APPLICATION OF INVERSE GAS-LIQUID CHROMATOGRAPHY FOR DETERMINATION OF THERMODYNAMIC PROPERTIES OF TEST COMPOUNDS IN OIL SHALE HIGH-BOILING OILS

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Inverse gas-liquid chromatography was used to determine specific retention volumes V_g^0 and excess enthalpy of mixing $\overline{H}^E$ for test compounds (alkanes, alkenes, aromatic hydrocarbons, alcohols, ketones, ethers and other heterocompounds) in oils of different shale oils at 298.2 K. The oil fractions boiling over 398 K at 267 Pa (573 K) of Mandra, Sysola, Jarenga and Perelyub shale oil have been investigated as stationary phases.

Introduction

The present depression urges us ever more to regard oil shales as energetic and chemical raw material. From the point of view of using different shale oils, their yields and properties (composition) play an essential role. Determination of the latter is very expensive and time-consuming even when the up-to-date equipment is used, because approximately two thirds of shale oil boils over 300 °C [1].

For industrial purposes, it is often sufficient to know the thermo-dynamic properties of oil, i.e., its behaviour in different technological processes (heating, mixing with different solvents, etc.). These properties can be predicted basing on the corresponding through study of test compounds behaviour in oil.

Shale oils are complicated multicomponent mixtures, which as a rule form non-ideal solutions with test compounds [2]. The properties of formed solutions deviate from these of an ideal solution and it is practically possible to evaluate them using thermodynamic excess mixing functions. To eliminate the effects caused by the interactions between the molecules of test compounds, it is expedient to use the test compound in negligible amounts, i.e., to carry out the experiment at infinitive dilution.

The determination of physical-chemical properties of test compounds on using gas chromatography is based on their relation to the chromato-graphic parameters. As it is known from classic chromatography, the main

parameter measured in inversed gas chromatography (IGC) is retention time. The specific feature, however, is that the investigated low-volatile compound is used as a stationary phase. The thermodynamic properties of test compounds are estimated by using their retention volume temperature dependence [3].

Theoretical Part

Retention time depends on the partition of the solute between gaseous and liquid phases, column volume, rate of carrier gas, inlet and outlet pressures [4]. If there are no interactions between liquid phase and injected compound, then solute moves together with gas flow and the retention time depends on the carrier gas flow rate and column length.

Taking into account the matter stated above, the adjusted retention time can be found as follows:

$$t_p = t_r - t = K V_L / V, \tag{1}$$

where t - time from injection moment to retention of ideally behaved, nonabsorbed compound;
t_r - sample retention time;
V_L - volume of liquid phase;
V - flow rate of carrier gas;
K - partition coefficient.

There exist definite relations between partition coefficient, retention volume and activity coefficient [5]. Experimentally the easiest way is to measure specific retention volume. It can be represented in the following way:

$$V_g^0 = 273.2 \, j \, (t_r - t) \, V / T \, g_L, \tag{2}$$

where g_L - amount of liquid phase
T - temperature;
j - coefficient, that takes into account the changes in ambient pressure and is expressed as follows:

$$j = 3[(P / P_0)^2 - 1] / 2[(P / P_0)^3 - 1], \tag{3}$$

where P_0 - carrier gas inlet pressure;
P - carrier gas outlet pressure (ambient pressure).

Differentiation of the Equation (2) to reciprocal of temperature gives:

$$R [d (\ln V_g^0) / d (1 / T)] = b, \tag{4}$$

within $b = H_s/R$,

where H_s - solution enthalpy;
R - universal gas constant.

It is known that thermodynamically

$$H_s = \Delta H_v - \overline{H}^E ,$$

(5)

where ΔH_v - enthalpy of evaporation;

$\overline{H}^E$ - partial excess enthalpy of mixing.

It means that experimentally, using IGC, it is possible to predict the test compound partial excess enthalpy of mixing $\overline{H}^E$ in liquid phase using the temperature dependence of retention volume [7].

