



Kukersite oil shale kerogen solvent swelling in binary mixtures

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HIGHLIGHTS

- ▶ Examined kukersite kerogen structure using solvent swelling in binary mixtures.
- ▶ Established that specific kerogen-solvent interactions play a role in swelling.
- ▶ High swellability with mixed solvents over a broad range of solubility parameters.
- ▶ Electron donor strength plays a key role in determining extent of swelling.

ARTICLE INFO

Article history:

Received 20 January 2012

Received in revised form 12 April 2012

Accepted 20 June 2012

Available online 10 July 2012

Keywords:

Oil shale

Kerogen

Kukersite

Solvent swelling

Binary solvent mixture

ABSTRACT

This work presents experimental data on volumetric swelling of Estonian kukersite oil shale kerogen in 11 different binary mixtures, prepared using nine different solvents. Variations in equilibrium swelling ratios have been studied as a function of mixture composition. The results confirm the important role of specific interactions in determining the swelling behavior of this kerogen. Swelling of kukersite kerogen in mixtures with high electron donor number solvents (such as pyridine, propylamine, and NMP) show the highest values of equilibrium swelling ratios over the very broad solubility parameter range. In terms of maximizing swelling of this kerogen, binary solvent mixtures do not offer particular advantage relative to pure, strong electron donor solvents.

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1. Introduction

Volumetric expansion in solvents (solvent swelling) is a widely used, low-cost technique for determining the solubility parameters of fossil fuels with cross-linked macromolecular structures. The swelling data may be used to determine Hansen's three-dimensional solubility parameters [1], to characterize solvent-macromolecule interactions, and utilizing suitable theoretical models [2–4], for calculating cross-link densities, molecular weights between cross-links, and the number of repeat units per cross-link of a macromolecular structure.

Swelling is a complex phenomenon, especially in heterogeneous macromolecular networks such as oil shale kerogens or coals. Many coal related studies have shown that although volumetric swelling is a valuable tool for understanding macromolecular structure, swelling theories, especially those based on regular solution theory, are not reliably applicable to systems containing specifically interacting heteroatoms, especially those

with hydrogen bond-forming capabilities [5,6]. However, oil shale swelling studies indicate that most oil shales investigated follow regular solution theory reasonably closely [3,4,7–9]. Hence, there is not always a complexity of swelling behavior in oil shale kerogens like that usually seen with coals.

The cross-link density of a macromolecular network directly determines its swellability and existence of cross-links, covalent and non-covalent, prevents infinite swelling (i.e., dissolution). In principle, all oil shale kerogens can have two types of cross-links, just as have been discussed for coals. Non-covalent cross-links, or strong specific kerogen-kerogen intramolecular interactions, can be broken by specifically interacting solvents that interact with the kerogen similarly or more strongly than do other parts of the kerogen structure. Such solvents render the structure more swellable and penetrable by other solvents. It has also been observed in both coal and polymer swelling studies that mixed solvents of certain types can significantly increase both the rate and extent of equilibrium swelling [10,11], through a combined effect of increasing the penetrability of the macromolecular structure and increasing the thermodynamic/chemical compatibility of the mixture with the macromolecular structure.

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Our previous studies [12,13] on kukersite oil shale kerogen swelling has shown that the maximum swelling occurs in high electron donor number (EDN) solvents such as pyridine, methyl ethyl ketone or 1-methyl-2-pyrrolidone (NMP), indicating the role of specific interactions such as hydrogen bonds. In this regard the kukersite oil shale kerogen differs somewhat from oil shale kerogens that have been shown to follow regular solution theory reasonably closely [3,4,7–9].

The objective of this study is to investigate further the role of specific interactions in kukersite kerogen, through use of solvent pairs. This paper presents experimental data on the equilibrium swelling of kukersite oil shale kerogen in 11 different binary mixtures using the usual volumetric swelling technique (so called “test tube” technique) at room temperature. It presents simple global behavioral results – changes in solvent mixture composition relative to initial mixture composition as compositional distributions inside the swollen network were not studied here. While a large number of studies are available on oil shale kerogen swelling in a single solvent, much less attention has been directed at swelling in multicomponent solvent mixtures, despite the potential that such information offers for understanding the macromolecular structure.

2. Experimental

2.1. Oil shale sample and solvents

The oil shale kerogen sample used here was obtained from kukersite oil shale (from a commercial grade oil shale with organic matter content of about 35%) and it had a 91% organic matter content. The kerogen was isolated from the parent oil shale by a flotation technique [14]. The flotation technique was selected as chemical isolation methods may change the organic structure of oil shales. In the context of this paper, it is important to note, that oil shale kerogens have macromolecular structures that are practically insoluble in organic solvents at room temperature. The yields of solubles, or extractables, from kukersite oil shale (the object of this study) in typical organic solvents do not exceed 1.5% of the organic matter [29].

