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## Dissolution and Dispersion of Coal in Ionic Liquids

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In “good” solvents such as pyridine, coal particles swell and fracture to some degree as soluble material is extracted, but they remain as more-or-less coherent particles. It is shown here that certain ionic liquids (ILs) are capable of solubilizing, disintegrating, and dispersing certain coals as very fine particles to a remarkable extent. The solubility of two coals, a Powder River Basin coal and an Illinois No. 6 coal, also increased significantly in IL/*N*-methyl pyrrolidinone (NMP) and IL/pyridine mixtures, relative to the solubility of the coals in NMP and pyridine. A third coal, Upper Freeport, gave yields that were lower than those obtained in pyridine alone. This coal may be anomalous in its behavior. It is suggested that many if not most coals are densely cross-linked networks where a portion of soluble material remains trapped, even upon swelling in good solvents, which fracture and only partially fragment coals at ambient temperatures. Certain ILs fragment and disperse some coals to a much greater extent, however, apparently releasing much of this trapped material.

### Introduction

An understanding of the solvent swelling and solubility of coal is of both fundamental and practical importance. Fundamentally, the nature of coal/solvent interactions and their effect on swelling and solubility provides important insights into the physical and chemical structure of coal. In a more applied problem, hydrogenation and hydrogenolysis in the early stages of coal liquefaction is limited until coal particles have been fragmented and partially solubilized, thus allowing a more intimate contact with catalysts.<sup>1–4</sup>

Low- and medium-rank coals are polar, interacting through hydrogen bonds involving phenolic OH, carboxylic acids (in lower rank coals), and other groups containing heteroatoms. Ionic interactions also appear to play an important role in coal cohesion.<sup>5–7</sup> Nonpolar hydrocarbon solvents, such as toluene or hexane, thus have limited ability to swell coals and extract only small amounts of soluble material. It is only those solvents that have acceptor groups that form strong hydrogen bonds, such as pyridine or *N*-methylpyrrolidinone (NMP) that swell coal particles and dissolve a portion that appears to vary systematically with rank.

Nonanthracitic coals have often been perceived as being similar to polymer cross-linked networks. In such materials

there is a “sol” and “gel” fraction that varies with cross-link density. The gel fraction comprises the portion that consists of cross-linked chains. It is insoluble but swells in the presence of “good” solvents to a degree that depends on cross-link density. Although the soluble (sol) fraction is extractable using appropriate solvents, if the cross-link density of the network is high and the chains are relatively stiff, a significant portion of the soluble fraction can be trapped and inaccessible. Such may be the case with many coals.

There is a different school of thought that regards coal as predominantly an associated structure of smaller molecules held together by secondary interactions, such as hydrogen bonds,  $\pi$ – $\pi$  interactions, and charge transfer complexes. This idea is based mainly on the seminal and important research of Iino and co-workers, who demonstrated that there is a synergistic effect if carbon disulfide, CS<sub>2</sub>, is used with NMP.<sup>8–22</sup> In certain coals, a much greater extraction yield is

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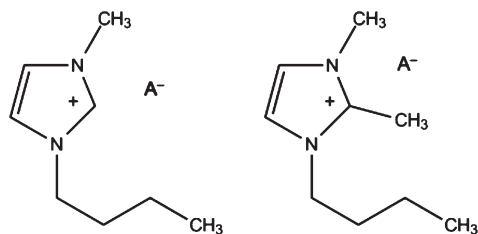
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**Figure 1.** The structures of the 1-butyl-3-methyl-imidazolium (left) and 1-butyl-2,3-dimethyl-imidazolium (right) ionic liquids used in this study. A is the anion, e.g., Cl in 1-butyl-3-methyl-imidazolium chloride, [bmim][Cl],  $\text{CF}_3\text{SO}_3$  in 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate, [bmim][ $\text{CF}_3\text{SO}_3$ ], etc.

obtained using this mixed solvent system than with individual solvents such as pyridine. Furthermore, the addition of a third component, such as tetracyanoethylene, further increases the extraction yield.<sup>12,13</sup> However, very large extraction yields seemed to be confined to just one or two specific coals, Upper Freeport being the most widely studied. This coal and one or two others may be anomalous, in that the NMP/ $\text{CS}_2$  soluble fraction obtained from other coals is comparable to the yields obtained with pyridine extraction.

