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SOLVENT SWELLING OF DICTYONEMA OIL SHALE

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The present work investigates volumetric swelling of Estonian Dictyonema oil shale, as a representative of black shales of the Baltoscandian basin, in 22 solvents. This study shows that kerogen of Dictyonema oil shale is characterized by a low degree of swelling indicating a highly cross-linked structure. The relatively high swellability in high Guttmann's electron donor number solvents indicates the importance of non-covalent cross-links, such as hydrogen bonding, in swelling process and raises concern regarding the use of regular solution-based approaches. Despite this, the solubility parameter, a fundamental thermodynamic property, was tentatively determined from swelling data.

Introduction

Solvent swelling is a frequently applied low-cost technique to obtain experimental information on cross-linked macromolecular substances, including solid fuels such as coal [1, 2] and oil shales [3-6]. Solvent uptake data can determine solubility parameters and, by using suitable swelling models, the macromolecular structure can be characterized by estimating crosslink densities (or number average molecular weights between cross-links) [1, 6, 7]. The crosslink density (degree of cross-linking) has been a useful input parameter in coal devolatilization/pyrolysis modeling [8].

The present study uses the equilibrium solvent swelling data to characterize Dictyonema oil shale (Termadocian black shale) from Estonia – as a representative of the black shales of the Baltoscandian basin. Organic matter content of Dictyonema oil shales is typically 10–20% with an average elemental composition of (wt%) C: 58.3–76.0; H: 5.3–7.4; N: 1.88–4.24; S: 1.61–4.56; O: 12.22–34.3 [9]. The organic component of Dictyonema oil shales is known to contain relatively low amounts of solvent-soluble compounds – below 2.5%, organic matter basis [10]. Most importantly, as

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being a low oil yield oil shale [11] (exemplary Fischer assay, ISO-647-74, yields (wt%, daf): oil – 19.6, semicoking gas – 16.5, semicoke – 45.4 and water – 18.5 [12]), its processing by *ex situ* retorting technologies is not considered economical. However, despite this, Dictyonema oil shale may be a prospective resource of energy and chemicals.

The specific objectives of this paper were to evaluate the role of specific interactions (non-covalent crosslinks) in swelling and to get some indication whether or not approaches based on classical regular solution theory could be used for determining, at least for indicative purposes, crosslink density in the case of Dictyonema oil shale.

Materials and methods

The Dictyonema oil shale sample of North-Estonia was taken from a layer about 10 m underground. Its organic content is 13 wt%. The sample was characterized as follows: ash 86%, carbonates 2%, and elemental analysis results (wt%) C – 6.7, H – 0.9, N – 0.3, residue – 92.1 (giving H/C ratio of 1.56). The elemental composition of the organic matter was determined by an elemental analyzer Exeter Analytical model CE440.

Dictyonema oil shales are known to contain significant amounts of clay minerals (mostly illite and smectite [13]) that can swell/shrink in organic solvents. For example, mixed-layer clays with 70% clay content, mostly illite and smectite, [14] have been shown to swell/shrink in solvents with solubility parameter values between 15 to 25 $(MPa)^{½}$ (for example, the swelling ratios measured were 0.99 in hexane, 1.11 in acetone, 1.13 in acetonitrile or 1.19 in N,N-dimethylformamide). Therefore, acid treatment with HF was used to transform original shale minerals into nonswellable form, despite the fact that acid treatment may result in some changes in the kerogen [15]. For HF treatment, 0.5 litres of 1:1 HF (with water) was added slowly to 100 grams of previously crushed/ground (size < 1 mm) shale in an 1-liter flask at 0 °C. After mixing for 24 hours, the suspension was filtered and distilled-water washing was used to neutralize the acid-treated sample. The sample was dried in air at 100 °C for 1 hour. No original clay minerals were observed after acid treatment, the only original mineral left was pyrite. The major mineral formed was hieratite (K_2SiF_6). Finally, the sample was ground and sieved to get a size fraction of 0.32–100 µm. The organic content of the acid treated shale was roughly estimated to be about 25 wt%.

