling after methylation (albeit significantly lower than for the parent coal). Conversely, the alcohols see a strong reduction in swelling power upon methylation of the coal. This indicates that O-methylation has capped a large part of the oxygen functionality in the coal and prevented it from taking part in hydrogen-bonded crosslinking. The fact that swelling of the methylated coal does not significantly exceed that of the untreated coal, together with the observation from Table XX that swelling of acetylated coal exceeds that of methylated coal in the non-polar solvents, may be further indication of incomplete O-methylation.

4.2.3 Swelling vs. Solubility Parameter

A comparison of swelling ratio versus solvent solubility parameter (see Table VIII) for the untreated LY1277, and the densified and thermally modified coals is shown in Figure 37. The classical bell-shaped curve discussed in Section 1.5 is apparent for both of the treated coals (again, however, note the limited number of solvents in the test suite).

The relative position of the curves in Figure 37 is evidence of the densification and thermal modification processes as discussed in Section 4.2.1. All seven solvents (polar and non-polar alike) yield



Figure 37. Variation of Volumetric Swelling with Solvent Solubility Parameter.

significantly reduced swelling ratios for ADLY compared to LY1277. It appears that a much higher concentration of hydrogen bonding (or ionic bonding/van der Waals forces⁽¹¹⁹⁾) is present than in the untreated coal, and that many of these coal-coal bonds are thermodynamically more favourable (and thus stronger) than prospective coal-solvent bonds. The fact that such a specific solvent as pyridine experiences a significantly greater resistance to swelling after ammoniadigestion suggests that many of the new crosslinks in this coal are covalent (i.e. much stronger than hydrogen bonding). This is in contrast to the findings of Hodges et al.⁽¹¹⁹⁾ who were unable to detect covalent bonding by infrared spectroscopy.

Thermal modification of the ammonia-digested compact leads to reduced swelling for all solvents, which may indicate that the structure has adopted a minimum energy configuration due to decarboxylation and replacement of hydrogen bonds with additional covalent bonds⁽⁶⁴⁾.

The position of the peaks for each curve in Figure 37 is identical at approximately 20-25 MPa^{1/2}. On first reflection, this is not a great recommendation for the utility of solubility parameter theory for brown coals and brown coal derived products, since structural changes of the type discussed in Section 4.2.1, and above, would be expected to shift the curves relative to the abscissa. Just as solvents are assigned three-dimensional solubility parameters, all contributing to the total solubility parameter (Section 1.5), structural changes to coals which result in a greater degree of covalent or hydrogen bonding should be reflected in a change in the solubility parameter of the coal. However, any conclusions on the utility of solubility parameter theory, based on such a small suite of solvents, are tenuous at this stage.

A greater number of solvents are included in the plot of swelling ratio versus solubility parameter, for LYROM and its O-acetylated and O-methylated derivatives, shown in Figure 38. As was the case for the



Figure 38. Variation of Volumetric Swelling with Solvent Solubility Parameter.

untreated LYROM (see Figure 16), the trend apparent for the smaller suite of solvents disappears completely, and a large degree of scatter is evident in the swelling data. However, if the data points for the "poor" hydrogen bonding solvents (see Table VIII) are again isolated, as shown in Figure 39, the bell-shaped curve becomes apparent again. There is also a slight possibility that the maxima for the curves in Figure 39 are shifted towards lower solubility parameters as the coal is derivatised. As discussed above, this reduction in the solubility parameter of derivatised coals might be expected, due to the reduction in the ability of the coal to enter into hydrogen bonding, either with itself or the solvent. Caution must again be exercised in the interpretation of this data due to the small number of solvents which qualify as being non-specific for brown coals. Attempts (not shown here) to further resolve any trend in swelling versus solubility parameter in terms of the three-dimensional parameters were unconvincing.

4.2.4 <u>Swelling vs. Solvent Electron-Donor and Electron-Acceptor</u> <u>Numbers</u>

Figures 40 to 42 show swelling ratio versus DN, AN, and DN-AN respectively for LYROM and its O-acetylated and O-methylated derivatives. The data in Figure 40 follows a similar trend to that observed by Marzec et al.^(3, 66). Whereas a slight peak occurs in the swelling data for LYROM at a DN of approximately 27, the peak appears to shift to approximately 30 after derivatisation of the oxygen functional groups in the coal. Unfortunately, ethylenediamine is the only solvent in the test suite with an electron donor number of greater than 33 so it is difficult to ascertain whether the peaks are real. However it is worth considering how the tentatively proposed shift fits with the decrease in hydrogen-bonding capacity of the coal after O-derivatisation of the coal.



Figure 39.Volumetric Swelling versus Solubility Parameter for Solvents with
Poor Hydrogen Bonding Capacity.



Figure 40. Variation of Swelling Ratio with Solvent Electron Donor Number.



Figure 41. Variation of Swelling Ratio with Solvent Electron Acceptor Number.



Figure 42. Coal Swelling Ratio versus Solvent DN-AN.

High solvent electron donor numbers are indicative of high polarity and strong hydrogen bonding capacity. It was shown in Section 4.2.2 that highly polar solvents are capable of swelling untreated coal to a greater extent than O-acetylated or O-methylated coals. Conversely, non-polar solvents were able to swell the derivatised coals to a greater extent than the untreated coal. However, this does not preclude the possibility that, all other things remaining equal in a given suite of solvents, a higher polarity might lead to greater swelling of the derivatised coals. Indeed, what might be expected from the relative behaviour of the polar and nonpolar solvents, after derivatisation of the coal, is a flattening of the swelling/solvent DN curve as the non-polar solvents become more powerful, and the polar solvents less powerful, than they were for the original coal. Figure 40 shows that this is the case, and the premise of a shift of the peak in the curve towards solvents with higher electron donor numbers is entirely consistent with the structural changes believed to be occurring due to derivatisation of the oxygen functionality in the coal.

A shift in peak is also apparent in the plot of swelling versus solvent electron acceptor number (Figure 41). The apparent shift in maximum swelling from an AN of 15 – 20 (see Section 3.2.2) to an AN of at least 20 is consistent with the shift in the same direction of the peak in swelling versus solvent DN discussed above. High solvent electron acceptor numbers are also indicative of high polarity and strong hydrogen bonding capacity. Figure 42 shows a similar relationship between DN-AN and swelling ratio as was shown in Figure 24.

4.2.5 <u>A Combined Solubility Parameter / Electron Donor-Acceptor</u> <u>Approach to Predicting Swelling</u>

A combined solubility parameter / electron donor-acceptor number approach to predicting swelling was employed with mild success for untreated Loy Yang brown coals in Section 3.2.3 (See Figure 26). In view of the structural changes effected by O-derivatisation, it is worth revisiting the combined approach in order to test the significance of apparent trends identified in the previous Section.

It has been demonstrated that swelling of the derivatised coals in the present suite of solvents is a maximum when:

- (i) the total solubility parameter of the solvent is around 21.5 MPa^{$\frac{1}{2}$} (Figure 39), or when the absolute value of (δ -21.5) is closest to zero,
- (ii) the electron acceptor number of the solvent is around 20 (Figure 41), or the absolute value of (AN-20) is closest to zero, and
- (iii) the difference between electron donor and electron acceptor numbers of the solvent (or the absolute value of DN-AN) is a maximum (Figure 42).

It follows then that swelling should be a maximum when the relation:

 $|DN - AN| - |(\delta_0 - 21.5)| - |(AN - 20)|$ is a maximum.

Figure 43 shows a plot of Q against the proposed relationship and, again, only a reasonable trend is evident, with some significant scatter shown in the plot. However it is noted that the anomaly in the comparison of swelling in water and in nitromethane for Loy Yang coal, as discussed in Section 3.2.3, is not apparent for the derivatised coals.



Figure 43.Prediction of Volumetric Swelling Ratio by a Combined SolubilityParameter / Electron Donor-Acceptor Approach.

4.2.6 Swelling vs. Kamlet-Taft Solvatochromic Parameters

Swelling data for the derivatised Loy Yang coals was fitted (by an iterative technique) to the solvatochromic parameters in Table IV (see also Section 3.2.4). The plots of predicted versus measured swelling ratio for the acetylated and methylated coals are shown in Figures 44 and 45 respectively. Both show a reasonable correlation ($r^2 = 0.63$ and 0.85 respectively). A line representing a perfect prediction has been included in both plots and the solvents that sit greater than 10% away from this line have been identified.

Iterative fitting of measured swelling with the Kamlet-Taft solvatochromic parameters (see Section 3.2.4) yielded coefficient values of 1.06, -0.21, 0.55, -0.02, and 0.17 respectively for the acetylated coal, and 1.85, -0.14, 0.25, -0.04, and 0.27 respectively for the methylated coal. The effects of coal modification on the Kamlet-Taft coefficients are shown in Figure 46.

The solvent's ability to stabilise a charge by virtue of its dielectric properties (π^* scale) appears to be most important to swelling of all three samples (it is unclear why the magnitude of the **s** coefficient is smaller for the acetylated than for the methylated coal). The ability of the solvent to donate an electron pair (as indicated by the β scale) also appears to be relatively important, however this importance diminishes as the coal is derivatised and the hydrogen bonding capacity of the coal is diminished. This is in accordance with an expected reduction in the affinity of solvent electron donor sites for alkylated, compared to protonated, oxygen functional groups. Whilst the solvent's electron acceptor ability (α scale) appears to slightly inhibit coal swelling, for all three coal types, the negative **a** coefficients are probably a reflection on the fact that strong electron acceptors are not often strong electron donors – the latter being the most likely to interact with functional groups in coals.