In previous work in this laboratory we have shown that the NMP/ $\text{CS}_2$  mixed solvent system can extract cations from various clays and apparently form complexes that strongly absorb light in the visible region.<sup>23</sup> The individual solvents cannot form such complexes, but nevertheless can extract smaller amounts of the cations from the clays. Because many coals have significant contents of minerals and inorganic ions, the ability to complex with these species could be important in determining solubility. This is because organic carboxylate salts (in lower rank coals) and  $\pi$ -cation interactions can act as cross-links in coal.<sup>5–7</sup> Pure NMP and solvents like pyridine apparently do not form complexes with cations, but the 1:1 NMP/ $\text{CS}_2$  mixed solvent does. This may be an important factor in the enhanced extraction yields obtained from certain coals using this binary solvent system. This suggests that a study of the ability of ionic liquids, ILs, to swell and solubilize coals would be interesting.

ILs consist of large organic cations associated with various anions that melt at or below 100 °C. Many are liquids at room temperature. They have outstanding chemical and thermal stability, are nonflammable at ordinary temperatures, and have a negligible vapor pressure. (e.g., see refs 24 and 25 and citations therein.) A particularly versatile group of ILs is based on imidazolium cations, and the structures of the ILs used in this study are illustrated in Figure 1. The properties of these solvents can be “tuned” by varying the imidazolium substituent groups and the nature of the anion, so that unusual combinations of reagents, both organic and inorganic, can be brought into the same phase or multiphase processes can be designed. We have found that certain ILs can fragment, disperse, and solubilize some low- and medium-rank coals to a remarkable degree. We report our initial results here.



**Figure 2.** PRB coal where the as-received sample and coals treated with 0.1N HCl are first extracted with pyridine and then placed in contact with fresh solvent.

### Materials and Methods

The ionic liquids were all purchased from Sigma-Aldrich and used as-received. The supplier reports an HPLC assay for 1-butyl-3-methylimidazolium chloride as  $\geq 99\%$ . The other ILs used in this study are somewhat less pure, but all were assayed at  $\geq 95\%$ . The Illinois No. 6 and the Upper Freeport coals used in this study were Argonne Premium Coal samples. Chevron USA Inc., an affiliate of Chevron Corporation, provided a Powder River Basin (PRB) sub-bituminous coal.

Coals were mixed with ionic liquids in centrifuge tubes held at 100 °C in an oil bath. Samples for microscopic observation were simply smeared onto glass slides at room temperature. Micrographs were obtained in transmission using a Leica DM 4000 research microscope.

### Results

First, it is useful to recall what is usually observed when a solvent such as pyridine is placed in contact with a low- or medium-rank coal. As an example, we consider what happens when a PRB sub-bituminous coal and samples of this coal treated with 0.1N HCl are first extracted with pyridine and the residue placed in contact with fresh solvent in a graduated cylinder. The results are shown in Figure 2. A solvent phase remains separate from a solid phase that consists of swollen coal particles. We found that this coal in the as-received form has about 11% pyridine soluble material, while about 15% dissolves in NMP. The yields from this and other extractions (to be described later) are summarized in Table 1. The residue swells to about 1.9 times its original dimensions when put in contact with fresh amounts of pyridine. In previous work, we observed that in addition to covalent cross-links, low-rank

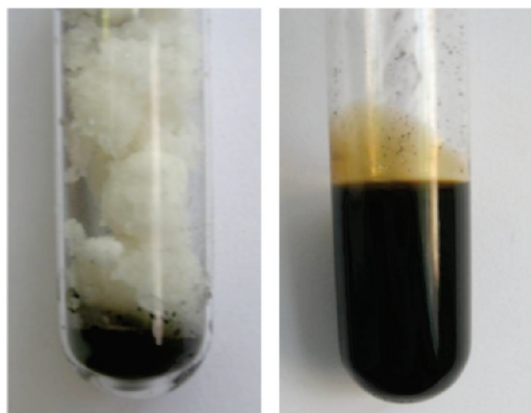
**Table 1. Extract Yields Obtained from Coals in Specified Solvents and Mixed Solvents**

coal	extract yield				
	NMP	pyridine	ionic liquid (IL)	IL + NMP	IL + pyridine
Powder River Basin	15.3%	11.2%	> 19.2%	30.4%	20.5%
Illinois No. 6	15.8%	34% <sup>a</sup>	> 22.5%	40.2%	25.3%
				46.3%	27.2%
Upper Freeport	20.5%	35% <sup>a</sup>	> 14.4%	23.4%	29.2%