Experimental Part

Equipment

The gas chromatograph "LHM-80" with modified oven to keep the temperature stable ($\pm$ 0.05 K) was used. The ultrathermostat was used to heat up the water used afterwards as chromatograph oven heating agent. The temperature of injector during the experiments was 383 K. As detector katharometer was used. High sensitivity of detector makes very little concentrations of compounds detectable and so affords to work in the area of infinite dilution. Detector temperature was 423 K. Stainless steal columns 1.0 × 0.004 m were used.

Chemicals and Method of Measuring

Column was filled with "Inerton AW-HMDS" (0.315-0.400 mm) as an inert solid support that was impregnated with heavy fraction of oil shale as liquid phase. The characteristics of different liquid phases are given in Table 1. For filling 1 g ($\pm$ 0.0001 g) heavy oil fraction of shale oil was taken, and dissolved either in ether or chloroform. The weighed inert support was added to solution. The amount of liquid phase was approximately 13-17 % from the solid support amount. Ether or chloroform was separated from solid filling by distillation in a rotor extractor. The total filling mass of column weighed a little bit more than 7 g. The column was weighed before every working day. Total loss of liquid phase measured all over the working period was below 1 % from its

Table 1. **Characteristic Data for Oils of Oil Shales from Different Deposits Boiling over 573 K, %**

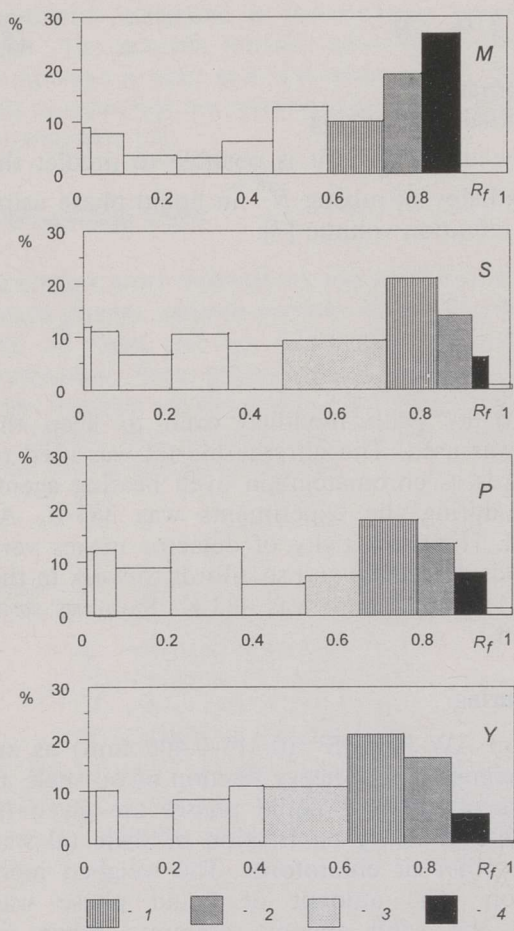| Oil shale	Yield of semicoking oil	Oil boiling over 573K					
		Yield	Elemental composition				
			H	C	H/C	N	O+S
Mandra	10.4	6.6	12.4	86.5	1.72	0.8	0.3
Sysola	7.3	5.7	9.9	83.2	1.43	1.4	3.5
Yarenga	15.8	11.8	8.4	81.8	1.23	1.1	8.7
Perelyub	11.9	9.7	9.6	82.0	1.41	0.8	7.6

Fig. 1. Thin layer chromatography resalts: *1* - yellow, *2* - sky blue, *3* - brown, *4* - blue; *M* - Mandra, *S* - Sysola, *P* - Perelyub, and *Y* - Yarenga deposit

Table 2. **Characteristic Data for Oil Shales from Different Deposits, %**

Characteristic	Mandra	Sysola	Yarenga	Perelyub
Analytical moisture W^a	1.9	9.4	5.6	2.7
Ash A^d	64.3	65.9	22.4	47.2
Carbon dioxide of carbonates $(CO_2)^d_M$	0.3	5.3	1.6	7.2
Total sulfur S^d_t	2.6	2.5	7.9	5.8
Elemental composition organic matter basis:				
C	77.2	63.8	70.4	73.5
H	10.4	8.6	7.9	8.9
O	8.8	20.2	14.7	6.4
N	1.0	1.6	1.5	1.6
S	2.6	5.8	5.5	6.4
H/C	1.62	1.62	1.35	1.45
Organic matter $100 - A^d - (CO_2)^d_M$	27.7	21.4	76.0	45.6

total amount and was therefore neglected. Temperature range of experiments was 303-366 K.