Solvent swelling experiments were performed with 22 solvents. All solvents were of analytical grade and used without further purification. They were selected to cover a wide range of solubility parameter values. The solvents are listed in Table 1 together with their key characteristics: molar volumes [16], solubility parameters (Hildebrand or total [6, 17, 18]; three dimensional Hansen solubility parameters [16]), Guttmann's electron donor numbers (EDN) and electron acceptor numbers (EAN) [19, 20].

Table 1. **Key characteristics of solvents used in swelling studies: molar volumes (V_m), solubility parameters (Hildebrand δ; dispersion δ_D; polar δ_P; hydrogen-bonding δ_H) and Guttmann's electron donor numbers (EDN), and electron acceptor numbers (EAN)**

	Solvents	V_m, cm^3/mol	δ, $(MPa)^{1/2}$	δ_D, $(MPa)^{1/2}$	δ_P, $(MPa)^{1/2}$	δ_H, $(MPa)^{1/2}$	EAN	EAN
1	Acetone	74.0	20.3	15.5	10.4	7.0	17.0	12.5
2	Acetonitrile	52.6	24.3	15.3	18.0	6.1	14.1	18.9
3	Aniline	91.5	21.3	19.4	5.1	10.2	35	
4	DMF	77.0	24.5	17.4	13.7	11.3	26.6	16.0
5	Ethanol	58.5	26.0	15.8	8.8	19.4	19.2	37.1
6	MEK	90.1	19.0	16.0	9.0	5.1		
7	Methanol	40.7	29.3	15.1	12.3	22.3	19.1	41.3
8	NMP	96.5	23.1	18.0	12.3	7.2	27.3	13.3
9	*n*-Propanol	75.2	24.5	16.0	6.8	17.4	19.8	37.7
10	Propylamine*	83.0	18.2	16.9	4.9	8.6	55.5	
11	Pyridine	80.9	21.9	19.0	8.8	5.9	33.1	14.2
12	Tetrahydrofuran	81.7	18.6	16.8	5.7	8.0	20.0	8.0
13	Benzylalchohol	103.6	24.8	18.4	6.3	13.7	23.0	36.8
14	Methylnaphthalene	138.8	20.3	20.6	0.8	4.7		
15	Benzene	89.4	18.8	18.4	0.0	2.0	0.1	8.2
16	Hexane	131.6	14.7	14.9	0.0	0.0	0.0	0.0
17	*o*-Xylene	106.8	18.0	17.8	1.0	3.1	5	
18	Toluene	102.7	18.2	18.0	1.4	2.0	0.1	
19	Nitrobenzene	71.5	20.5	20.0	8.6	4.1	4.4	3.3
20	Nitroethane	54.3	22.7	16.0	15.5	4.5	5	14.8
21	Nitromethane	63.9	26.0	15.8	18.8	5.1	2.7	
22	Dichloromethane**	106.8	20.3	18.2	6.3	6.1	0.0	20.5

DMF stands for dimethylformamide; NMP stands for *n*-methyl-2-pyrrolidinone; MEK stands for methyl ethyl ketone;

* ethylamine EDN and EAN values were used for propylamine;

** 1,2-dichloroethane EDN and EAN values were used for dichloromethane.

The volumetric solvent swelling procedure used was described in our previous paper [3]. In short, a few grams of oil shale sample was placed into a glass-tube with a cap (glass tube inside diameter 5.5 cm and length 8 cm without a cap region) and centrifuged three times at 6000 rpm for 5 minutes. The height of the sample was measured using a caliper ruler. Solvent in excess was added to the tube, mixed to achieve complete wetting/mixing and centrifuged three times at 6000 rpm for 5 minutes. The height of the sample was recorded after centrifugation and re-measured in 48 hours. The swelling behavior of Dictyonema oil shale is described by the volumetric swelling ratio calculated as $Q = h_2/h_1$, where h_1 – initial height of the un-swollen sample and h_2 – equilibrium height of swollen oil shale. In order to more conveniently compare/analyze results, also swelling ratio on a dry mineral matter-free basis, Q_{dmmf}, and molar solvent uptake as $(Q_{dmmf} - 1)/V_m$ were used. The Q_{dmmf} were determined from the equation (1):