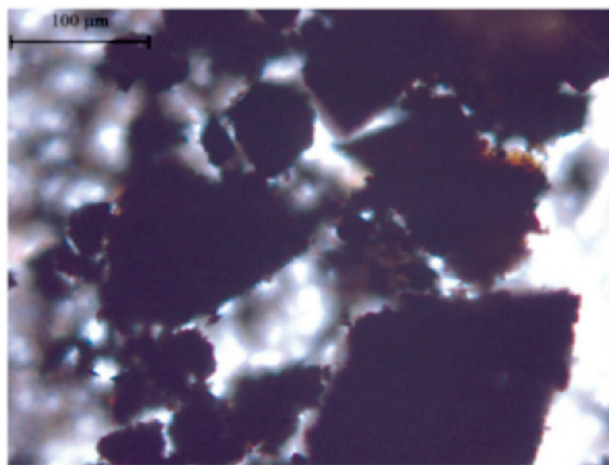
<sup>a</sup> Data from ref 7.

coals are also cross-linked through the formation of salt bridges and  $\pi$ -cation interactions. These limit the degree of swelling and the amount of soluble material that can be recovered.<sup>5–7</sup> We therefore also washed the coal with 0.1N HCl in water and found that the extract yield (in pyridine) increased to 17%, while the swelling of the insoluble residue increased to a factor of 2.4 times the original (volume) dimensions. FTIR spectra (not shown) demonstrate a conversion of  $\text{COO}^-\text{M}^+$  groups, presumably present as clusters that cross-link the coal, to  $\text{COOH}$  groups.

When the same coal is placed in contact with an IL we obtained surprising results. We chose to initially use 1-butyl-3-methylimidazolium chloride,  $[\text{bmim}][\text{Cl}]$ . This IL is a solid at room temperature, but apparently melts near 80 °C (the observed melting temperature depends on the water content of this hydrophilic material). A mixture of the powdered IL and an as-received sample of the PRB coal (10% by weight) were placed in a centrifuge tube. Figure 3 shows the two powders in contact at room temperature ( $\sim 25$  °C). Upon heating to 100 °C, a dark black solution/dispersion was immediately obtained and the mixture remained a liquid on cooling to room temperature, as also shown in Figure 3. A gel slowly formed on the surface over time (hours) as a result of the absorption of moisture from the atmosphere. Because the IL has almost zero vapor pressure, this is easily removed by reheating to 100 °C.



**Figure 3.** An Illinois No. 6 coal and the IL  $[\text{bmim}][\text{Cl}]$  (white material) before and after heating to 100 °C.

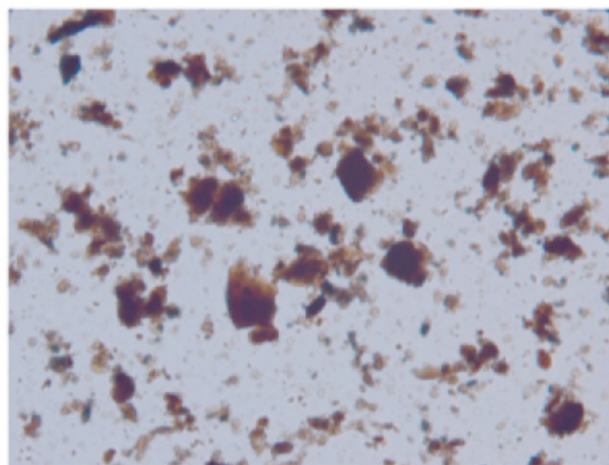


It is difficult to determine precisely what portion of the coal has dissolved and how much is present as dispersed particles. The suspension could not be filtered using conventional filter paper (cellulose dissolves in this solvent) and when attempting to use Teflon or glass fiber filters filtration stopped very early in the process, as a viscous gel would form as the coal/solvent mixture became more concentrated. Centrifugation at ordinary speeds was also inefficient, because there are very fine, swollen coal particles in these mixtures. However, by centrifuging hot tubes, pouring off the supernatant solution, remixing with IL and pouring off the second extraction after centrifugation, we estimate that more than 19% of this coal (by weight) had dissolved in the IL. We will return to this question of solubility later. First, we wish to point out what we believe to be some remarkable and interesting characteristics of this coal/IL dispersion.

