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SOLUBILITY OF MAOMING OIL SHALE KEROGEN

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The solubility of Maoming oil shale kerogen is studied by using the CS_2 – N-methyl-2-pyrrolidinone mixed solvent extraction. It is found that Maoming oil shale kerogen contains abundant soluble fractions (255.95 g/kg TOC). These solvent-soluble molecules are distributed or 'trapped' in the networks with abundant noncovalent bond interactions between soluble and insoluble molecules.

Introduction

Solvent extraction has always been one of the most commonly used techniques for studying the composition of coal and sedimentary organic matters. The primary aim of solvent extraction of coal was to isolate the material, or materials, from which coal has derived its coking properties. Studying the nature and amount of soluble materials existing in source rocks may provide the information about the potential of crude oil [1].

It is generally known that the solubility of oil shale kerogen is poor and shale can be converted to shale oil by pyrolysis. The nature of shale oil depends upon the structural characteristics of kerogen and the pyrolysis conditions used. Chemical and physical properties of oil shale kerogen are important for selecting the processing technology and determining what end products will be produced.

There are many studies on the chemical structure of Maoming oil shale kerogen, but no physical properties have been reported. Is oil shale kerogen really poor in solubility? How many portions of the kerogen are soluble? In recent ten years, an efficient mixed solvent consisting of CS_2 and N-methyl-2-pyrrolidinone (CS_2/NMP, 1 : 1, v/v) has been used in the studies of coal [2] and source rocks [1], and very high extraction yields are obtained.

Therefore, effective solvent extraction is a new method to investigate the solubility of oil shale kerogen. Abundant soluble materials present in oil shale kerogen have an important impact on its properties.

The purpose of this study was to use CS_2 and N-methyl-2-pyrrolidinone (CS_2/NMP) mixed solvent extraction to investigate the solubility of Maoming oil shale kerogen and in which form these soluble molecules exist in kerogen. Chloroform was also used as the extraction solvent for comparison.

Experimental

Solvent Extraction

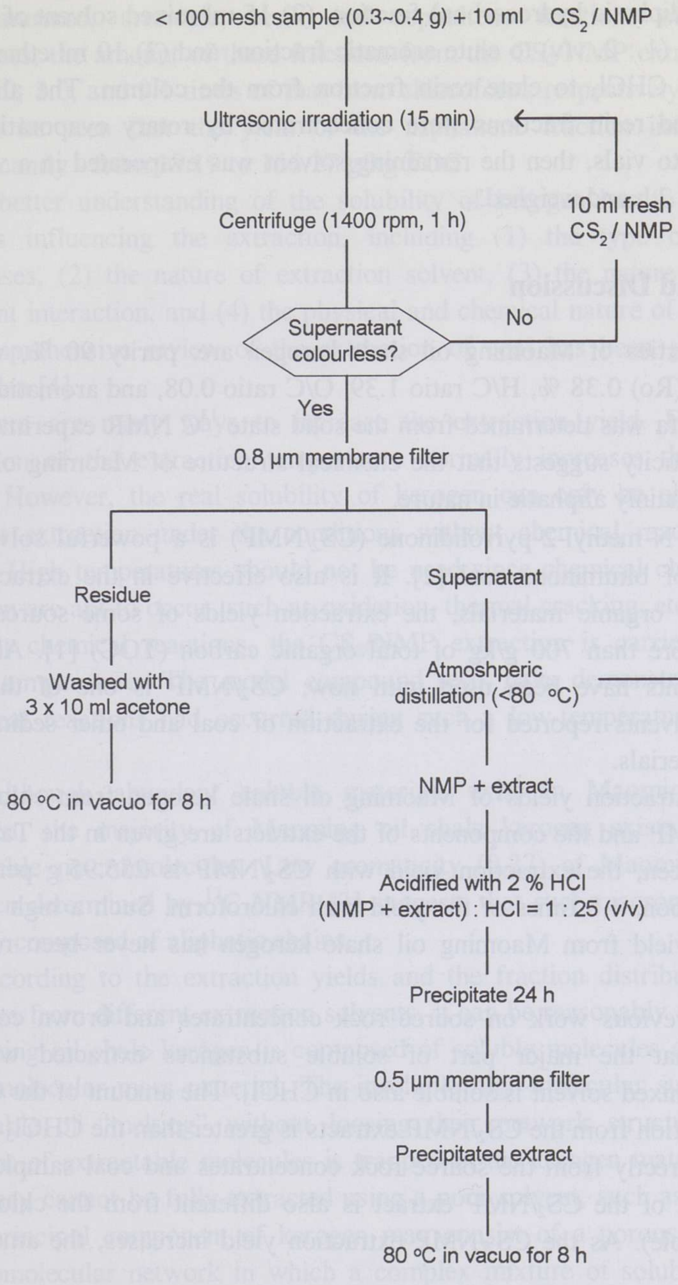
CS_2/NMP (1 : 1, v/v) mixed solvent extraction was used to study the solubility of Maoming oil shale kerogen, and it was carried out under ultrasonic irradiation (38 kHz) for 1 hour at room temperature (Figure) as described below.