$$Q_{dmmf} = \frac{Q - \dfrac{x_{\min} \cdot \rho_{org}}{x_{org} \cdot \rho_{\min} + x_{\min} \cdot \rho_{org}}}{1 - \dfrac{x_{\min} \cdot \rho_{org}}{x_{org} \cdot \rho_{\min} + x_{\min} \cdot \rho_{org}}}, \quad (1)$$

where x_{org} is the kerogen mass fraction, x_{min} is the mass fraction of mineral matter, ρ_{org} is the kerogen density (taken 1.15 g/cm^3, estimated from densities of Type II kerogens [21–23]) and ρ_{min} is the density of mineral matter (taken 2.65 g/cm^3, the density of oil shale mineral illite [24]).

Results and discussions

Table 2 presents swelling data of dried acid-treated Dictyonema oil shale samples in 22 solvents. The data is re-plotted in Fig. 1 to illustrate graphically variation of swelling ratios (dry mineral free matter basis) with Hildebrand solubility parameters of solvents. This is a traditional way to present swelling results for estimation of solubility parameter. Formation of a bell-shape curve

Table 2. **Swelling characterized by means of swelling ratio *Q* and swelling ratio on dry mineral ash free basis Q_{dmmf}. The Q_{dmmf} was calculated using equation (1)**

No	Solvent	*Q*	Q_{dmmf}
1	Acetone	0.95	0.89
2	Acetonitrile	0.95	0.89
3	Aniline	1.09	1.20
4	DMF	1.06	1.15
5	Ethanol	1.00	0.99
6	MEK	0.97	0.92
7	Methanol	0.98	0.96
8	NMP	1.03	1.07
9	*n*-Propanol	0.97	0.93
10	Propylamine	1.05	1.12
11	Pyridine	1.07	1.16
12	Tetrahydrofuran	1.06	1.13
13	Benzylalchohol	1.01	1.01
14	1-methylnaphthalene	0.99	0.97
15	Benzene	0.99	0.97
16	Hexane	0.96	0.91
17	*o*-Xylene	0.97	0.93
18	Toluene	1.02	1.04
19	Nitrobenzene	1.00	1.00
20	Nitroethane	0.98	0.96
21	Nitromethane	0.97	0.93
22	Dichloromethane	1.02	1.05

DMF stands for dimethylformamide;
NMP stands for *n*-methyl-2-pyrrolidinone;
MEK stands for methyl ethyl ketone;

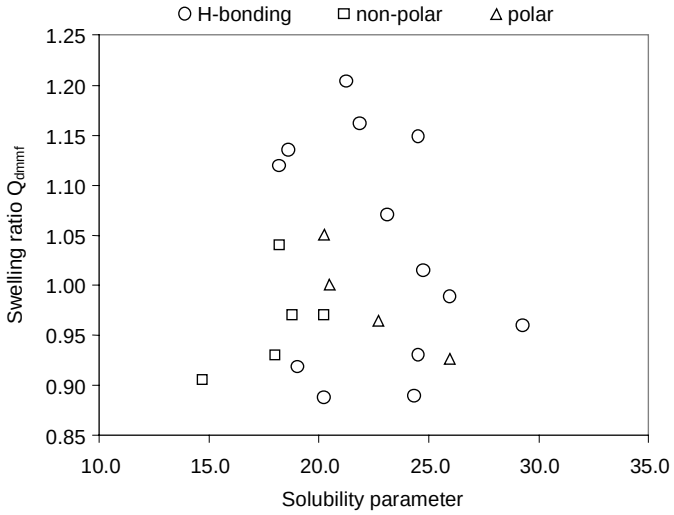

Fig. 1. Equilibrium swelling ratios, dry mineral matter free kerogen basis, as a function of solvent solubility parameters (Hildebrand solubility parameter). Circles correspond to swelling in hydrogen-bonding solvents, triangles in polar solvents and squares in non-polar solvents. See Table 1 to identify solvents by solubility parameter values and Table 2 by swelling ratio values.