The **h** coefficients all but eliminate the effects of solvent solubility parameter on coal swelling for all three coals. However the **e** coefficient, which was insignificant for the untreated LYROM, becomes a little more significant for the derivatised coals. Interpretation of this phenomenon is difficult, however, in simple terms, it may confirm the general tendency noted from Tables XXI and XXII for the higher ξ parameter solvents (triethylamine and quinoline) to more strongly swell the derivatised coals than the untreated LYROM.



Figure 44.Prediction of Volumetric Swelling Ratio using Kamlet-Taft
Solvatochromic Parameters.



Figure 45.Prediction of Volumetric Swelling Ratio using Kamlet-Taft
Solvatochromic Parameters.



LYROM Acetylated Methylated

Figure 46. Comparison of Kamlet-Taft Coefficients between LYROM and its Chemically Modified Derivatives.
<u>CHAPTER 5.</u>

VICTORIAN BROWN COAL BRIQUETTES

5.1 INTRODUCTION

Background to the manufacture of briquettes from Victorian brown coal is given in Section 1.11, along with discussion on possible binding mechanisms, and on the weathering problems affecting briquettes produced from Morwell coal. Briquettes are widely believed to be predominantly held together by hydrogenbonding forces, and it is presumably these forces that are weakened in the disintegration of the briquettes in stockpiles. In this Chapter, both factory and laboratory produced briquettes are probed with organic solvents and with water. Swelling is measured and discussed in terms of the bonding within the briquetted structure.

5.2 FACTORY PRODUCED BRIQUETTES

Pycnometric swelling data for factory produced Yallourn Township, Morwell and Loy Yang briquettes are given in Table XXIII (see also Appendix 5). Figures 47 to 49 show plots of swollen volume versus solvent uptake and indicate that the initial volumes of the Yallourn Township, Morwell and Loy Yang briquettes at zero solvent uptake, and hence zero swelling, are 0.6322, 0.6325, and 0.6218 cm³/g respectively. As discussed in Section 3.2, care should be exercised in interpreting these values, however they are useful as measures of unswollen volume in later calculation of swelling ratios. As was the case for the ROM coal (Chapter 3), the correlation coefficients for the lines of best fit in Figures 47 to 49 are 0.99, and the gradients of the lines of best fit are approximately 1.

The densities of the briquette samples in each solvent were calculated as shown in Section 3.2 and are shown in Table XXIV. The densities in water are lower than might be expected, as discussed in Section 3.2, because drying under N₂ at 60°C makes the surface of the coal somewhat hydrophobic. Although the same drying treatment was employed here, the briquette samples had experienced much higher temperatures than 60°C in their production process, both in drying of the raw coal before briquette production (at temperatures in excess of 100°C),

 Table XXIII.
 Pycnometric Swelling Data for Factory Produced Briquettes.

Solvent	Yallourn Township			Morwell			Loy Yang		
	Solvent uptake		Swollen	Solvent uptake		Swollen	Solvent uptake		Swollen
	% wt./wt.	cm ³ /g (d.b.)	volume (cm ³ /g)	% wt./wt.	cm³/g (d.b.)	volume (cm ³ /g)	% wt./wt.	cm ³ /g (d.b.)	volume (cm ³ /g)
Water	38.23	0.383	1.105	40.70	0.408	1.108	32.64	0.327	1.056
Methanol	83.01	1.051	1.804	75.02	0.950	1.617	86.37	1.094	1.700
Ethanol	97.17	1.228	2.006	87.14	1.101	1.838	93.00	1.176	1.870
Pyridine	286.67	2.924	3.580	273.32	2.788	3.436	286.60	2.924	3.567
Acetone	92.01	1.170	1.717	83.98	1.068	1.571	87.79	1.116	1.631
Benzene	21.49	0.246	0.861	19.72	0.226	0.855	21.24	0.243	0.866
n-Hexane	12.68	0.194	0.708	12.51	0.191	0.776	11.35	0.173	0.736



Figure 47.Swollen Volume versus Solvent Uptake for Yallourn Township
Briquette.



 Figure 48.
 Swollen Volume versus Solvent Uptake for Factory Produced

 Morwell Briquette.
 Morwell Briquette.



Figure 49.Swollen Volume versus Solvent Uptake for Factory Produced Loy
Yang Briquette.

Solvent	Density of Briquette (g/cm ³)					
Solvent	Yallourn	Morwell	Loy Yang			
Water	1.386	1.429	1.372			
Methanol	1.329	1.499	1.649			
Ethanol	1.287	1.358	1.439			
Pyridine	1.526	1.543	1.555			
Acetone	1.827	1.988	1.943			
Benzene	1.626	1.589	1.604			
n-Hexane	1.945	1.709	1.779			

 Table XXIV.
 Densities of Factory Produced Briquettes in Various Solvents.

Note: Helium densities = 1.415, 1.434 and 1.410 g/cm³ respectively

and in the presses due to frictional forces on the coal. It is interesting to note the greater penetration of water for the Morwell briquette than for the Yallourn and Loy Yang briquettes in view of the weathering problem described in Section 1.11, however the difference is not as large as may have been expected.

Measured densities for LY1277 and for briquetted Yallourn, Morwell and Loy Yang coals are compared in Figure 50. The briquette samples may be expected to show less solvent penetration than LY1277 due to their compressed porosity (see Section 2.1). However, in reality solvent accessibility is insensitive to a reduction in pore volume (essentially only macropore collapse) and chemical effects appear to be dominant, confirming the similar observation for the ammonia-digested coals in Section 4.2.1. Whilst the densities of all four samples in water are relatively similar, both alcohols show densities in the order Loy Yang briquette \approx LY1277 > Morwell briquette > Yallourn briquette. The observed differences are likely to be due to the different levels of carboxyl and hydroxyl functional groups on the coal surface to which highly polar solvents have a great affinity⁽³²⁾. Of the highly polar solvents have a great affinity, all but water (which is influenced by the higher level of carboxylate cations) generally show the same orders of penetration for the coal samples.

Pyridine is rather less discriminatory than the alcohols, and its ability to penetrate the briquette samples is higher than that for the LY1277. The specific nature of the interaction between pyridine and coal has been discussed in Sections 1.4 and 3.2, and its great ability to disrupt hydrogen bonding is readily apparent from Figure 50.

The briquette densities measured in acetone were very high, and much greater than that for unbriquetted LY1277. The enhanced penetrative power of acetone for briquettes is consistent with observations of higher levels of extraction (see Table XI) and greater disintegration than was observed for the alcohols. Benzene and n-hexane were also capable of extensive penetration of the briquette particles, although they are not strong swelling agents and are unable to disrupt hydrogen bonding. No extraction was observed for these solvents (i.e.



□LY1277 ■Yallourn Township ■ Morwell 13/5/88 ■Loy Yang 7/5/86

Figure 50. Comparison of Measured Densities between LY1277 and Yallourn, Morwell and Loy Yang Briquettes.

solvents remained uncoloured after 4 weeks of contact with the briquette samples). The ability of benzene, and especially n-hexane to strongly penetrate the briquette samples without causing appreciable extraction or swelling may be related to the low viscosities of these solvents (Table VIII) – acetone also has a low viscosity – which will in turn impact on the surface tension and wetting angles for these solvents when exposed to the coal surface.

Table XXV shows swelling ratios for the briquette samples calculated by dividing swollen volumes (Table XXIII) by the unswollen volumes derived from Figures 47 to 49. Swelling ratios for LY1277 and for briquetted Yallourn, Morwell and Loy Yang coals are compared in Figure 51. Some interesting observations are apparent:

- (i) The swelling of Morwell briquette in water was identical to that of the Yallourn Township briquette. This is a most surprising finding given the well-documented weathering problems associated with Morwell briquettes. The reason for this better than expected result is discussed further below.
- (ii) The hydrogen bonding responsible for briquette integrity significantly reduces swelling for most solvents employed here when compared to the unbriquetted LY1277. However pyridine is capable of completely disrupting the hydrogen bonds between coal particles in the briquette, so that the swelling of the briquettes in pyridine is identical to that observed for unbriquetted coal.
- (iii) Swelling of all three briquette samples is essentially the same for a given solvent. Swelling is more sensitive to the type of bonding in the briquette than to surface chemical differences between the coals used in their production.

Table XXVI shows the differences between briquette swelling (average of all three briquette types) and unbriquetted LY1277 swelling. The solvents can be

Cabrant	Q					
Solvent	Yallourn	Morwell	Loy Yang			
Water	1.75	1.75	1.70			
Methanol	2.85	2.56	2.73			
Ethanol	3.17	2.91	3.01			
Pyridine	5.66	5.43	5.74			
Acetone	2.72	2.48	2.62			
Benzene	1.36	1.35	1.39			
n-Hexane	1.12	1.23	1.18			

 Table XXV.
 Swelling Ratios for Factory Produced Briquettes.



□LY1277 ■Yallourn Township ■ Morwell 13/5/88 ■Loy Yang 7/5/86

Figure 51. Comparison of Swelling Ratios between LY1277 and Yallourn, Morwell and Loy Yang Briquettes.