Helium was used as the carrier gas. Its inlet pressure was measured using Hg manometer with the accuracy of ± 1.0 mm Hg. The outlet pressure of the carrier gas was measured using barometer with the accuracy of ± 0.5 mm Hg. The rate of carrier gas was measured using a soap bubble flowmeter and was hold during the experiments in the range of 0.9-
-1.1 cm^3/s. Twenty three test compounds were used, e.g. alkanes, alkenes, ketones, alcohols, aromatics and others.

Heavy Fractions of Shale Oil

The oils of possibly different origin - Mandra, Sysola, Jarenga and Perelyub - were tested [8]. In Table 2 the characteristics of these oil shales are given. Oil shale was milled in a ball mill. Oils were obtained by semicoking oil shale in a 50 g alumina retort (standard Fischer assay). The lighter part of every oil was distilled off under vacuum (368 K and 267 Pa), and further the cube residues were used. Their characteristics are given in Table 1. The heavy part of shale oil was also separated using thin layer chromatography (silica gel). The results in Fig. 1 show different patterns for different oils when eluated with *n*-hexane.

Results and Discussion

The retention volumes of test compounds at different temperatures were calculated using the equation from [9]:

$$V_g^0 = t_r \, F j \, T_k \, (P_0 - P_V) / \, m \, T_0 \, P_0 \qquad (6)$$

where F - gas rate;
t_r - adjusted retention time;
m - weight of liquid phase;
T_k - column temperature;
P_0 - carrier gas inlet pressure;
P_V - pressure of saturated water at a temperature T_0:
T_0 - ambient temperature.

These dependences have linear character and in case of the same heavy oil fraction noticeably differ for different test compounds. For all studied thermodynamic systems, the correlation coefficient was greater than 0.98 and the reliability of the correlation exceeded 0.99. It means that the experimental data can be used for extrapolation of V_g^0 value at the 298.2 K. In Table 3 the specific retention volumes of test compounds at 298.2 K in different heavy oil fractions are given.

Temperature dependences of V_g^0 were used for the calculation of partial excess enthalpies of mixing $\overline{H}^E$ of test compounds with different heavy oil fractions. The results are given in Table 4. In case of infinite dilution, where the interactions between test compounds molecules can be

neglected, the sign of $\overline{H}^E$ can be considered to characterize the interactions between solute and oil molecules. The positive sign (+) evidences weak and negative sign (-) strong interactions between solute and oil, respectively. If the interactions between oil molecules are strong,

Table 3. **Specific Retention Volumes V_g^0 (m³/kg) of Test Compounds in High-Boiling Oils**