The extraction vessel containing ca 0.3 g sample and 10 ml mixed solvent was sealed to prevent the loss of CS_2. After centrifugation at 1500 rpm for 60 min the supernatant was separated by decantation. Fresh mixed solvent was added to the residue, which was again extracted under ultrasonic irradiation for 30 min and centrifuged. These procedures were repeated until the supernatant became colorless (about 4~7 times). The residue was then washed with 10 ml acetone three times under ultrasonic irradiation (15 min) to remove any CS_2 and NMP.

The supernatant was filtered through a membrane filter with an average pore size of 0.5 μm and solid residue on the paper, if any, was combined with the residue described above. After removing CS_2 (stripped below 40 ^{0}C), the filtrate was acidified with 250 ml of a 2 % aqueous HCl solution per 10 ml filtrate. The precipitated extract was filtered under vacuum through a membrane paper. The solid extract was water-washed, dried in *vacuo* at 80 ^{0}C for 8 hour and weighed. The extraction yield was determined from the weight of the extracts obtained. For comparison Maoming oil shale kerogen was also extracted by $CHCl_3$ in a Soxhlet apparatus.

Fractionation of the Extracts

The maltene fraction of the extract was separated with pentane and analyzed by gravity column chromatography on silica gel and neutral alumina. The maltene fraction (ca. 20 ~ 50 mg) in ca 0.2 ml solvent was adsorbed onto 0.2 g of silica gel and the solvent was removed under a gentle flow of nitrogen.



Extraction procedure of the crude source rock concentrates

The adsorbed sample was then added to the top of a glass column (30 cm × 0.75 cm i. d.) packed with a hexane slurry of 3 g of silica gel in the lower part of the column and 2 g of neutral alumina in the upper, and sequentially eluted with following solvents: (1) 20 ml *n*-hexane to elute saturated (aliphatic hydrocarbon) fraction, (2) 15 ml mixed solvent of hexane and CH_2Cl_2 (1 : 2, v/v) to elute aromatic fraction, and (3) 10 ml ethanol and then 10 ml $CHCl_3$ to elute resin fraction from the column. The aliphatic, aromatic and resin fractions were concentrated by rotary evaporation and transferred to vials, then the remaining solvent was evaporated in a vacuum at 30 ^{0}C for 2 h and weighed.

Results and Discussion

Main properties of Maoming oil shale kerogen are: purity 90 %, vitrinite reflectance (Ro) 0.38 %, H/C ratio 1.39, O/C ratio 0.08, and aromaticity (fa) 0.270. The fa was determined from the solid state ^{13}C NMR experiment [3]. Low aromaticity suggests that the chemical structure of Maoming oil shale kerogen is mainly aliphatic in nature.

CS_2 – N-methyl-2-pyrrolidinone (CS_2/NMP) is a powerful solvent for extraction of bituminous coal [2]. It is also effective in the extraction of sedimentary organic materials, the extraction yields of some source rocks reach to more than 700 g/kg of total organic carbon (TOC) [1]. Although many solvents have been used until now, CS_2/NMP is one of the most effective solvents reported for the extraction of coal and other sedimentary organic materials.

The extraction yields of Maoming oil shale kerogen from chloroform and CS_2/NMP and the components of the extracts are given in the Table. As it can be seen, the extraction yield with CS_2/NMP is 255.95 g per kg of organic carbon, 4.8 times of the yield with chloroform. Such a high solvent extraction yield from Maoming oil shale kerogen has never been reported before.