The elemental composition of the organic matter was 73.3 wt.% C, 8.8 wt.% H, 1.6 wt.% N, 16.3 wt.% O + S (by difference), determined using an Exeter Analytical model CE440 elemental analyzer. This indicates that the kerogen has high oxygen content (above 10%). Generally, for kukersite oil shale kerogens hydroxyl and carbonyl groups have been shown to contribute about half of the total organic oxygen, for example 42% and 13% respectively, on a total organic oxygen basis [15].

The samples were ground to <100 µm particle size. All samples were pre-dried 1 h at 105–110 °C in air (a standard oil shale drying procedure) before swelling measurements.

The nine solvents used in preparing the binary solvent mixtures were all of reagent grade. Some solvent characteristics of interest in this study are shown in Table 1, including total (or Hildebrand) solubility parameter [3,16,17], Gutmann's electron donor number (EDN) and acceptor number (EAN) [18–20], and molar volume [21].

2.2. Swelling procedure

Solvent mixtures of desired composition were prepared and used for swelling the kerogen. The solvent mixtures were used in large excess so that each solvent in the mixture was present in an amount much larger than the previously established solvent uptake volume (in pure solvent swelling experiments). This was done in an attempt to minimize any change in solvent mixture

Table 1
Properties of the solvents used.

Solvent	Solubility parameter, δ (MPa) ^{1/2}	EDN	EAN	Molar volume (cm ³ mol ⁻¹)
Benzene	18.8	0.1	8.2	89.4
Diethyl ether	15.6	19.2	3.9	104.8
Nitrobenzene	20.5	4.4	14.8	102.7
Nitromethane	26.0	2.7	20.5	54.3
NMP ^a	23.1	27.3	13.3	96.5
n-Propanol	24.5	19.8	37.7	75.2
Propylamine ^b	18.2	55.5	4.8	83.0
Pyridine	21.9	33.1	14.2	80.9
Toluene	18.2	0.1	3.3	106.8

^a NMP stands for 1-methyl-2-pyrrolidone.

^b Ethylamine EDN and EAN values were used for propylamine.

composition associated with possible selective absorption of solvent components by the kerogen.

In order to get sufficiently reliable data we have re-examined the swelling procedure presented in our previous paper [12]. It was found that the swelling results, especially for the isolated kerogen as used here, were somewhat affected by the centrifugation procedure. Therefore, solvent swelling in this study was determined following a modified experimental procedure.

An oil shale kerogen sample, up to 0.25 g, was placed into a constant diameter glass tube, fitted with a cap to minimize solvent loss during the experiment. The glass tube had an inside diameter of 5.5 mm and length 8 cm, excluding the cap. The tube was centrifuged three times at 6000 rpm for 5 min each. The reason for this was that it was found that shifting the position of the tube relative to the rotor in between spinning periods gave an easier to read initial height. The height of the dry kerogen sample was thus measured after the third centrifugation. Solvent was then added to the tube, in excess, and mixed to achieve complete wetting/mixing with the kerogen and then the tube was again centrifuged three times at 6000 rpm for 5 min each.

A preliminary swelling measurement could already be taken then, because the swelling was fast enough to be essentially complete by this point in time. The actual reported final height of the sample was then measured after allowing 24 and/or 48 h of swelling in solvent. It was found that the extra time rarely resulted in additional swelling beyond what was observed in the first few minutes, but only the longer time results are reported here, to ensure that all samples were truly equilibrated.

The volumetric swelling is characterized by the parameter Q , defined as the final swollen volume divided by the initial unswollen volume. To help better interpret the results to be shown below, Fig. 1 illustrates the reproducibility of data for swelling in a series of propanol-benzene mixtures. It can be seen that the swelling ratio deviation is generally below ± 0.02 , with only one exception visible in the concentration range from 10 to 20 mol% of propanol. One other occurrence of a larger uncertainty was observed in the case of benzene–NMP mixture (not shown here) that showed comparably large variation at a concentration of about 40 mol% of NMP.

3. Results and discussion

3.1. Pre-prepared binary mixture composition based analysis

Figs. 2–4 give changes in swelling ratios as a function of the molar compositions of the pre-prepared solvent mixtures. These figures show that the highest swelling capacities obtained in binary mixtures are not much greater than the maximum swelling ratio in the neighborhood of 1.4–1.45 obtained with the pure, high EDN solvents such as pyridine, NMP and propylamine. No synergistic effects of solvent pairs that resulting in an increase in maximum

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