	ΔV (swollen volume-unswollen volume) cm ³ /g					
Solvent	LY1277	Briquettes (average)	% reduction			
Water	1.23	0.46	62.64			
Methanol	1.70	1.08	36.56			
Ethanol	2.08	1.28	38.69			
Pyridine	3.08	2.90	5.84			
Acetone	1.51	1.01	33.04			
Benzene	0.85	0.23	73.03			
n-Hexane	0.59	0.11	81.31			

 Table XXVI.
 Reduction in Swelling of Coal Due to Briquetting.

grouped according to the magnitude of the reduction in swelling caused by briquetting. Benzene, n-hexane, and water suffered a 60-80% reduction in the amount by which they are able to swell low rank coal after briquetting. The two alcohols suffered a 36-40% reduction, and acetone a slightly lower reduction (33%). Finally, as mentioned above, no significant reduction of swelling in pyridine was observed after briquetting of the coal.

The reduction in the ability of n-hexane and benzene to swell the coal after briquetting is not surprising in view of the popular theory of hydrogen bonding being responsible for the integrity of the briquetted coal. Neither of these two solvents is capable of disruption of hydrogen bonding (see Table VIII). Hexane, in particular, is almost incapable of swelling the briquette samples at all (Figure 51). To a rough approximation, the 70-80% reduction in swelling for these non-specific solvents gives a measure of the extent of interparticle hydrogen bonding in a briquette.

That water, a good swelling solvent for unbriguetted LY1277 with a strong hydrogen bonding capacity (Table VIII), suffered a large reduction in swelling power (60%) after briquetting may be explained in part by the increased hydrophobicity of briquettes compared to coal dried under less severe conditions. However the observed reduction in swelling would appear to be too large to attribute solely to hydrophobic surface effects. It may be true also that water is not an especially strong swelling agent for briquettes because briquette moisture is already playing in integral role in the hydrogen bonding between particles in the briquette⁽³¹⁾. There is no readily apparent thermodynamic motive for the disruption of a hydrogen bond between coal particles, involving a water molecule, by another water molecule. It is true that all coal materials were dried at 60°C under N₂ prior to pycnometry experiments, however there are no reports of briquettes falling apart after extensive drying well below the optimum moisture content for binderless briquetting ($\approx 15\%^{(31)}$), despite the importance of water to the hydrogen bonding process. The water that forms bridges between functional groups on the coal surface must be strongly bound and difficult to remove thermally without decomposing the coal to char⁽⁹¹⁾.

The alcohols are capable of disrupting only some (\approx 50%) of the hydrogen bonding in the briquette, whilst acetone is capable of disrupting about 55% of the hydrogen bonding. This order is despite the alcohols having a strong hydrogen bonding capacity, whilst that of acetone is only moderate (Table VIII).

The differences between the reductions in swelling shown in Table XXVI for these three solvents are small, however, and maybe they should be grouped together.

Swelling of the Morwell briquette was identical to that of the Yallourn Township briquette, which was contrary to the expected result based on its weathering behaviour. Pycnometric experiments were conducted on -8.00, +5.60 mm briquette fragments, so that internal stresses could not develop as significantly as for whole briquettes.

Green et al.⁽²⁰⁾ describe experiments in which sub-bituminous coal was exposed to n-propylamine vapour for varying lengths of time followed by air-drying to determine the degree of reversibility of the observed swelling. Swelling was found to be reversible after short contact times with the solvent vapour, however it was irreversible if contact times were large enough to allow substantial swelling. The observed irreversibility was attributed to fractures or dislocations within the coal due to mechanical stresses created by uneven swelling of the network⁽²⁰⁾, with the non-uniform swelling being due to kinetic effects or to differences in the swelling behaviour of the microscopic subcomponents (vitrinite, fusinite etc.) within the coal. Kinetic effects are seen where the inner regions of the coal particles are penetrated by the solvent at different rates to the outer regions. The swelling of the most accessible regions produces large stresses when constrained by the more rigid inner regions. This difference in swelling may be expected to occur even if the inner and outer regions of the coal have the same equilibrium swellability⁽²⁰⁾. It should be noted here that when similar experiments were performed on wafer-thin sections of a homogeneous vitrinite from Illinois No. 6 coal even advanced swelling was completely reversible⁽²⁰⁾. This would illustrate the important effect of the comparatively unswollen inner regions of

larger pieces of coal on the irreversibility of advanced swelling.

The weathering of Morwell briquettes is believed to be due to the internal stresses caused by uptake of moisture, and the associated swelling. Thus further tests were conducted to examine the effect of particle size on observed particle decrepitation.

The following Morwell briquette samples were prepared and immersed in water without prior drying (as per water immersion testing employed by Chiodo⁽⁸²⁾):

- (i) Whole briquette
- (ii) Approx. ¹/₂ briquette
- (iii) Approx. 4 cm x 1 cm fragments
- (iv) Approx. 2 cm x 1 cm fragments
- (v) Approx. 1 cm x 1 cm fragments

Previous briquette factory experience (anecdotal) was that <u>freshly produced</u> Morwell briquettes quickly disintegrated when immersed in water, whilst those produced from Yallourn Township coal remained intact indefinitely. None of the samples above showed any signs of disintegration after 6 hours, after which time the water was drained and the samples were placed in an air-forced oven at 60°C overnight. Bad cracking was evident after overnight drying except for the 1 x 1 cm fragments. The samples were cooled to room temperature and immersed in water once more, whereby the cracks appeared to widen after about 1 hour, especially for the larger particles. It was clear that differential expansion within the briquette particles was responsible for the observed surface cracking because the smallest particles did not crack appreciably.

5.2.1 Swelling Rates

An attempt was made to measure swelling rates for factory produced Yallourn briquettes in a small suite of organic solvents using the centrifuge method as proposed for American sub-bituminous coals by Otake and Suuberg⁽¹⁰⁷⁾ (see Chapter 2). Swelling curves are shown Figure 52.



Figure 52. Swelling Rates for Factory Produced Yallourn Briquettes.

Unfortunately, this method was found to be inappropriate for lower rank coals because the rate of swelling was so fast that at least 90% of the total swelling was achieved inside the first time interval. This phenomenon has also been observed for a range of low rank coals from around the world by Jones et al.⁽⁸⁷⁾, who found the equilibrium swelling value to be reached within one hour of introduction of solvent to the coal.

The tendency of the strong swelling solvents to show a peak in the initial stages of the swelling curve followed by a gradual relaxation to the equilibrium position has also been noted by Takanohashi et al.⁽¹²⁶⁾ for a range of coals in N-methyl pyrrolidinone (NMP).

5.3 LABORATORY PRODUCED BRIQUETTES

5.3.1 Effects of Ion-Exchange

The poor weathering resistance of Morwell coal briquettes has been largely attributed⁽¹²⁷⁾ to the high concentrations of carboxylate cations in the coal, mainly Ca and Mg. It is believed that these cations render the coal hydrophilic and, when exposed to high humidity, rapid hydration of the cations results in rapid swelling and disintegration of the briquettes. Ionexchanged calcium has been shown to reduce hydroliquefaction yields for low rank coals^(128, 129), possibly because Ca²⁺ ions can act as a crosslink between coal fragments to form -COO⁻...Ca²⁺...⁻OOC- bridges⁽⁸⁾. The same is likely to be true of other divalent cations (including magnesium). The extent of cation exchange has been shown to be inversely proportional to the degree of swelling and extraction of a Beulah Zap lignite in pyridine⁽¹³⁰⁾ because of the ability of divalent cations to covalently bind oxygen functionalities, providing crosslinks (monovalent cations are probably capable of electrostatic crosslinking)⁽¹³⁰⁾. Similarly, removal of alkali and alkaline earth ions from sub-bituminous coal by SO2-treatment resulted in enhanced swelling due to reduced coal-coal interactions⁽¹³¹⁾.

Figure 53 shows the effects of cation exchange of Yallourn and Morwell coals on both the rate and extent of swelling in water. Two clear trends are evident. Firstly, the initial rate of swelling of the briquetted Morwell coal is significantly greater than for the Yallourn coal in all cases. Secondly, the magnesium-exchanged samples exhibited the greatest rate and degree of swelling in water for both Morwell and Yallourn coals.

Chiodo⁽⁸²⁾ concluded that swelling would be influenced by exchanged cations in the order monovalent > divalent > trivalent, on the basis that sodium-exchange resulted in greater swelling of Yallourn and Morwell coals than barium-exchange. On the other hand, McAllan et al.⁽¹³²⁾ identified exchanged calcium and magnesium as being major contributors to briquette weathering, whilst sodium had little effect and acid-washing improved water resistance. However, the inorganic cation content of the coal alone was insufficient to explain the very rapid weathering of Morwell briquettes. The latter results are difficult to interpret clearly since McAllan et al. used a loading technique (contacting the coal with chloride or acetate solutions of each cation and evaporating to 15% moisture content). This has the dual complicating effects of failing to clearly delineate between ion-exchanged and physically incorporated cationic species, and of retention of significant quantities of the anion. Indeed, McAllan et al. found that when loaded as the chloride, the cations under test exhibited lower water uptake than when loaded as the acetate, confirming the complicating influence of anion addition. Further,

McAllan et al. did not precede their cation addition with an acid-washing step, ostensibly to avoid the potential loss of humates. Hence the interpretation of data became a matter of complex multi-variable analysis with competing influences of the cations (and anions) added to the coals with those already present in the untreated coals.