Our previous work on source rock concentrates and brown coals [1] indicates that the major part of soluble substances extracted with the CS_2/NMP mixed solvent is soluble also in $CHCl_3$. The amount of the $CHCl_3$-soluble fraction from the CS_2/NMP extracts is greater than the $CHCl_3$ extract extracted directly from the source rock concentrates and coal samples. The composition of the CS_2/NMP extract is also different from the chloroform extract (Table). As the CS_2/NMP extraction yield increases, the amount of

Extraction Yield and Fractionation of the Extracts of Maoming Oil Shale Kerogen (g/kg TOC)

Solvent	Yield	Saturated	Aromatic	Resin	Asphaltene	S/A	R/As
$CHCl_3$	53.60	11.35	6.26	17.80	18.19	1.81	0.98
CS_2/NMP	255.95	36.37	17.92	35.39	166.27	2.03	0.21

* S/A – Saturated/Aromatic ratio; R/As – resin/asphaltene ratio.

the saturated, aromatic, resin and asphaltene fractions obtained also increases, the amount of these fractions from the CS_2/NMP extraction being 3.2, 2.9, 2.0, and 9.1 times of that from chloroform, respectively (see Table). It can be seen that the yield of the asphaltene fraction increases most significantly - from 18.19 to 166.27 g/kg TOC.

A better understanding of the solubility of kerogen has to consider all factors influencing the extraction, including (1) the type of extraction processes, (2) the nature of extraction solvent, (3) the nature of kerogen--solvent interaction, and (4) the physical and chemical nature of the extracts. A comprehensive review of the extraction of coal has been given by van Krevelen [4].

There are many ways to increase the extraction yield. For example, elevation of the extraction temperature normally increases the extraction yield. However, the real solubility of kerogen can only be obtained from solvent extraction under the conditions without chemical reactions taking place. High temperatures should not be used since chemical changes in the kerogen are apt to occur, such as oxidation, thermal cracking, etc. In order to prevent chemical reactions, the CS_2/NMP extraction is carried out under room temperature. The model compound tests have demonstrated that no chemical reactions had occurred during such a low-temperature extraction [1].

Although abundant soluble materials exist in Maoming oil shale kerogen, the majority of Maoming oil shale kerogen exists as solvent--insoluble macromolecules. Low aromaticity (0.27) of Maoming oil shale kerogen determined by ^{13}C NMR [3] suggests that such macromolecules are mainly composed of aliphatic chains.

According to the extraction yields and the fraction distributions of the extracts from different extraction solvents, it can be reasonably assumed that Maoming oil shale kerogen is composed of soluble molecules and insoluble high molecular mass material. The insoluble high-molecular substances are incapable of "melting" without loosing their network structure. A large amount of extractable molecules is trapped in the kerogen matrix so tightly that they cannot be fully extracted using a poor solvent, such as chloroform. The principal component of kerogen may consist of a porous cross-linked macromolecular network in which a complex mixture of soluble molecules is intimately sorbed.

The aliphatic and aromatic fractions are composed of nonpolar hydrocarbons. The heteroatoms and the corresponding polar non-hydrocarbons are concentrated in the resin and asphaltene fractions. Non-covalent bond interactions, such as hydrogen bonds, Van der Waals forces, charge transfer and polarization forces, may exist between the polar heteroatomic functional groups. Such noncovalent bond molecular interactions may also exist between the polar functional groups of the soluble fractions and the insoluble high molecular mass material. Therefore, there are abundant noncovalent bond interactions in these macromolecular structures. Some noncovalent bond interactions are so strong that they cannot be disrupted by $CHCl_3$. CS_2/NMP has a stronger ability to disrupt these non-covalent bond interactions and so gives higher extraction yield. Although these noncovalent bond interactions are individually much weaker than covalent bonds, their cumulative effects have a great impact on the physical properties of kerogen.

Conclusions

Abundant soluble fractions (255.95 g/kg TOC) are present in Maoming oil shale kerogen. The solvent-soluble molecules are distributed or 'trapped' in the networks with noncovalent bond interactions between soluble and insoluble molecules.

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