# Dissolution, Swelling Properties, and Complex Formation of Clays in NMP/$CS_2$ Mixed Solvents

*Pakorn Opaprakasit, Paul C. Painter, and Michael M. Coleman*

The Energy Institute
Penn State University
University Park, PA 16802

## Introduction

Solvent swollen coals and the extract solutions that can be obtained from them are complex systems, displaying a rich range of behavior that can vary from coal to coal and with the nature of the solvent. Certain coals, notably Upper Freeport have a significantly enhanced solubility in this mixed solvent system and suspensions of the extracted parent coal and certain solutions of the extracts form gels and display viscoelastic behavior[1]. The nature of the interactions in this mixed solvent system and the mechanism by which small amounts of certain additional additives further enhance coal solubility remains largely unknown, although some progress has been made as a result of recent studies[2,3].

Dyrkacz[3] reported the results on a systematic study of this solvent pair, using both spectroscopic and physical property measurements, and concluded that the presence of some type of NMP chain oligomer at particular concentrations may indeed be an important factor. However, even though the results suggested that there was weak complex formation between the mixed solvent components, there was no evidence that these complexes were long-lived.

In recent work we have proposed that π-cation complexes can form in coal and act as cross-links or junction zones similar to those found in ionomers[4,5]. Accordingly, we decided to determine if NMP/$CS_2$ could also form complexes with this solvent system and present some preliminary results here.

## Experimental

Montmorillonite clay was obtained from Nanoclay co. under the brand name Cloisite $Na^+$. Infrared spectroscopic measurements were recorded on a Digilab model FTS 45 FTIR spectrometer at a resolution of 2 $cm^{-1}$. UV-Vis spectroscopic measurements were performed on a Perkin Elmer spectrometer model Lambda 2S.

## Results and Discussion

**Clay Swelling and Cation Extractability of Solvents in Contact with Clay.** Information concerning clay/solvent interaction could be important, because most coals have a significant amount of mineral matter that could act as a source of the cations that can form ionomer-like junction zones or cross-links in the organic component of coal through π–cation interactions[4]. For example, montmorillonite clays contain alkali and alkali earth cations in the interlayer spaces of their aluminosilicate sheets. These cations bind to the sheet layers by an ionic interaction. It therefore seemed intriguing to examine what fraction of these cations could be extracted by NMP and $CS_2$, and whether the amount of extracted cation is enhanced by the 1:1 mixed solvent.

We will start by examining the swelling properties of the montmorillonite, Cloisite $Na^+$. This clay was placed in various solvents and its volume change was recorded after 2 days of contact. The results show that the non-polar solvents used in this study are more effective swelling agents than their polar-solvent counterparts. The swelling ratios observed in toluene and $CS_2$ are almost identical at 2.1, while those in more polar solvents, pyridine and NMP, are 1.9 and 1.3, respectively. Interestingly, the swelling ratio observed in the NMP/$CS_2$ mixed solvent is similar to that observed in neat NMP (1.3), which is much lower than that in neat $CS_2$. These results show that $CS_2$ alone is an effective swelling agent. However, when mixed with NMP, this ability is diminished.

We next examined the ability of solvents to extract cations from the montmorillonite clay by measuring the amount of $Na^+$ extracted from Cloisite $Na^+$ after 2 days of clay/solvent contact. The $Na^+$ cation was chosen to represent the clay cations, because of its abundance in this type of clay and its extractability was calculated using a calibration curve generated from standard solutions. The results are summarized in **table 1**. The extraction yield from $CS_2$ and toluene is, as expected, below the detection limit of the instrument, indicating that although these non-polar solvents swell the clay considerably, they are not capable of extracting this cation from the clay galleries or interlayers. The yield obtained from pyridine and NMP is 1 and 6%, respectively. This result indicates that NMP and pyridine can disrupt the clay/cation interactions and extract $Na^+$ species. NMP is roughly an order of magnitude more effective than pyridine. The corresponding result for an NMP/$CS_2$ mixed solvent is somewhat greater than pure NMP, 8% (2 days extraction). However, when the clay was placed in the solvent for 30 days, the amount of extracted $Na^+$ increases by a factor of almost 10, to 41%. It is apparent that NMP is the most effective single solvent in extracting $Na^+$ cations, but the addition of $CS_2$ enhances the extraction yield considerably. The mechanism of this enhancement, however, remains unknown.