Figure 53. Effects of Cation Type on Swelling of Freshly Prepared Ion-Exchanged Briquettes in Water (hollow symbols = Yallourn coal; solid symbols = Morwell coal).

Schafer⁽¹³³⁾ has shown that the equilibrium moisture content of low rank coals increases with the nature of the carboxylate cation and its concentration in accordance with the degree of hydration of that cation in solution. Thus the equilibrium moisture content increases in the following order:

$$Fe^{2+} > Mg^{2+} > Ca^{2+} > Cu^{2+} > Ba^{2+} > Al^{3+} \approx Fe^{3+} \approx Na^{+} > K^{+}$$

McAllan et al.⁽¹³²⁾ and Woskoboenko and Ryan⁽¹³⁴⁾ have shown that the extent of briquette weathering is dependent on the rate of swelling due to the uptake of water rather than its magnitude alone. The larger the difference between the briquette moisture content and the equilibrium moisture content of the coal feedstock under ambient humidity conditions, the larger and faster the degree of drying or moisture adsorption by the briquette and the greater the loss of strength due to stresses generated within the briquette by the shrinkage or swelling associated with this equilibration⁽³¹⁾.

Whilst the swelling curves in Figure 53 confirm the strong influence of exchanged magnesium on equilibrium moisture content, the order of the other cations is not the same as in Schafer's series above. Furthermore, the order is not the same for both coal types, and the general shape of the rate curves appears to be coal dependent, rather than cation dependent.

Table IX (Chapter 2) shows that Morwell coal is much more highly exchanged than Yallourn coal. Calcium and magnesium levels, in particular, are much higher for Morwell coal, which explains why these two species are the "prime suspects" in any analysis of the poor weathering characteristics of Morwell briquettes. However, the data shown in Figure 53 would appear to eliminate calcium as a candidate for causing increased swelling and decrepitation in briquetted coal.

5.3.2 Effects of Ageing

Laboratory briquettes (Section 2.3.5) were produced from untreated Yallourn and Morwell coals and stored carefully for varying times prior to the measurement of swelling in water. Chiodo⁽⁸²⁾ had found aged briquettes to weather less rapidly than fresh briquettes (i.e. moisture equilibration reduced weathering). Anecdotally, there had also been evidence that if freshly produced Morwell briquettes were stored carefully (away from weathering environments) immediately after production (i.e. when warm) and then stockpiled in the open at a later stage, then their weathering characteristics were much better than usual (although still not as good as for Yallourn Township briquettes).

Figures 54 and 55 show the effects of ageing of laboratory-produced briquettes on the swelling behaviour in water for Yallourn and Morwell coals respectively. Whereas the Yallourn briquettes (Figure 54) appear to produce essentially the same swelling curve regardless of the extent of ageing, the Morwell briquettes (Figure 55) exhibit a significant "curing" with time. It would appear from the current work that if the undercover storage is continued for long enough after production (in the case of the factory produced briquettes shown in Figure 51, 12 months), Morwell briquettes can improve to the extent that their behaviour when exposed to water is similar to that of Yallourn Township briquettes.

The effects of exchanged cations on this curing effect are examined for both briquette types in Figures 56 to 59. Figures 56 and 57 show for Yallourn briquettes that, contrary to the impression given by Figure 54, there is indeed some curing with time with respect to at least some of the exchanged cations, notably magnesium and iron(III), even within the reduced timeframe shown in Figure 54. It is also instructive to compare the magnitude of swelling shown in Figure 54 with that of Figures 56 and 57. Magnesium exchange has significantly increased the rate and extent of swelling of the Yallourn coal.



Figure 54.Effects of Ageing on Swelling of Laboratory-Produced YallournBriquettes in Water.



Figure 55.Effects of Ageing on Swelling of Laboratory-Produced MorwellBriquettes in Water.



Figure 56.Effects of Ageing and Cation Type on Swelling of Ion-Exchanged
Yallourn Briquettes in Water (solid symbols = Ca^{2+} exchanged coal;
hollow symbols = Mg^{2+} exchanged coal).



Figure 57. Effects of Ageing and Cation Type on Swelling of Ion-Exchanged Yallourn Briquettes in Water (solid symbols = H^+ exchanged coal; hollow symbols = Na⁺ exchanged coal; hollow symbols with crosshair = Fe³⁺ exchanged coal).



Figure 58.Effects of Ageing and Cation Type on Swelling of Ion-Exchanged
Morwell Briquettes in Water (solid symbols = Ca^{2+} exchanged coal;
hollow symbols = Mg^{2+} exchanged coal).



Figure 59. Effects of Ageing and Cation Type on Swelling of Ion-Exchanged Morwell Briquettes in Water (solid symbols = H^+ exchanged coal; hollow symbols = Na⁺ exchanged coal; hollow symbols with crosshair = Fe³⁺ exchanged coal). Figures 58 and 59 show for Morwell briquettes that, with the possible exception of sodium, all exchanged cations exhibit significant curing with time.

It has been shown in Section 5.3.1 and in this Section that magnesium is by far the greatest contributor to briquette swelling in water of the likely exchangeable cations. It has also been shown that the swelling of briquettes due to uptake of water by magnesium-exchanged coals is reduced significantly with controlled ageing of the briquettes. The large difference between the rate and extent of swelling in water of Yallourn and Morwell briquettes is almost entirely attributable to exchanged magnesium. Table IX (Chapter 2) shows that the untreated Morwell coal contains approximately 3 times the acid-extractable magnesium of untreated Yallourn coal. Similarly, the magnesium exchange procedure employed here also resulted in a level of magnesium in the Morwell coal that was 3 times that of the Yallourn coal.

5.3.3 Diffusion Mechanism

Swelling rate curves can be used to determine the diffusion mechanism governing the uptake of water into the briquette structure. Diffusion of solvents into coals may vary between two extremes^(125, 135). If diffusion is controlled by the concentration gradient between the centre and the outside of the particle, the diffusion mechanism is termed "Fickian". If the diffusion of solvent is completely controlled by relaxation of the coal network to accommodate the solvent then the diffusion mechanism is termed "relaxation" or "Case II". Figure 60 shows the normalized plots for the theoretical Fickian and Relaxation diffusion modes⁽¹²⁵⁾. Fickian diffusion gives a curve that rises monotonically, whilst the Case II mechanism results in a gradual rise near the origin.



Figure 60. Normalised Theoretical Modes for Fickian and Relaxation Controlled Diffusion into a Sphere⁽¹²⁵⁾.

Analysis of the rate curves for Morwell briquettes (Figure 61) shows that diffusion, and hence swelling, is relaxation controlled (a Case II mechanism) and that the propensity to relax decreases with age, so that swelling becomes more relaxation controlled.

Rates of swelling of laboratory produced Yallourn and Morwell briquettes in water are shown in Figure 62, both with and without prior evacuation of the pores. It can be seen that the rate of swelling is highly dependent on the rate of displacement of air, from within the pore structure, into the advancing water. Whilst the briquettes from which this air has been removed reach 99% of their total swelling in approximately 2 hours, the unevacuated samples take approximately 7 hours to reach 75% of this total. Similar results have been found by Green et al.⁽²⁰⁾ for the adsorption of pyridine vapour by an Illinois No. 6 coal. Experiments under vacuum were performed in duplicate and the swelling curves shown in Figure 62 illustrate the excellent repeatability obtained with the modified Wykenham-Farrance apparatus (see Section 2.4.3).

Comparison of the diffusion mechanisms (Figure 63) shows that uptake is relaxation controlled for both briquette types. Evacuation of the pores prior to contact with the water alters the diffusion mechanism towards a Fickian mode (although it is still slightly relaxation controlled). The higher rate of swelling of Morwell briquettes would indicate a greater propensity for relaxation than for Yallourn briquettes.

5.3.4 Effects of Ionic Strength

Matturro et al.⁽¹³⁶⁾ observed an unusual effect of increasing the ionic strength of a methanol solution in contact with a bituminous coal on the swelling behaviour of that coal. Although a 1.0 M solution of tetra butyl ammonium hydroxide resulted in greater swelling than a 0.25 M solution, the initial *rate* of swelling was six times faster for the more dilute ionic



Figure 61.Effects of Ageing on Diffusion of Water into Laboratory-Produced
Morwell Briquettes.



Figure 62. Swelling of Laboratory Produced Briquettes in Water (with and without pore evacuation).



Figure 63. Normalised Swelling Curves for Laboratory-Produced Yallourn and Morwell Briquettes (solid symbols = ambient pressure; hollow symbols = evacuated).

solution. The effect was attributed to the coal becoming less permeable to the swelling solvent (methanol) in the presence of high ionic strength solution. The bituminous coal was thus considered to be behaving as a polyelectrolyte⁽¹³⁶⁾. It follows that lower rank coals such as Victorian brown coals, with their far greater concentration of ionisable functionalities, would be expected to exhibit a marked polyelectrolytic behaviour.