should be expected when randomly distributed weak non-specific interactions dominate in swollen network. The swelling ratios and corresponding solvent solubility parameters in Fig. 1 show no clearly determinable pattern suggesting that chemical character causes specific interactions between solvents and kerogen plays important role in the swelling process. There are several observations that can be made regarding the swelling behavior of Dictyonema oil shale from this figure. It is useful to mention that our other unpublished data on several non-acid treated Dictyonema oil shales, both dried and non-dried, support the trends to be shown below.

First, comparison with literature data available on oil shales and coals reveals that Dictyonema oil shale is characterized by a considerably lower swelling capacity indicating the existence of tightly cross-linked structure. The maximum swelling ratio observed in mineral matter free bases was as low as 1.2 (see Fig. 1 and Table 2). For comparative purposes the following are some swelling extent maxima on dry ash free basis of some other oil shales: 1.4–1.7 for Kukersite oil shale, up to 1.8 for Rundle oil shale, 1.6–1.9 for Green River oil shale, 1.3–1.7 for Paris Basin Toarcian oil shale or about 1.6 for Göynyk oil shale. Note that these values are approximate, as these were estimated using equation (1) from available literature data [3–6]. Second, Dictyonema oil shale practically does not swell in non-polar solvents, and considerable swelling can be seen mostly in hydrogen-bonding solvents with high Gutmann's electron donor numbers (EDN). Generally, oil shale kerogens, the complex crosslinked macromolecules, are known to have

two types of cross-links: covalent and non-covalent ones. While the covalent crosslink density is constant, then the non-covalent crosslinks or specific shale-shale interactions can be disrupted by specifically interacting solvents causing higher swelling in these solvents. As Dictyonema oil shale shows significantly higher swellability in hydrogen bonding solvents with high EDN values (indicating importance of non-covalent or specific interactions such as hydrogen bonds), the data is re-plotted in Fig. 2 by means of molar solvent uptake as a function of EDN. The molar solvent uptake is used instead of the swelling ratio in order to eliminate the effect of solvent molar volume on solvent absorption extent. Figure 2 reveals that there could be a better correlation with swelling capacity. It can be seen how the molar solvent uptake increases with EDN increase up to a limiting value as expected [25] – the limiting molar solvent uptake is reached at about solvent EDN value of 25. It would follow that the greatest swelling extents are to be expected in hydrogen bonding solvents with highest EDN values, while some exceptions, toluene and dichloromethane (with practically zero EDN values and relatively high EAN values), could still result in comparatively greater swelling extents. Finally, noticeable shrinking, instead of swelling, was observed with several non-polar and polar solvents. It is worth noting that the shrinking appeared also in swelling of non-acid treated Dictyonema oil shale, in the case of both non-dried and dried samples. Although the shrinking is not a common experimentally seen behavior, still it is not