Figure 4 compares micrographs ( $\times 200$ ) of the original PRB coal (left) and the broken and dispersed material obtained after contact with  $[\text{bmim}][\text{Cl}]$  (right). The larger particles of the coal dispersed in the IL are less than 50  $\mu\text{m}$  in size, while the numerous smaller particles are 10  $\mu\text{m}$  or smaller in diameter. The IL has disintegrated the original coal particles (the initial particles were mostly of the order of 100  $\mu\text{m}$  in size). If the solvent phase is removed quickly using a small amount of water, it can be observed that the remaining particles are not glassy, but rubbery, showing that they are solvent-swollen gels. This is a very interesting result—we have never seen coal behave like this in any other solvent.

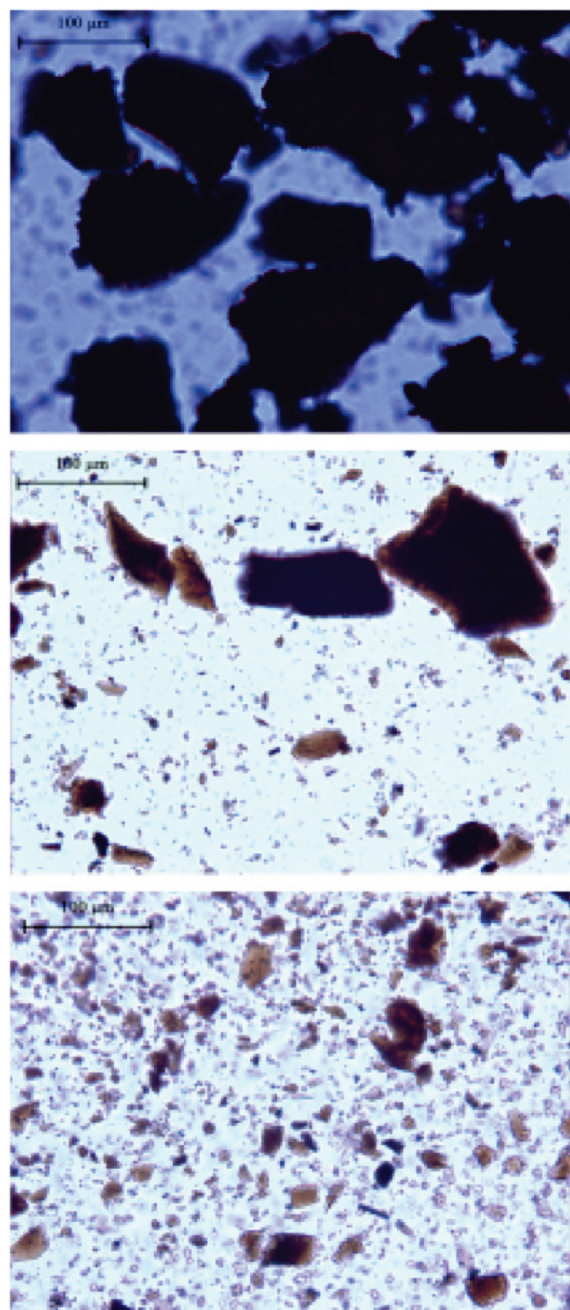
Illinois No. 6 coal appears to be broken up and dispersed to an even greater extent than the PRB coal. Figure 5 compares micrographs ( $\times 200$ ) of the original coal and a smear of the dispersion obtained after 2 h in contact with  $[\text{bmim}][\text{Cl}]$ . There are a few residual large particles (middle micrograph), but the bulk of the sample appears to have become dispersed as small particles, many of the order of 10  $\mu\text{m}$  or less in diameter (bottom micrograph). After 72 h at 100 °C there appears to have been an increase in dispersion, although this is hard to quantify using this approach. However, the particles certainly appear to be less opaque, perhaps because they are thinner, as can be seen in the micrograph shown in Figure 6.

Because of the difficulties we encountered in attempting to filter and centrifuge the viscous dispersion obtained by mixing both the PRB and Illinois No. 6 coal with this IL, we diluted the IL/coal suspension with NMP, filtered the dispersion, and



**Figure 4.** Optical micrograph ( $\times 200$ ) of a PRB coal suspended in water and smeared between micrograph slides (left) and a micrograph ( $\times 200$ ) of a smear of the same coal after heating to 100 °C with the IL  $[\text{bmim}][\text{Cl}]$  then cooled to room temperature (right).