A very important property of water is its ability to provide an ionising medium of high dielectric constant (insulating power – to lower the attraction between solvated ionic species⁽⁸⁵⁾), which accounts for its strong solvent power for polyelectrolytes⁽³⁵⁾. Brown coals contain ionisable groups and therefore swell in contact with pure water due, in part, to the osmotic pressure of the ion-rich water in the pore system on the (relatively) ion-poor bulk water. This swelling can be suppressed by adding salts to the bulk water phase⁽⁸⁾, as shown in Figures 64.

Figure 64 shows the effects of a relatively small increase in the ionic strength of water (i.e. 10^{-3} M KNO₃) on the swelling of ion-exchanged Morwell briquettes. In all cases, swelling was suppressed significantly.

Brown coal behaves much like an ion-exchange resin in aqueous media⁽¹³⁷⁾ due to the dynamic exchange of inorganic cations in the water with acidic oxygen containing functional groups in the coal⁽³²⁾. The electrical double-layer thus formed is shown schematically in Figure 65. The electrical double-layer consists of an inner portion (Stern Layer) in which counter-ions (H+, Na+, Ca2+, Mg2+, Fe2+ and Al3+) are firmly bound to the coal surface, and an outer diffuse layer in which ions are distributed according to the influence of the electrical forces and random thermal motion⁽³²⁾.


Figure 64. Swelling of Laboratory Produced Ion-Exchanged Morwell Briquettes in Water (solid symbols) and 10⁻³ Molar KNO₃ (hollow symbols).

Sung et al⁽³⁶⁾ have shown that, at low concentrations, alkali-soluble coal suspensions exhibit highly viscoelastic behaviour due to intramolecular expansion when ionised functional groups are mutually repelled. The forces between these ionised groups are very much larger (about an order of magnitude⁽³⁶⁾) than the dispersion forces or the attractive dipole-dipole interactions between uncharged groups⁽³⁵⁾. As the concentration of the coal extract in suspension is reduced, the increased dilution eventually results in a shortage of counter-ions in the electrical double-layer. This in turn results in charge repulsion between the functional groups at each coal surface. At constant pH, increasing the ionic strength of the suspension resulted in a corresponding increased adequacy of supply of counter-ions at the surface and chain expansion no longer occurred.

The reduction in swelling of briquettes as ionic strength is increased is a result of the dual effects of:

- a decrease in the concentration profile, and hence, osmotic pressure, between the pore water and the bulk water, and
- (ii) a reduction in mutual repulsion between ionised functional groups on the coal surface due to an increase in the supply of counter-ions in the electrical double-layer.



Figure 65. Schematic Representation of Electrical Double Layer at Coal/Water Interface (Stern-Gouy-Chapman Model)⁽³²⁾.

- a Coal surface which carries a net negative charge due to partial ionization of carboxyl groups.
- **b** Stern layer containing firmly bound carboxylate cations (H^+ , Na^+ , Ca^{2+} , Fe^{2+} , Mg^{2+} and Al^{3+} .
- c Diffuse part of double layer.
- **d** Double layer thickness (k^{-1}) .
- e,f Counter-ion and co-ion concentration profiles.
- **g** Shear plane at which zeta-potential is measured.

CHAPTER 6.

SUMMARY

6.1. INTRODUCTION

The aims of this study on the solvent-induced swelling behaviour of Victorian brown coals were to examine and explain the interaction between brown coal and specific solvents, and to probe the bonding mechanisms in very low rank coals (in this case Victorian brown coal). Ideal outcomes of the study would be a clearer picture of the structure of brown coals, and a means of predicting swelling behaviour for any set of solvent properties. The conclusions of the study are summarised in the following Sections.

6.2. PREDICTION OF SOLVENT INDUCED SWELLING IN VICTORIAN BROWN COALS

Much of the research on coal swelling has revolved around the use of solvent solubility parameters as diagnostic and predictive tools. The applicability of solubility parameters to coal hinges on similarities between the coal and highly crosslinked polymers (i.e. do the coals follow conventional swelling theory).

Most work has been carried out on coal residues (after thorough solvent extraction) because conventional swelling theory requires that the free energy of equilibrium be between the pure solvent and the insoluble coal matrix only. Many researchers have also excluded specific solvents (e.g. pyridine) from their work on swelling because of the specific chemical interactions known to occur. However there seemed to be little point, especially in regard to the objectives of the present study, in limiting any conclusions to the insoluble portion of coals, which can be changed significantly in physical structure from their parents⁽⁹⁴⁾. It was considered important to study the behaviour of whole coals in contact with a wide variety of solvents (specific and non-specific) so that the behaviour of coals in industrial processes could be better understood.

Correlation of brown coal swelling behaviour with solvent solubility parameter in Chapter 3 predicted a maximum in the coal swelling at approximately 20-25 MPa^{1/2}. This prediction is significantly different from that of Karim⁽⁵⁸⁾ (33 MPa^{1/2}), however there is a paucity of commonly available solvents having solubility parameters around 33 MPa^{1/2} and, in view of the data presented, it was considered unwise to place too much faith in the ability of the solubility parameter concept alone to predict the degree of coal swelling. Solvents having very similar solubility parameters exhibited a wide range of swelling abilities.

The higher rank coals to which the solubility parameter approach has been applied in the literature are higher in covalent bonding, lower in functional group content, and lower in hydrogen bonding than lower rank coals. Thus the list of solvents capable of specific interaction with higher rank coals is much smaller than that for Victorian brown coal. If the data points for the "poor" hydrogen bonding (i.e. nonspecific) solvents; nitromethane, acetonitrile, nitrobenzene, dichloromethane, benzene, cyclohexane and n-hexane were isolated, a maximum in coal swelling occurred at a solvent solubility parameter of approximately 22 MPa^{1/2}. However, the utility of the solubility parameter approach to Victorian brown coal has to be seriously questioned when so few of a large suite of solvents qualify for inclusion in the analysis.

It is concluded that the solubility parameter estimated by Karim for Latrobe Valley brown coals⁽⁵⁸⁾ is unlikely and, in any event, reliance on this figure in the selection of suitable swelling solvents for brown coals would unfairly discriminate against several strong swelling agents having solubility parameters in the range 20-30 MPa^{1/2}.

When solvent solubility parameter was resolved into its 3-dimensional components, maximum swelling was observed at a δ_d of 17-19 MPa^{1/2}, δ_p of 9-15 MPa^{1/2}, δ_h of 6-12 MPa^{1/2}, and δ_a of 10-20 MPa^{1/2}. With optimum values already determined for δ_0 (20-25 MPa^{1/2}), a good swelling solvent for Loy Yang brown coal might then be expected to have a total solubility parameter of

≈22.5 MPa^½, and three-dimensional solubility parameters (δ_d , δ_p , δ_h , and δ_a) of approximately 18, 12, 9 and 15 MPa^½ respectively. N,N-dimethyl formamide was closest of the solvents studied here to satisfying the solubility parameter criteria listed above and, indeed, this solvent produced the largest swelling ratio for LYROM coal. The lack of other solvents in this study having similar total, and three-dimensional, solubility parameters to N,N-dimethyl formamide means that caution must be exercised in making any strong conclusions on the ability of the solubility parameter approach to accurately predict coal swelling. Nevertheless, use of both total and three-dimensional solubility parameters, rather than total solubility parameter alone, does appear to provide some promise as a tool to predicting and understanding swelling behaviour.

Brown coal swelling showed a minimum when the solvent electron-donor number (DN) minus its electron-acceptor number (AN) was closest to zero, i.e. when DN and AN were of similar magnitude. The degree of swelling increased either side of this point. Indeed, the electron donor/acceptor approach predicts that large differences between solvent DN and AN will result in a large amount of coal extract, and high extraction should also lead to large swelling values⁽⁶⁶⁾.

In contrast to the solubility parameter approach (which suffers from the uncertainty caused by specific interaction between coal and solvent), the electron donor/acceptor approach is *about* specific interactions and these trends show promise for the prediction of solvent swelling of brown coal.

It is concluded that a combination of total and three-dimensional solubility parameters and solvent electron donor/acceptor numbers may be used to predict the solvent swelling behaviour of unextracted brown coals with some success⁽¹³⁸⁾. Correlation of coal swelling to a single parameter, chosen so as to represent some measure of the strength of favourable interactions, can be misleading. It is the balance of favourable to unfavourable forces that is crucial⁽⁷³⁾.

6.3. THE EFFECTS OF PHYSICAL AND CHEMICAL MODIFICATION OF THE COAL STRUCTURE ON SWELLING BEHAVIOUR

To further probe the coal structure using solvent swelling techniques it was considered instructive to modify the coal structure by thermal, physical and chemical treatments and to observe the effects of these changes in structure on swelling behaviour. In Chapter 4, the solvent swelling of chemically densified, thermally modified, and O-alkylated brown coals was investigated in terms of the solvent properties discussed in Chapter 3. A comparison of swelling for the modified coals with that of the untreated coals was used to further elucidate those structural features which govern the solvent swelling behaviour of Victorian brown coals.

The chemically densified coal was expected to show less solvent penetration than the other samples due to its lower porosity. However, in reality, solvent accessibility was insensitive to a reduction in pore volume, and chemical effects were dominant. Both polar and non-polar solvents yielded significantly reduced swelling ratios for the chemically densified coal compared to the parent coal. It appears that a much higher concentration of hydrogen bonding (or ionic bonding/van der Waals forces⁽¹¹⁹⁾) is present than in the untreated coal, and that many of these coal-coal bonds are thermodynamically more favourable (and thus stronger) than prospective coal-solvent bonds. Even such a specific solvent as pyridine experienced a significantly greater resistance to swelling after ammonia-digestion of the coal, suggesting that many of the new crosslinks in this coal are covalent (i.e. much stronger than hydrogen bonding). This is in contrast to the findings of Hodges et al.⁽¹¹⁹⁾ who were unable to detect covalent bonding in ammonia-digested coal by infrared spectroscopy.