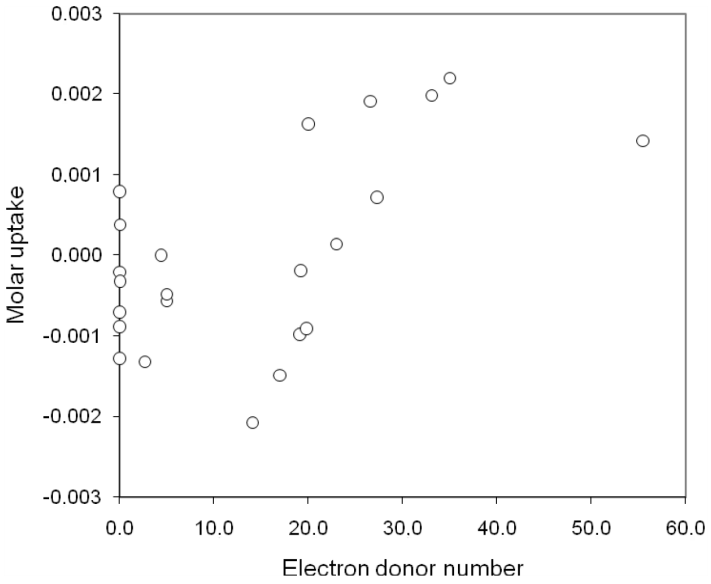

Fig. 2. Degree of swelling represented as a molar solvent uptake, $(Q_{dmmf} - 1)/V_m$, *versus* solvent Guttman's electron donor number. The shrinking behavior is the reason for the negative values of the molar solvent uptake in the case of several solvents.

unusual phenomenon in solvent swelling studies, and a slight shrinking has been observed also in other occasions: for example in the cases of petroleum asphaltenes [26], explained based on non-uniformity of the sample particle size, or in swelling of clay minerals [14]. One plausible reason for the shrinking behavior of Dictyonema oil shale could be rearrangement of kerogen structure in the presence of swelling agent assuming that the dry-state structure may not be the thermodynamically most stable one [27].

The major implication of the results shown in Table 2, also represented in Fig. 1 and 2, is that for Dictyonema oil shale, the highest swelling extents can be seen in specifically interacting solvents (in hydrogen bonding solvents with high EDN values, such as pyridine, NMP, tetrahydrofuran, propylamine), and this emphasizes the concern regarding the use of regular-solution based approaches. However, at present, there is no consensus as to what degree of non-ideality one should use regular solution based approaches. Therefore, simple models have been extended to quite complex systems, including coals [7] and oil shales [6], to estimate at least semi-quantitatively useful properties. Thus, the following is pursued only for comparative purposes as information on some other shales is available from literature: for Green River [6], Beypazari [4] and Göynük [4] oil shales using the Flory-Rehner model and its extension, the Kovak model [1, 28]. The main advantage of these models is that structure properties can be estimated from swelling data using a few key parameters: the macromolecule volume fraction in swollen network (from swelling ratio) and the Flory-Huggins interaction parameter (calculable from solubility parameter values of the macromolecule and the solvent).

In order to get a reasonable estimate on volume fraction of kerogen in swollen network (equal to reciprocal value of the selling ratio) from swelling data, the lowest swelling ratio (Q_{dmmf} = 0.89 for acetone) was taken to be 1, and others were corrected accordingly by adding 0.11 to corresponding swelling ratios Q_{dmmf}. It could be assumed that the shrinking was caused by re-arrangement of molecular structures, and thus the lowest swelling ratio was taken to be a so-called „reference state". Of course, this assumption is debatable.

Another largest source of uncertainty comes from the interaction parameter (χ) as the choice of proper value of χ is not presently clear. There has been a very limited amount of work found on the coal-solvent [29], and not at all for oil shale kerogen-solvent, interaction parameters. Therefore the solvent-kerogen interaction parameters were calculated in accordance with the suggestive equation [30]:

$$\chi = \chi_s + \frac{V_s}{RT}(\delta_s - \delta)^2, \tag{2}$$

where χ is interaction parameter, χ_s is taken constant with a value of 0.35, R is ideal gas constant, T is temperature, V_s is molar volume of the solvent, δ_s is solubility parameter of solvent and δ is solubility parameter of macromolecule, here of kerogen.

Table 3 presents tentative estimates of solubility parameters of Dictyonema oil shale kerogen (Hildebrand solubility parameter and three Hansen partial solubility parameters) from swelling data using Gee's approach [31, 32] – a graphical determination of solubility parameter, based on the assumption that the solubility parameter of a macromolecule matches the solubility parameter of solvents of maximum swelling (in principle the bell-shape curve seen Fig. 1). The formula of Gee is given as:

$$\frac{Q}{Q_{\max}} = \exp[-aQ(\delta_s - \delta)^2], \tag{3}$$

where Q and Q_{max} are the swelling ratio and the maximum swelling ratio respectively, δ_s and δ are the solubility parameters of solvent and macromolecule respectively, and a is a constant. The macromolecule solubility parameter can be determined from a rearranged equation (3) by plotting $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ versus δ_s of solvents used [31, 32]. Figure 3 shows an exemplary evaluation of the solubility parameters based on the Gee's approach for Hildebrand solubility parameter. The Hildebrand solubility parameter value of 22 $(MPa)^{1/2}$ corresponds to the linear regression line interception of the horizontal axis or the ratio of intercept and slope. Again, the data scattering seen on the plot indicates that the randomly distributed weak interactions, which are the basis for regular solution theory, are of secondary importance. The three-dimensional Hansen solubility parameters were similarly estimated. It is noteworthy that close values of solubility parameter were obtained in the case of all solvents and in the case of reduced number of solvents (for the solvents with EDN < AEN), indicating rudeness of the method used.

Tentative calculations for the number average molecular weights between cross-links are presented in Table 4 for two equations (swelling models): Flory-Rehner and Kovac equations [1, 28]. The results seem to underestimate the number average molecular weights between the cross-links for Dictyonema oil shale. Generally, oil shale thermo-chemical conversion tarry products, both thermobitumen and pyrolysis tar, show much higher number average molecular weight values [33, 34].

Table 3. **Solubility parameters [$(MPa)^{1/2}$] determined tentatively by Gee's method. The total solubility parameter (in principle the Hildebrand solubility parameter) calculated from three determined Hansen solubility parameters are shown for comparison**

	$\delta_{Hildebrand}$	δ_D	δ_P	δ_H	$\delta_t = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$
All solvents	22	19	6	12	23
Selected solvents*	22	18	6	11	22

* the selected solvents are solvents with EDN < EAN

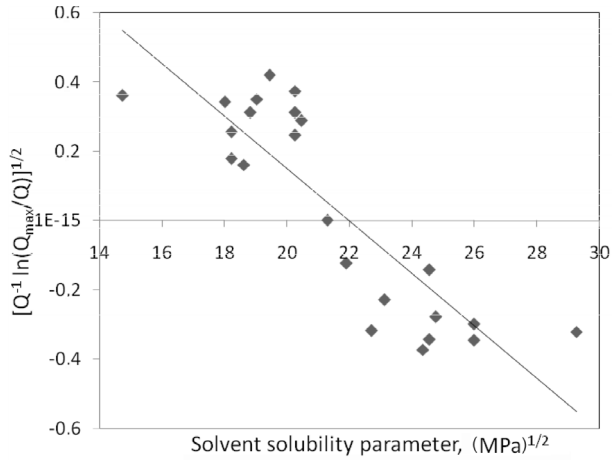

Fig. 3. Determination of the Hildebrand solubility parameter by plotting $[Q^{-1} \ln(Q_{max}/Q)]^{1/2}$ as a function of solubility parameters (δ_s) of solvents. The scattery on the plot indicates the role of non-covalent interactions (especially hydrogen bonds) and that of the randomly distributed weak interactions, which are the basis for regular solution theory, are of secondary importance.

Table 4. **Average values of calculated number average molecular weights per cross-links for Dictyonema oil shale. Literature values for other oil shales (Green River [6], Göynük [4], Beypazari [4]) are shown for comparison**

Oil shale	Flory-Rehner	Kovac $N = 1$	Kovac $N = 2$	Kovac $N = 3$
Dictyonema	83	373	274	241
Göynük	247	933	678	593
Beypazari	208	790	576	504
Green River (5.2% mineral)	215	808	581	505

N is the number of rotatable segments between branch points in the Kovac equation.

Conclusions

The low swelling capacity of Dictyonema oil shale in organic solvents suggests a highly cross-linked structure of the kerogen. Sensitivity of swellability to solvent donor numbers indicates the importance of non-covalent crosslinks (kerogen-solvent specific interactions such as hydrogen bonds) and suggests that models, that expect randomly distributed week interactions, may not be suitable for describing Dictyonema oil shale. The simplest models used show underestimation of the number average molecular weights between crosslinks.

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