**Figure 5.** Optical micrograph ( $\times 200$ ) of an Illinois No. 6 coal suspended in water and smeared between micrograph slides (top) and micrographs ( $\times 200$ ) of a smear of the same coal after heating to 100 °C for two hours with the IL [bmim][Cl] then cooled to room temperature (middle and bottom).

precipitated the soluble coal extract in water. Both the residue and extract were then Soxhlet extracted with water to remove residual [bmim][Cl] and NMP. We found that about 30% of the PRB coal had dissolved in the IL/NMP mixture, while more than 40% of the Illinois No. 6 coal dissolves in this mixture (see Table 1). Adding pyridine to the IL/coal suspension gave a lower yield of soluble material relative to adding NMP, about 25% for the Illinois No. 6 coal. This is somewhat surprising because the parent coal is more soluble in pyridine

than in NMP. Soxhlet extracting the IL/coal suspension did not change this number significantly. Lower yields of soluble material were also obtained for the PRB coal using pyridine with the IL/coal slurry, again relative to using NMP. Yields were still higher than those obtained from coal in the absence of [bmim][Cl], however.

Because of its unusually high solubility in NMP/CS<sub>2</sub> mixtures, we also examined the results of mixing Upper Freeport coal with [bmim][Cl]. This coal remains anomalous and did not form a dispersion of coal fragments and dissolved material, as can be seen in Figure 7. As a result, we obtained lower yields of soluble material when NMP or pyridine was added to this coal/IL mixture, as reported in Table 1.

Not all ILs will form this type of dispersion with the PRB or Illinois No. 6 coals. Figure 8 shows what is observed when Illinois No. 6 coal is mixed with the IL, [bmim][CF<sub>3</sub>SO<sub>3</sub>]. Upon initial contact at room temperature, the coal particles are apparently unaffected and the solvent appears clear (apart from suspended particles). Upon heating to 100 °C, however, a viscous black dispersion is formed (see Figure 8), similar in gross appearance to what is observed using the IL [bmim][Cl] (Figure 3). Unlike this latter dispersion however, upon cooling to room temperature the coal particles can clearly be seen both at the bottom of the tube and floating around in the slightly discolored solvent. They do not appear to be broken up significantly. We found that most of the ILs we examined gave similar results to those shown in Figure 8, only those imidazolium salts with chlorine anions formed a fine dispersion of coal particles in a coal/IL solution with the Illinois No. 6 and PRB coal samples. A summary of our observations for these two coals is presented in Table 2.

## Discussion

It is well-known that coals and other materials can spontaneously fracture in the presence of solvents. In a paper published more than 30 years ago, Keller and Smith<sup>26</sup> first commented on earlier observations by Bangham et al.<sup>27</sup> that charcoal “virtually exploded” when inserted into methanol and went on to show that coal particles spontaneously fractured in the presence of certain solvents. However, the particle sizes remained rather large, in the context of what is being discussed here. Most of the original coal particles were larger than 250 µm in size and were reduced to about 60 µm or larger in size. In a classic study of the fracture of cross-linked glassy polymers, Turner Alfrey et al.<sup>28</sup> noted that flat round discs of styrene-divinylbenzene copolymers would break apart with “an audible ping, splash” on being placed in contact with certain solvents. Again, the material was fractured into several large pieces. Brenner<sup>29</sup> observed that coal particles expand, become cracked, and greatly distorted in the presence of good solvents, but they were not fractured or dispersed to the extent reported here. Van Niekerk et al.<sup>30</sup> also recently observed a similar fracturing of millimeter-sized particles of South African coals.

Fracturing is a consequence of the high stresses that can be generated by the swelling process. In synthetic polymers this