Thermal modification of the ammonia-digested compact resulted in reduced swelling for all solvents, indicating that the structure had adopted a minimum energy configuration due to decarboxylation and replacement of hydrogen bonds with additional covalent bonds⁽⁶⁴⁾.

As expected, swelling of acetylated coal in non-polar solvents was enhanced due to the reduction of polar crosslinking in the coal and an increase in the relative importance of dispersive forces in the coal solvent system^(2, 125). An observed reduction in swelling of the acetylated coal in the more polar solvents was also to be expected because the very basis of the specific interactions between these solvents and the untreated coal (i.e. hydrogen bonded crosslinks) had been removed. O-methylated coal was also found to swell less than its parent in highly polar solvents due to a reduction in the secondary crosslinking so susceptible to attack by these solvents.

Comparison of the swelling behaviour of the solvent extracted intermediaries with that of the derivatised coals confirmed that whilst pyridine may destroy the secondary crosslinking in the coal, it does not irreversibly affect oxygen functionality, which can contribute to specific interaction with highly polar solvents and limit interaction with non-polar solvents. Acetylation does succeed in neutralising these modes of interaction, so that dispersive forces gain prominence and swelling in non-polar solvents increases.

It was shown in Chapter 4 that highly polar solvents are capable of swelling untreated coal to a greater extent than O-acetylated or O-methylated coals. Conversely, non-polar solvents were able to swell the derivatised coals to a greater extent than the untreated coal.

6.4. WEATHERING OF VICTORIAN BROWN COAL BRIQUETTES

In chapter 5 it was shown that the swelling of -8.00, +5.60 mm fragments of 1 year old factory produced Morwell briquettes in water was identical to that of Yallourn Township briquettes. This was a most surprising finding given the welldocumented weathering problems associated with Morwell briquettes. The three types of Victorian brown coal briquettes studied exhibited no significant differences in their <u>equilibrium</u> swelling behaviour. Swelling of all three briquette samples (Morwell, Yallourn and Loy Yang) was essentially the same for any given solvent. Swelling is more sensitive to the type of bonding in the briquette than to surface chemical differences between the coals used in their production. The hydrogen bonding responsible for briquette integrity significantly reduces swelling for most solvents (including water) when compared to unbriquetted coal.

The weathering of Morwell briquettes is believed to be due to the internal stresses caused by uptake of moisture, and the associated swelling. Thus tests were conducted to examine the effect of particle size on observed particle decrepitation. These tests made it clear that differential expansion within the briquette particles was responsible for the observed surface cracking because the smallest particles did not crack appreciably, whilst whole briquettes did deteriorate.

Victorian brown coal briquettes appear to fracture upon weathering via a mechanism whereby the differential swelling of the outer regions of the briquette compared to the inner regions causes mechanical stresses large enough to overcome the hydrogen bonding responsible for the briquette's original integrity. Whether this differential swelling is due to kinetic effects or to the differences in swellability of the subcomponents of the coal used in manufacturing the briquette is unimportant here, especially since there is very little that can be done industrially to change either phenomenon. The important thing is to acknowledge that the spontaneous fracture of Victorian brown coal briquettes upon weathering is due to rupture of the hydrogen-bonded network. The only industrially viable option for elimination (or minimisation) of this fracture is then to restrict the total swelling (and thus the internal stress) by reducing the affinity of the solvent (in this case, water) for the hydrogen-bonded briquette network.

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Chiodo⁽⁸²⁾ concluded that swelling would be influenced by exchanged cations in the order monovalent > divalent > trivalent, on the basis that experimental briquettes produced from sodium-exchanged Yallourn and Morwell coals swelled to a greater extent than their barium-exchanged counterparts. On the other hand, McAllan et al.⁽¹³²⁾ identified exchanged calcium and magnesium as being major contributors to briquette weathering, whilst sodium had little effect and acid-washing improved water resistance.

It has been shown in Chapter 5 that magnesium is by far the greatest contributor to briquette swelling in water of the likely exchangeable cations. Calcium has been eliminated as a candidate for causing increased swelling and decrepitation in briquetted coal.

Untreated Morwell coal contains approximately 3 times the acid-extractable magnesium of untreated Yallourn coal. The initial rate of swelling of freshly briquetted Morwell coal is significantly greater than for Yallourn coal. The large difference between the rate and extent of swelling in water of Yallourn and Morwell briquettes is almost entirely attributable to exchanged magnesium. The magnesium exchange procedure employed in this study also resulted in a level of magnesium in the Morwell coal that was 3 times that of the Yallourn coal. Magnesium exchanged samples exhibited the greatest rate and degree of swelling in water for both Morwell and Yallourn coals. Magnesium exchange significantly increases the rate and extent of swelling of the Yallourn coal.

It has also been shown that the swelling of briquettes due to uptake of water by magnesium-exchanged coals is reduced significantly with controlled ageing of the briquettes. Chiodo⁽⁸²⁾ had found aged briquettes to weather less rapidly than fresh briquettes (i.e. moisture equilibration reduced weathering). Anecdotally, there had also been evidence that if freshly produced Morwell briquettes were stored carefully (away from weathering environments) immediately after production (i.e. when warm) and then stockpiled in the open at a later stage, then their weathering characteristics were much better than usual (although still not as good as for Yallourn Township briquettes). It would

appear from the current work that if the undercover storage is continued for long enough after production (perhaps years), Morwell briquettes can improve to the extent that their behaviour when exposed to water is similar to that of Yallourn Township briquettes. Whilst this observation is of great interest, it is considered impractical to stockpile briquettes in commercial quantities for very long periods of time. A greater understanding of the chemical changes which produce the observed ageing effect may make it possible to accelerate the increased resistance to weathering of Morwell briquettes in a cost-effective manner.

Analysis of the rate curves for swelling of briquettes in water shows that diffusion, and hence swelling, is relaxation controlled and that the propensity to relax decreases with age, so that swelling becomes more relaxation controlled. The higher rate of swelling of Morwell briquettes would indicate a greater propensity for relaxation than for Yallourn briquettes.

6.4 <u>A MODEL FOR VICTORIAN BROWN COAL BASED ON ITS SOLVENT</u> SWELLING BEHAVIOUR

The discussion of swelling behaviour shown by ROM coals in Chapter 3 has centred on the coal being a highly crosslinked macromolecular structure containing somewhat smaller extractable species within its open pore network.

The observations of swelling behaviour reported here are entirely consistent with the notion that coal is a both covalently and non-covalently crosslinked and entangled macromolecular network comprising extractable species which are held within the network by a wide range of non-covalent, polar, electron donor/acceptor interactions⁽¹³⁹⁾. Low rank coals have a high degree of oxygen functionality so that polar interactions associated with hydroxyl, phenolic, carbonyl and carboxylic groups are a feature of their molecular structure⁽¹²⁾. Solvents capable of significant extraction of whole brown coals are also capable of significant swelling, but not dissolution, of the macromolecular coal network,

which supports the view that the network is comprised of both covalent and ionic bonding.

Aida and Squires⁽¹⁰⁴⁾ found a Q value of 2.90 for Illinois No. 6 (sub-bituminous) coal immersed in pyridine. Clearly, the lower rank Victorian brown coal with Q equal to 5.71 is affected far more by the pyridine molecule's ability to disrupt hydrogen bonding than the higher rank Illinois coal which comprises substantially more covalent bonds.

The correlation coefficient for the line of best fit for swelling versus solvent uptake for run-of-mine coal was found in Chapter 3 to be 0.999, indicating a remarkably constant relationship between uptake and swelling. This was somewhat surprising because it indicates that chemical specificity is relatively unimportant to swelling. Although chemical effects are presumably responsible for the increased uptake of some solvents (i.e. the most polar ones) compared to others, the relationship between uptake and swelling remains constant. Thus the extent of swelling is solvent specific, but the mechanism appears not to be. Some solvents, most particularly pyridine and ethanol, produced spectacular swelling of the dried coal particles. The extent of swelling is more remarkable when it is considered that the swollen coal particles remained intact, i.e. they did not dissolve, although the extent of extraction (as indicated visually by the colour of the bulk solvents in contact with the coals) correlated extremely well with the measured swelling. It was demonstrated that the reason for enhanced uptake and swelling of some solvents compared to others lies in the chemical interactions between solvent and coal, rather than physical size effects.

Victorian brown coals have been shown to exhibit polyelectrolytic behaviour due to a high concentration of ionisable surface functionalities. This causes them to swell in aqueous solvent due, in part, to the osmotic pressure of the ion-rich water in the pore system on the (relatively) ion-poor bulk water. This swelling can be suppressed by adding salts to the bulk water phase⁽⁷⁾. The reduction in swelling of coal as ionic strength is increased is a result of the dual effects of a decrease in the concentration profile, and hence, osmotic pressure, between the pore water and the bulk water, and a reduction in mutual repulsion between ionised functional groups on the coal surface due to an increase in the supply of counter-ions in the electrical double-layer.

