SOLVENT EXTRACTION
OF JORDANIAN OIL SHALE KEROGEN

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Jordanian oil shale kerogen was studied by solvent extraction with chloroform and two mixed solvents – methanol/acetone/chloroform (M/A/C) and CS₂/N-methyl-2-pyrrolidinone (CS₂/NMP). It was found that the extraction yield and the composition of the extracts are quite different in the case of different solvents. Such results suggest that Jordanian oil shale kerogen structure is characterized by three-dimensional networks cross-linked by covalent bonds and noncovalent bond intermolecular interactions. The nonpolar aliphatic and aromatic fractions are trapped or "protected" in these networks. The mixed solvents M/A/C and CS₂/NMP have stronger ability to disrupt these noncovalent bond interactions and give higher extraction yields. This may explain why, as the extraction yield increases, the amount of nonpolar saturated and aromatic fractions also increases.

Introduction

Sedimentary organic matter consists of solvent-soluble and -insoluble fractions. Solvent extraction has always been one of the most commonly used techniques for studying their composition. It is of great importance to determine the quantity of extractable substances present in kerogen considering the debated concept about the presence of mobile phase (component) and rigid phase (network) in kerogen [1]. Many studies on solvent extraction have been reported, but mostly on Soxhlet extraction carried out using conventional solvents at temperatures near the boiling point of the solvent. Chemical reactions such as decomposition and oxidation may occur in certain cases, especially in solvents with high boiling point.

It is generally known that the solubility of oil shale kerogen is poor and it can be converted to shale oil under high-temperature pyrolysis. The nature of shale oil depends upon the structural characteristics of kerogen and the pyrolysis conditions used. The chemical and physical properties of oil shale

kerogen are important for selecting the processing technology and determining what end products will be produced.

Is Jordanian oil shale kerogen really poor in solubility? The purpose of this work was to study the solubility of Jordanian oil shale kerogen using chloroform, methanol/acetone/chloroform (M/A/C) and CS_2/N-methyl-2-pyrrolidinone (CS_2/NMP) as the extraction solvent.

Experimental

Solvent Extraction

Jordanian oil shale kerogen was extracted with chloroform and with the mixed solvent M/A/C (23 : 30 : 47 by weight) in a Soxhlet apparatus for 72 h. CS_2/NMP (1 : 1 by volume) mixed solvent extraction was carried out under ultrasonic irradiation (38 kHz) for 1 h at the room temperature as described in the previous paper [2]. The residue was 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 0.5μm and solid residue on the paper, if any, was combined with the residue described above. After removing CS_2 (stripped below 40 °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 °C for 8 h and weighed. The extraction yield was determined from the weight of the extracts obtained.

Fractionation of the Extracts

The asphaltene fraction of the extract was precipitated with pentane. The soluble part (malthenes) was analyzed by gravity column chromatography on silica gel and neutral alumina. (The details of the fractionation procedure see in the previous paper [2].) The malthene fraction (ca. 20~50 mg) was adsorbed onto a glass column (30 cm × 0.75 cm i.d.) packed with a hexane slurry of 3 g silica gel in the lower part of the column and of 2 g 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 by volume) to elute aromatic fraction

(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, and weighed after the remaining solvent was evaporated in a vacuum at 30 °C for 2 h.

Results and Discussion

The main properties of Jordanian oil shale kerogen are as follows: vitrinite reflectance Ro 0.49 %; elemental composition, wt%: C 68.34, H 8.43, O 7.29; atomic ratio: H/C 1.48, O/C 0.08. High H/C atomic ratio indicates that the chemical structure of Jordanian oil shale kerogen is mainly aliphatic in nature.

Chloroform is widely used as a solvent in extraction of sedimentary organic matter, such as coal and kerogen. Other solvents such as benzene, toluene, acetone and some mixed solvents are also commonly used. Because of their low extraction yields, no great progress has been made. 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 [2, 3].

The model compound tests have demonstrated that no chemical reactions had occurred during such a low-temperature extraction and the extracted materials are real soluble molecules present in kerogen [4].

The amount of soluble fractions present in Jordanian oil shale kerogen is much higher than expected. Although abundant soluble materials are present in Jordanian oil shale kerogen, the majority of the kerogen exists as solvent-insoluble macromolecules. High H/C atomic ratio suggests that Jordanian oil shale kerogen is mainly composed of aliphatic chains.

The composition of the M/A/C and CS_2/NMP extracts is also different from that of the chloroform extract as shown in the Table. As the extraction yield increases, the amount of the saturated, aromatic, resin and asphaltene fractions obtained also increases proportionally.

Extraction Yields and Composition of the Extracts from Jordanian Oil Shale Kerogen with Different Solvents (g/kg C)

Solvent*	Extraction yield	Composition of the extracts			
		Saturated	Aromatic	Resin	Asphaltene
E_1	42.42	3.10	2.23	4.71	32.38
E_2	128.77	11.05	4.05	13.62	100.05
E_3	190.66	14.34	5.27	19.00	152.05

* E_1 = chloroform, E_2 = methanol/acetone/chloroform, E_3 = CS_2/NMP.

According to the extraction yields and the fraction distributions of the extracts obtained with different extraction solvents, it can be reasonably assumed that Jordanian oil shale kerogen is composed of soluble molecules and insoluble high-molecular-mass material. The insoluble high-molecular substances have the covalent bond linking network structure and are incapable of "melting" without loosing their network structure. The principal component of kerogen may consist of a porous and covalent bond cross-

linked macromolecular network, in which a complex mixture of soluble molecules is intimately sorbed. The solvent extractable molecules are trapped in the kerogen matrix. Some soluble molecules are trapped so tightly that they cannot be fully extracted using a poor solvent, such as chloroform.

The aliphatic and aromatic fractions of the extracts are composed of nonpolar hydrocarbons. The heteroatoms and the corresponding polar nonhydrocarbons in the extracts are concentrated in the resin and asphaltene fractions. Noncovalent bond interactions, such as hydrogen bonds, van der Waals forces and charge transfer, may exist between the polar hetero-atomic functional groups and be interacted with the polar functional groups in the insoluble kerogen matrix. Kerogen structure is characterized by three-dimensional networks cross-linked by covalent bonds and noncovalent bond intermolecular interactions. Some noncovalent bond interactions are so strong that they cannot be disrupted by chloroform.

The mixed solvents M/A/C and CS_2/NMP have a stronger ability to disrupt these noncovalent bond interactions and give higher extraction yields. The nonpolar aliphatic and aromatic fractions are trapped or "protected" in these networks. This may explain that as the extraction yield increases, the amount of nonpolar saturated and aromatic fractions also increases. 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

- Jordanian oil shale kerogen structure is characterized by three-dimensional networks cross-linked by covalent bonds and noncovalent bond intermolecular interactions.
- The principal component of kerogen may consist of a porous and covalent bond cross-linked macromolecular network, in which a complex mixture of soluble molecules is intimately sorbed.
- Some noncovalent bond interactions are so strong that they cannot be disrupted by chloroform. The nonpolar aliphatic and aromatic fractions are trapped or "protected" in these networks.
- The solubility in the solvent depends upon its ability to disrupt the noncovalent bond interactions between the soluble and the insoluble components in the kerogen.

Acknowledgments

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