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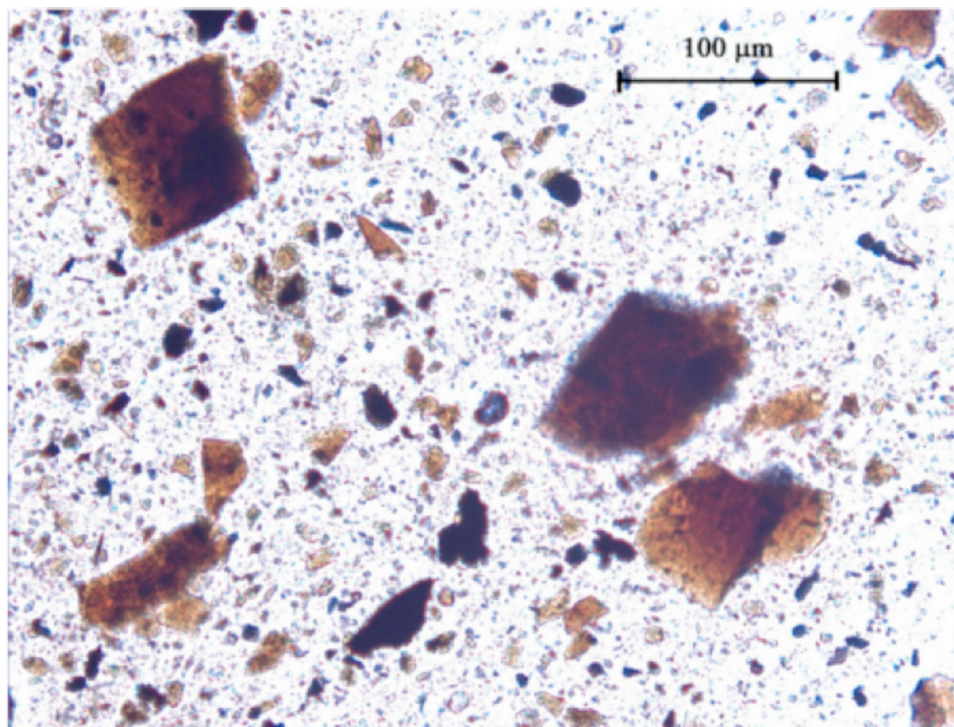
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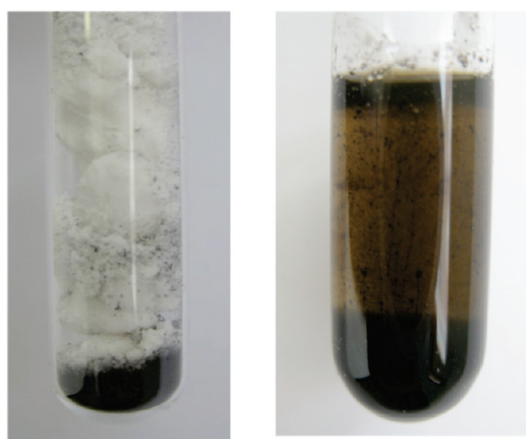
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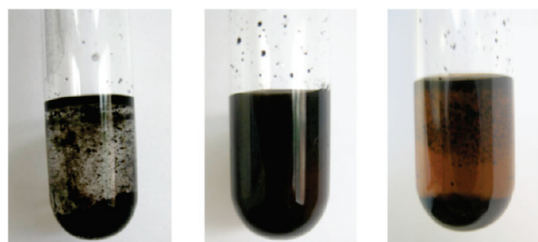
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**Figure 6.** Optical micrograph ( $\times 200$ ) of a smear of an Illinois No. 6 coal after heating to 100 °C with the IL [bmim][Cl] for 72 h and then cooled to room temperature.



**Figure 7.** Upper Freeport coal sample and IL (white material) before and after heating to 100 °C.



**Figure 8.** Illinois No. 6 coal and IL (white material) before mixed with the IL, [bmim][CF<sub>3</sub>SO<sub>3</sub>] at room temperature (left), at 100 °C (middle), and after cooling back to room temperature (right).

was attributed to the large increase in stress that occurs when a glassy core that is diminishing in size is trying to hold a thick swollen shell in compression.<sup>28</sup> In coals, a mismatch in the

swelling tendencies of different types of macerals, the presence of mineral inclusions and various other heterogeneities that lead to uneven swelling also play a part.<sup>29,30</sup> However, we suggest that the extent of disintegration and subsequent dispersion of coals observed when mixed with certain ILs is unusual. Presumably, this is a consequence of a rapid and large build up of stresses when two of the coals studied here are immersed in [bmim][Cl].

The ability of certain ILs to disintegrate and disperse at least some coals must surely be related to the intermolecular interactions between the components of these mixtures. These cover a wide range, from the electrostatic (between ILs and mineral surfaces and chelated ions in the coals), ion–dipole, and dipole–dipole interactions to in some cases even hydrogen bonding (the C2 hydrogen, the hydrogen attached to the carbon between the two nitrogen atoms in the imidazolium ring, hydrogen bonds<sup>24</sup>). It is also well-known that ILs can engage in  $\pi$ -cation interactions.<sup>31–33</sup> We have observed in previous work that these latter interactions appear to act as cross-links in various coals. It is possible that the replacement of metal cations with bulky IL groups plays a role in the fracturing and dispersion we observe.