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SOLVENT MOLECULAR MODELS



Water [H₂O]



Methanol [CH₃OH]



Ethanol [C₂H₅OH]



Nitromethane [CH₃NO₂]



Ethylenediamine [(CH₂NH₂)₂]



N,N-Dimethyl formamide [(CH₃)₂NCHO]



Dimethyl sulphoxide [(CH₃)₂SO]



n-Propanol [C₃H₈OH]



Dioxane [C₄H₈O₂]



Nitrobenzene [C₆H₅NO₂]



Acetonitrile [CH₃CN]



Isopropyl alcohol [(CH₃)₂CH₂OH]



Quinoline [C₉H₇N]



Pyridine [C₅H₅N]



Acetone [(CH₃)₂CO]



Dichloromethane [CH₂Cl₂]



Methyl acetate [CH₃OCOCH₃]



Ethyl acetate [C₂H₅OCOCH₃]



Methyl ethyl ketone [CH₃COC₂H₅]



Ethylene glycol dimethyl ether [CH₃OC₂H₂OCH₃]



Benzene (C₆H₆)



Tetrahydrofuran [C₄H₈O]



Cyclohexane [C₆H₁₂]



Diethyl ether [(C₂H₅)₂O]



Triethylamine [(C₂H₅)₃N]



n-Hexane [C₆H₁₄]
<u>APPENDIX 2.</u>

INFRARED SPECTRA



Yallourn Methanol Extract



Yallourn Ethanol Extract



Yallourn Acetone Extract



Yallourn Pyridine Extract



Morwell Acetone Extract



Morwell Pyridine Extract





Loy Yang Methanol Extract



Loy Yang Ethanol Extract



Loy Yang Acetone Extract



Loy Yang Pyridine Extract



Untreated Yallourn



Untreated Morwell



Untreated Loy Yang



Yallourn/Benzene (Difference)



Yallourn/Methanol



Yallourn/Pyridine



Yallourn/Pyridine (Difference)



Yallourn/Methanol (Difference)



Yallourn/Ethanol



Yallourn/Ethanol (Difference)



Appendix 2



Morwell/Methanol



Morwell/Methanol (Difference)



Morwell/Ethanol



Morwell/Ethanol (Difference)



Morwell/Pyridine



Morwell/Pyridine (Difference)



.

Loy Yang/n-Hexane



Loy Yang/n-Hexane (Difference)



Loy Yang/Benzene



Loy Yang/Benzene (Difference)



Loy Yang/Water



Loy Yang/Water (Difference)



Loy Yang/Acetone



Loy Yang/Acetone (Difference)



Loy Yang/Methanol



Loy Yang/Methanol (Difference)



Loy Yang/Ethanol



Loy Yang/Ethanol (Difference)



Approximatix 22

Loy Yang/Pyridine



Loy Yang/Pyridine (Difference)

APPENDIX 3.

PYCNOMETRIC DATA – LOY YANG ROM

Loy Yang ROM

Solvent	Uptake (wt./wt.)	٧p	MCs + MSi	VSa	VCs + VSi	<u>VCs + VSi</u> MCs + MSi	MCd	VSi	<u>VSi</u> MCd	VSa + VSi	VCs	<u>VCs</u> MCd	<u>VCs + VSi</u> MCd	Q	Δv	Dc
n-Hexane	37.42%	65.92	2.0738	64.0478	1.8725	0.9029	1.5091	0.8621	0.5713	64.9099	1.0104	0.6695	1.2408	1.9031	0.5888	1.4936
Benzene	74.08%	65.92	2.6124	63.6611	2.2592	0.8648	1.5007	1.2714	0.8472	64.9325	0.9878	0.6582	1.5054	2.3089	0.8534	1.5193
Water	117.83%	65.92	3.3311	63.0366	2.8837	0.8657	1.5292	1.8064	1.1813	64.8430	1.0773	0.7045	1.8857	2.8922	1.2337	1.4195
Acetone	117.13%	65.92	3.3213	62.6183	3.3020	0.9942	1.5296	2.2780	1.4893	64.8963	1.0240	0.6694	2.1587	3.3109	1.5067	1.4938
Methanol	136.19%	65.92	3.6683	62.2702	3.6501	0.9950	1.5531	2.6785	1.7246	64.9487	0.9716	0.6256	2.3502	3.6045	1.6982	1.5985
Ethanol	161.62%	65.92	4.0750	61.6607	4.2596	1.0453	1.5576	3.1822	2.0430	64.8429	1.0774	0.6917	2.7347	4.1943	2.0827	1.4457
Pyridine	295.53%	65.92	6.9236	59.3952	6.5251	0.9424	1.7505	5.2771	3.0146	64.6723	1.2480	0.7130	3.7276	5.7172	3.0756	1.4026

Vp = Volume of pycnometer (cm ³)
MCs = Mass of swollen coal (g)
MSi = Mass of imbibed solvent (g)
VSa = Volume of solvent added to pycnometer (cm ³)
VCs = Volume occupied by swollen coal (cm ³)
VSi = Volume of imbibed solvent (cm ³)
MCd = Mass dry coal in pycnometer (g)
Q = Swollen volume / Unswollen volume
ΔV = Swollen volume - Unswollen volume
Dc = Density of coal in solvent (g/cm3)

REGRESSION ANALYSIS

y = mx + c

- y = specific volume of swollen coal (cm³/g dry coal) x = volume of solvent imbibed (cm³/g dry coal)

m c fit 1.015420392 0.652039091 0.99893341

APPENDIX 4.

PYCNOMETRIC DATA – MODIFIED COALS

Loy Yang ROM / Ammonia digested

Solvent	Uptake (wt./wt.)	Vp	MCs + MSi	VSa	VCs + VSi	<u>VCs + VSi</u> MCs + MSi	MCd	VSi	<u>VSi</u> MCd	VSa + VSi	VCs	<u>VCs</u> MCd	<u>VCs + VSi</u> MCd	Q	Δv	Dc
n-Hexane	14.25%	65.92	1.2380	65.0678	0.8525	0.6886	1.0836	0.2357	0.2175	65.3035	0.6168	0.5692	0.7867	1.1947	0.1282	1.7568
Benzene	14.24%	65.92	1.2157	65.0324	0.8879	0.7304	1.0642	0.1733	0.1630	65.2057	0.7146	0.6715	0.8344	1.2671	0.1759	1.4891
Water	93.47%	65.92	2.6061	63.7504	2.1699	0.8326	1.3470	1.2622	0.9370	65.0126	0.9077	0.6738	1.6109	2.4463	0.9524	1.4840
Acetone	11.57%	65.92	1.3536	64.8779	1.0424	0.7701	1.2132	0.1785	0.1470	65.0564	0.8639	0.7121	0.8592	1.3047	0.2007	1.4044
Methanol	43.09%	65.92	1.9847	64.2039	1.7164	0.8648	1.3870	0.7569	0.5456	64.9608	0.9595	0.6918	1.2375	1.8793	0.5790	1.4455
Ethanol	47.61%	65.92	2.0198	64.0594	1.8609	0.9213	1.3683	0.8235	0.6013	64.8830	1.0373	0.7581	1.3600	2.0653	0.7015	1.3190
Pyridine	126.75%	65.92	4.0480	62.3433	3.5770	0.8837	1.7852	2.3083	1.2930	64.6515	1.2688	0.7107	2.0037	3.0429	1.3452	1.4070

Vp = Volume of pycnometer (cm³)
MCs = Mass of swollen coal (g)
MSi = Mass of imbibed solvent (g)
VSa = Volume of solvent added to pycnometer (cm ³)
VCs = Volume occupied by swollen coal (cm³)
VSi = Volume of imbibed solvent (cm ³)
MCd = Mass dry coal in pycnometer (g)
Q = Swollen volume / Unswollen volume
ΔV = Swollen volume - Unswollen volume

Dc = Density of coal in solvent (g/cm³)

REGRESSION ANALYSIS

y = mx + c

y = specific volume of swollen coal (cm³/g dry coal) x = volume of solvent imbibed (cm³/g dry coal)

m c fit 1.045666097 0.658536096 0.98541415

APPENDIX 4

APPENDIX 4

Loy Yang ROM / Ammonia digested / Thermally modified

Solvent	Uptake (wt./wt.)	Vp	MCs + MSi	VSa	VCs + VSi	<u>VCs + VSi</u> MCs + MSi	MCd	VSi	<u>VSi</u> MCd	VSa + VSi	VCs	<u>VCs</u> MCd	<u>VCs + VSi</u> MCd	Q	∆v	Dc
n-Hexane	3.07%	65.74	1.0100	65.0960	0.6443	0.6379	0.9799	0.0459	0.0468	65.1419	0.5984	0.6107	0.6575	0.9311	######	1.6375
Benzene	3.07%	65.74	1.1890	64.8033	0.9371	0.7881	1.1535	0.0406	0.0352	64.8438	0.8965	0.7772	0.8123	1.1503	0.1061	1.2867
Water	11.05%	65.80	1.3549	64.7412	1.0583	0.7811	1.2201	0.1352	0.1108	64.8763	0.9232	0.7567	0.8674	1.2283	0.1612	1.3216
Acetone	32.87%	65.74	1.7464	64.2848	1.4555	0.8335	1.3144	0.5493	0.4179	64.8341	0.9062	0.6895	1.1074	1.5681	0.4012	1.4504
Methanol	26.60%	65.74	1.6780	64.5372	1.2032	0.7170	1.3254	0.4464	0.3368	64.9836	0.7567	0.5709	0.9078	1.2854	0.2016	1.7515
Ethanol	25.78%	65.80	1.5610	64.3609	1.4386	0.9216	1.2410	0.4045	0.3259	64.7654	1.0341	0.8333	1.1592	1.6415	0.4530	1.2001
Pyridine	85.09%	65.74	3.2249	62.9542	2.7862	0.8640	1.7423	1.5124	0.8680	64.4666	1.2738	0.7311	1.5991	2.2644	0.8929	1.3678