**Table 1. The amount of extracted $Na^+$ cation from Cloisite $Na^+$ montmorillonite clay after 2 days of clay/solvent contact**

| Sample | Extraction Yield | |
|---|---|---|
| | g of $Na^+$ / 1 g of clay (x $10^5$) | Wt. %* |
| Toluene | 0 | 0 |
| $CS_2$ | 0 | 0 |
| Pyridine | 0.8 | 1 |
| NMP | 5.9 | 6 |
| NMP/$CS_2$ (2 days) | 7.2 | 8 |
| NMP/$CS_2$ (30 days) | 38.1 | 41 |

* Calculated on a basis of cation exchange capacity, $93 \times 10^{-5} gNa^+/1g$ of clay

**Interactions between Cations and NMP/$CS_2$ Solvent.** Given the results we previously obtained concerning π-cation interactions in coal[4,5], together with the results we obtained from swelling clays and cation extractability of solvents, it was decided to consider the changes that occur to $CS_2$, NMP and the 1:1 mixtures of these solvents in acid and base environments. Color change was used as a simple initial indicator of interactions. The results indicate that neat $CS_2$ is transparent and its color remains unchanged upon mixing with acid solutions. However, a color change is observed when this solvent is mixed with strong base solutions. The degree of color change seems to increase with the basicity of the added species. For example, the color of a $CS_2$/NaOH solution is more intense than that of a $CS_2$/triethylamine mixture. Although $CS_2$ is a non-polar solvent, this is not surprising, because $CS_2$ is a very polarizable molecule and charge/induced dipole interactions are known to occur in these systems. The resulting perturbation of the $CS_2$ π orbitals results in a shifting of absorption bands to the visible region. When pyridine and NMP alone are added to $CS_2$, however, the mixture remains transparent. Clearly, any interaction in these systems is not as strong, but could still occur.

A more precise measure of interactions than color change is provided by UV-Visible absorption spectroscopy. The spectra of the single and mixed solvents are shown in **figure 1.** The spectrum of $CS_2$ shows strong absorbancies in the UV region near 304 and 321 nm, while NMP also has a strong UV absorption near 252 nm, together with a shoulder at 275 nm. The bands can be assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively[6]. When these two compounds are mixed, the absorption maximum red-shifts to 359 nm. This absorption is most likely associated with the $n \rightarrow \pi^*$ transition of $CS_2$, whose energy gap is reduced as a result of an interaction. The mixture also absorb strongly throughout the region lower than 360 nm. These results are most likely due to a dipole/induced dipole interaction between the strong dipole of NMP and the highly polarizable S=C=S bonds. Additionally, when a small amount of NaOH is added, the absorption maximum further red-shifts to 374 nm, with a shoulder appearing in the visible region at 467 nm. This is consistent with the results obtained from the color change experiments, where a reddish-yellow solution was observed.

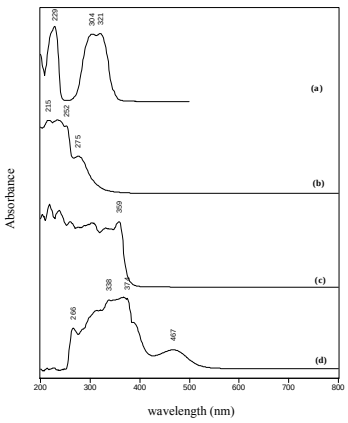


**Figure 1.** UV-Vis spectra of $CS_2$ (a), NMP (b), NMP/$CS_2$ 1:1 v/v binary solvent (c), and NMP/$CS_2$/NaOH 20:20:1 v/v (d)

We now turn to discuss the effect of additives on the FTIR spectra of the solvents. The results are shown in **figure 2**. The spectra of neat $CS_2$ and $CS_2$/HCl mixtures are very similar, with $\nu_3$ and $\nu_3 + \nu_1$ bands at 1527 $cm^{-1}$ and 2170 $cm^{-1}$, respectively. However, the main $\nu_3 + \nu_1$ band of $CS_2$ appears at a lower wavenumber, 2155 $cm^{-1}$, when mixed with strong bases, but still has a shoulder near 2170 $cm^{-1}$. The corresponding $\nu_3$ mode at 1527 $cm^{-1}$ also decreases in intensity and lower frequency shoulders appear, near 1500 $cm^{-1}$ in the spectrum of $CS_2$/NaOH mixtures. This indicates that the $CS_2$ $\pi$ bonds are strongly perturbed by cations.