The strength and extent of the interactions between coals and ILs will vary with the structure of the coal, the nature of the substituents on the imidazolium ring and the nature and size of the anion. The ILs that broke up and dispersed two of the coals we studied to the greatest extent both had Cl<sup>−</sup> counterions, and there is a significant difference in the size of the cations and anions in these materials. In a study of the ability of ILs to inhibit the aggregation of asphaltenes, Hu

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Table 2. Appearance of Illinois No. 6 Coal after Mixing with Specified Ionic Liquids

ionic liquid	room temperature appearance	appearance at 100 °C	appearance upon cooling to room temperature
[bmim][Cl]	two solids in contact	thick, black, solution/dispersion	thick, black, solution/dispersion
[bmmim][Cl]	two solids in contact	thick, black, solution/dispersion	thick, black, solution/dispersion
[bmim][BF <sub>4</sub> ]	clear liquid in contact with coal particles	slightly discolored liquid in contact with coal particles	slightly discolored liquid in contact with coal particles
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	clear liquid in contact with coal particles	thick, black, solution/dispersion	slightly discolored liquid in contact with coal particles
[bmim][PF <sub>6</sub> ]	clear liquid in contact with coal particles	clear liquid in contact with coal particles	clear liquid in contact with coal particles
[pmim][I]	slightly discolored liquid in contact with coal particles	thick, black, solution/dispersion	slightly discolored liquid in contact with coal particles

and Guo<sup>34</sup> observed that this disparity in size could result in local differences in charge density, promoting the ability of chlorine anions to engage in acid–base interactions and hence disrupt interactions between asphaltene molecules. However, one would then expect the most soluble of the coals studied (in an NMP/CS<sub>2</sub> mixed solvent), Upper Freeport coal, to also show increasing solubility in the presence of these ILs, but it does not. The interactions that promote swelling, fracture, dissolution, and dispersion in the PRB and Illinois No. 6 in certain ILs do not seem as favorable in this coal, and it remains a bit of a mystery because of its anomalous behavior.

It is also interesting and important that ILs allow a far larger proportion of the PRB and Illinois No. 6 coals, to dissolve in NMP and (to a lesser extent) pyridine. We suggest that this is because these coals consist of entities that are indeed cross-linked networks rather than associated structures. In rubber-like networks (i.e., lightly cross-linked) made up of flexible chains the “sol” fraction is usually readily extracted, the macromolecules being able to diffuse out by a reptation-type process. However, Aharoni and Edwards<sup>35</sup> pointed out a number of years ago that if both the network and sol are highly branched and rigid, the latter would be trapped. They showed that solvent extraction of such networks fails to remove highly branched macromolecules. Many coals appear to behave as if they are made up of

cross-linked, stiff chain entities. There are some classic studies that demonstrate that a proportion the soluble material in coals is extracted only with great difficulty, taking months in some cases,<sup>36,37</sup> while shock heating of coal to 420–450 °C results in a large increase in the extractability.<sup>38–42</sup> Brown and Waters<sup>43</sup> proposed that much of this latter material is trapped in the coal and can be released by a breakdown in the network, a position also argued by Given et al.<sup>44</sup> Although a reasonable hypothesis, it was also entirely possible that a significant portion of soluble material was obtained as a result of breaking just a few bonds, releasing high molecular weight but soluble material. However, the disintegration and dispersion of certain coals in specific ILs occurs under noncracking conditions, 100 °C or lower temperatures, indicating that there is indeed significant amounts of trapped soluble material in these coals.

## Conclusions

It has been demonstrated that certain ionic liquids fragment, swell, partially solubilize, and disperse a PRB and Illinois No. 6 coal as extremely fine particles to a remarkable extent. It is postulated that in part this is a result of the ability of ILs to disrupt intermolecular interactions in these coals. This significantly enhances the solvent extraction yields obtained from these two coals. Upper Freeport coal did not show the same behavior, however. It is proposed that the fragmentation breaks the coal network, allowing the dissolution of trapped material.

**Acknowledgment.** The authors gratefully acknowledge the support of Chevron USA Inc., an affiliate of Chevron Corporation.

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