Vp = Volume of pycnometer (cm³) MCs = Mass of swollen coal (g) MSi = Mass of imbibed solvent (g) VSa = Volume of solvent added to pycnometer (cm³) VCs = Volume occupied by swollen coal (cm³) VSi = Volume of imbibed solvent (cm³) MCd = Mass dry coal in pycnometer (g)

Q =Swollen volume / Unswollen volume $\Delta V =$ Swollen volume - Unswollen volume

Dc = Density of coal in solvent (g/cm³)

REGRESSION ANALYSIS

y = mx + c

y = specific volume of swollen coal $(cm^3/g dry coal)$ x = volume of solvent imbibed $(cm^3/g dry coal)$

m С fit 1.012116603 0.70619219 0.909395531 APPENDIX 5.

PYCNOMETRIC DATA – FACTORY PRODUCED BRIQUETTES

Yallourn Briquette

APPENDIX 5

Solvent	Uptake (wt./wt.)	Vp	MCs + MSi	VSa	VCs + VSi	<u>VCs + VSi</u> MCs + MSi	MCd	VSi	<u>VSi</u> MCd	VSa + VSi	VCs	<u>VCs</u> MCd	<u>VCs + VSi</u> MCd	Q	∆v	Dc
n-Hexane	12.68%	65.92	1.2640	65.1264	0.7939	0.6281	1.1217	0.2172	0.1936	65.3436	0.5767	0.5141	0.7077	1.1195	0.0755	1.9451
Benzene	21.49%	65.92	1.4659	64.8816	1.0387	0.7086	1.2066	0.2965	0.2457	65.1781	0.7422	0.6151	0.8608	1.3616	0.2286	1.6258
Water	38.23%	65.92	1.7256	64.5413	1.3790	0.7992	1.2484	0.4784	0.3832	65.0197	0.9006	0.7214	1.1047	1.7473	0.4725	1.3861
Acetone	92.01%	65.92	2.3926	63.7804	2.1399	0.8944	1.2461	1.4577	1.1699	65.2382	0.6821	0.5474	1.7173	2.7164	1.0851	1.8267
Methanol	83.01%	65.92	2.4670	63.4887	2.4316	0.9857	1.3480	1.4170	1.0511	64.9056	1.0147	0.7527	1.8039	2.8533	1.1717	1.3285
Ethanol	97.17%	65.92	2.5853	63.2906	2.6297	1.0172	1.3112	1.6105	1.2283	64.9011	1.0192	0.7773	2.0055	3.1723	1.3733	1.2865
Pyridine	286.67%	65.92	6.1545	60.2229	5.6974	0.9257	1.5917	4.6545	2.9243	64.8774	1.0429	0.6552	3.5795	5.6620	2.9473	1.5262

Vp = Volume of pycnometer (cm ³)							
MCs = Mass of swollen coal (g)							
MSi = Mass of imbibed solvent (g)							
VSa = Volume of solvent added to pycnometer (cm ³)							
VCs = Volume occupied by swollen coal (cm³)							
VSi = Volume of imbibed solvent (cm ³)							
MCd = Mass dry coal in pycnometer (g)							
Q = Swollen volume / Unswollen volume ΔV = Swollen volume - Unswollen volume							

Dc = Density of coal in solvent (g/cm³)

REGRESSION ANALYSIS

y = mx + c

y = specific volume of swollen coal (cc/g dry coal) x = volume of solvent imbibed (cc/g dry coal)

m c fit 1.021902519 0.632232646 0.989548255

Morwell Briquette

Solvent	Uptake (wt./wt.)	Vp	MCs + MSi	VSa	VCs + VSi	<u>VCs + VSi</u> MCs + MSi	MCd	VSi	<u>VSi</u> MCd	VSa + VSi	VCs	<u>VCs</u> MCd	<u>VCs + VSi</u> MCd	Q	Δv	Dc
n-Hexane	12.51%	65.92	1.1653	65.1163	0.8040	0.6899	1.0357	0.1979	0.1911	65.3142	0.6061	0.5852	0.7763	1.2273	0.1438	1.7088
Benzene	19.72%	65.92	1.2817	65.0049	0.9154	0.7142	1.0706	0.2414	0.2255	65.2464	0.6739	0.6295	0.8550	1.3518	0.2225	1.5885
Water	40.70%	65.92	1.5868	64.6709	1.2494	0.7874	1.1278	0.4601	0.4080	65.1310	0.7893	0.6998	1.1078	1.7515	0.4753	1.4289
Acetone	83.98%	65.92	2.0007	64.2122	1.7081	0.8537	1.0874	1.1612	1.0678	65.3734	0.5469	0.5030	1.5707	2.4834	0.9382	1.9883
Methanol	75.02%	65.92	2.0907	63.9885	1.9318	0.9240	1.1946	1.1348	0.9499	65.1232	0.7971	0.6672	1.6172	2.5568	0.9847	1.4987
Ethanol	87.14%	65.92	2.3495	63.6127	2.3076	0.9822	1.2555	1.3829	1.1015	64.9956	0.9247	0.7365	1.8380	2.9059	1.2055	1.3577
Pyridine	273.32%	65.92	5.7915	60.5898	5.3305	0.9204	1.5513	4.3254	2.7882	64.9152	1.0051	0.6479	3.4361	5.4325	2.8036	1.5435

Vp = Volume of pycnometer (cm ³)	
MCs = Mass of swollen coal (g)	
MSi = Mass of imbibed solvent (g)	
VSa = Volume of solvent added to pycnometer (cm ³)	
VCs = Volume occupied by swollen coal (cm ³)	
VSi = Volume of imbibed solvent (cm ³)	
MCd = Mass dry coal in pycnometer (g)	
Q = Swollen volume / Unswollen volume	
ΔV = Swollen volume - Unswollen volume	

Dc = Density of coal in solvent (g/cm³)

REGRESSION ANALYSIS

y = mx + c

y = specific volume of swollen coal (cc/g dry coal) x = volume of solvent imbibed (cc/g dry coal)

m c fit 1.006214088 0.632475489 0.992783143

APPENDIX 5

Loy Yang Briquette

Solvent	Uptake (wt./wt.)	Vp	MCs + MSi	VSa	VCs + VSi	<u>VCs + VSi</u> MCs + MSi	MCd	VSi	<u>vsi</u> MCd	VSa + VSi	VCs	<u>VCs</u> MCd	<u>VCs + VSi</u> MCd	Q	Δv	Dc
n-Hexane	11.35%	65.92	1.1936	65.1319	0.7884	0.6605	1.0719	0.1858	0.1733	65.3177	0.6026	0.5622	0.7355	1.1829	0.1137	1.7788
Benzene	21.24%	65.92	1.3870	64.9291	0.9912	0.7146	1.1440	0.2779	0.2429	65.2070	0.7133	0.6235	0.8664	1.3934	0.2446	1.6038
Water	32.64%	65.92	1.5580	64.6801	1.2402	0.7960	1.1746	0.3844	0.3272	65.0645	0.8558	0.7286	1.0558	1.6980	0.4340	1.3725
Acetone	87.79%	65.92	2.2384	63.9765	1.9438	0.8684	1.1920	1.3305	1.1162	65.3070	0.6133	0.5146	1.6308	2.6226	1.0090	1.9434
Methanol	86.37%	65.92	2.4137	63.7182	2.2021	0.9123	1.2951	1.4165	1.0937	65.1347	0.7856	0.6066	1.7003	2.7345	1.0785	1.6486
Ethanol	93.00%	65.92	2.5811	63.4190	2.5013	0.9691	1.3374	1.5721	1.1755	64.9912	0.9291	0.6947	1.8703	3.0078	1.2485	1.4394
Pyridine	286.60%	65.92	5.8356	60.5364	5.3839	0.9226	1.5095	4.4131	2.9236	64.9494	0.9709	0.6432	3.5668	5.7362	2.9450	1.5548

Vp = Volume of pycnometer (cm³)
MCs = Mass of swollen coal (g)
MSi = Mass of imbibed solvent (g)
VSa = Volume of solvent added to pycnometer (cm ³)
VCs = Volume occupied by swollen coal (cm³)
VSi = Volume of imbibed solvent (cm ³)
MCd = Mass dry coal in pycnometer (g)
Q = Swollen volume / Unswollen volume
ΔV = Swollen volume - Unswollen volume

Dc = Density of coal in solvent (g/cm³)

REGRESSION ANALYSIS

y = mx + c

y = specific volume of swollen coal (cc/g dry coal) x = volume of solvent imbibed (cc/g dry coal)

m	С	fit
1.002929374	0.621817605	0.994143029

APPENDIX 5