The spectra of $CS_2$ and $CS_2$ in cyclohexane are also examined, as shown in **figure 3**. Because $CS_2$ and cyclohexane should interact through weak dispersion forces only, this latter spectrum should reflect any changes due to the dilution of $CS_2$/$CS_2$ interactions and provide the appropriate basis for comparison of spectroscopic changes observed in more polar solutions. In this solvent, $CS_2$ has a $\nu_3$ band at 1524 with a shoulder at 1517 $cm^{-1}$ and a $\nu_3 + \nu_1$ combination mode at 2172 $cm^{-1}$. This band also has a shoulder, near 2159 $cm^{-1}$. The spectrum of neat $CS_2$ shows a broader band pattern that is probably due to some sort of self-association effect (presumably due to strong dispersion interactions). The corresponding bands of $CS_2$ in pyridine, however, shift to 2165 and 1519 $cm^{-1}$, and there is further shift to 2161 and 1520 $cm^{-1}$ in the presence of NMP. This shift indicates an interaction that again perturbs the $CS_2$ $\pi$-bonding system. However, the band shift observed in these two mixtures is different from that found in $CS_2$/strong base solutions, where the main band apparently does not shift but decrease in intensity, with a new absorption mode appearing as a shoulder at lower wavenumber. This suggests an interaction or transient complex formation with some $CS_2$ molecules, but not others.

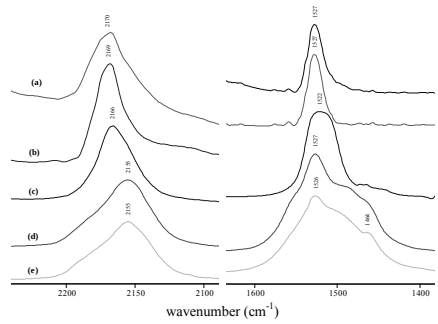


**Figure 2.** FTIR spectra of $CS_2$ + HCl (a), neat $CS_2$ (b), $CS_2$ + Triethylamine (c), $CS_2$ + NaOH (d), and $CS_2$ + $NH_4OH$ (e)

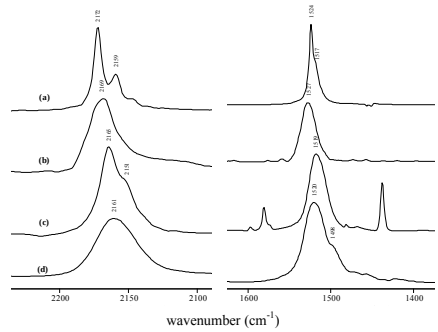


**Figure 3.** FTIR spectra of $CS_2$ in cyclohexane (a), neat $CS_2$ (b), $CS_2$ + pyridine (c), and $CS_2$ + NMP (d)

## Conclusions

The interaction between the "magic" binary solvent of NMP and $CS_2$, and its role in promoting extractability of Upper Freeport coal has been studied. It is likely that a complex formation of these mixed solvents and cations plays a key role. The results indicate that NMP/$CS_2$ is capable of extracting significant amount of and forming a complex to cations from montmorillonite clay. Given that Upper Freeport coal contains significant amounts of mineral matter, principally clays, the information obtained from these clay experiments may be important in reaching an understanding of the coal dissolution process. Nevertheless, the nature of the cations present in Upper Freeport coal remains uncertain and needs further investigation.

**Acknowledgement.** The authors gratefully acknowledge the support of the Office of Chemical Sciences, U.S. Department of Energy, under grant No. DE-FG02-86ER13537. P.O. is a recipient of and partially supported by the Development and Promotion of Science and Technology Talent Project (DPST), Thailand.

## References

(1) Iino, M.; Takanohashi, T.; Ohsuga, H.; Toda, K. *Fuel,* **1988,** *67,* 1639-1647.
(2) Chen, C.; Iino, M. *Prepr. Pap.- Amer. Chem. Soc., Div Fuel Chem,* **2000,** *45,* 89.
(3) Dyrkacz, G. R. *Energy & Fuels*, **2001**, 15, 918-929.
(4) Opaprakasit, P.; Scaroni, A. W.; Painter, P. C. *Energy & Fuels*, **2002**, 16, 543-551.
(5) Opaprakasit, P.: Ph.D. Thesis, the Pennsylvania State University, **2003**.
(6) Rao, C. N. R. *Ultra-Violet and Visible Spectroscopy Chemical Applications;* Butterworths: London, **1975**.