| No.	Test compounds	M	S	Y	P
1	Hexane	0.338	0.127	0.137	0.121
2	Heptane	1.110	0.421	0.652	0.408
3	Octane	3482	1.309	1.415	1.338
4	1-Hexene	0.296	0.136	0.142	0.128
5	1-Heptene	0.968	0.422	0.467	0.431
6	1-Octene	3.069	1.335	1.472	1.375
7	Cyclohexane	0.651	0.272	0.311	0.241
8	Methylcyclopentane	0.454	0.193	0.206	0.182
9	Benzene	0.699	0.546	0.768	0.541
10	Toluene	2.474	1.778	2.128	1.988
11	Ethylbenzene	8.488	4.977	5.520	5.460
12	Tetrachloromethane	0.677	0.408	0.511	0.460
13	Trichloromethane	0.468	0.501	0.591	0.517
14	Methyl alcohol	0.057	0.119	0.152	0.127
15	Ethyl alcohol	0.122	0.262	0.299	0.262
16	2-Propanol	0.181	0.357	0.401	0.339
17	2-Propanone	0.106	0.136	0.182	0.164
18	2-Butanone	0.360	0.424	0.572	0.526
19	Ethyl ether	0.099	0.071	0.076	0.069
20	Tetrahydrofuran	0.507	0.455	0.592	0.534
21	Ethyl acetate	0.352	0.350	0.428	0.394
22	Nitromethane	0.213	0.435	0.604	0.491
23	Acetonitrile	0.099	0.196	0.258	0.224
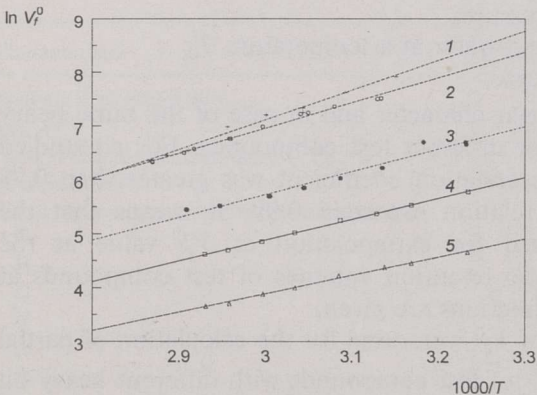
Fig. 2. Dependence of specific retention volumes of organic compounds on the temperature in heavy oil fractions of different oil shales *1* - Mandra (ethylbenzene), *2* - Yarenga (ethylbenzene), *3* - Sysola (1-octene), *4* - Yarenga (chloroform), *5* - Perelyub (2-propanone)

the sign and value of $\overline{H}^E$ depend on how successfully the molecules of test compounds can contest with the molecules of oil. As seen from Table 4, the interactions between oil and the test compounds are the strongest in case of Mandra oil shale and the weakest in case of Sysola oil shale. Consequently, the molecules in the Sysola oil are more bonded than in the Mandra oil. The interactions between oil and alcohols are weak, and the same can be said about the interactions between oil and other alkanes. The strongest interactions are between the oil of Yarenga shale and heptane as well as between the oil of Mandra shale and ethylbenzene. It could be explained by the conception that the molecules of some certain size suit better between the molecules of oil.

Table 4. **The Excess Enthalpy of Mixing $\overline{H}^E$ (kJ/mol) for Test Compounds Dissolved in Oils of Different Shales**

No.	Test compounds	M	S	Y	P
1	Hexane	1.60	8.65	6.00	5.45
2	Heptane	1.32	6.91	−3.63	4.47
3	Octane	2.26	6.90	4.91	3.42
4	1-Hexene	1.59	6.25	5.86	4.48
5	1-Heptene	1.18	6.60	4.53	3.14
6	1-Octene	1.28	5.92	3.83	2.80
7	Cyclohexane	2.58	9.24	5.98	9.39
8	Methylcyclopentane	1.84	8.66	5.93	7.69
9	Benzene	2.97	5.72	0.35	4.64
10	Toluene	1.71	5.16	2.69	1.47
11	Ethylbenzene	−2.99	4.77	3.61	1.52
12	Tetrachloromethane	1.27	7.46	2.57	2.30
13	Trichloromethane	1.02	3.43	0.44	0.20
14	Methyl alcohol	8.64	10.72	6.69	6.20
15	Ethyl alcohol	10.32	9.14	8.14	6.48
16	2-Propanol	12.31	9.59	9.51	8.88
17	2-Propanone	5.07	7.92	4.68	3.26
18	2-Butanone	1.95	4.51	0.99	−0.57
19	Ethyl ether	4.02	6.20	5.46	3.80
20	Tetrahydrofuran	1.14	5.45	1.40	2.67
21	Ethyl acetate	4.35	7.45	5.22	3.32
22	Nitromethane	9.35	11.12	6.41	7.08
23	Acetonitrile	7.82	10.25	6.48	5.93

Conclusions

1. The thermodynamic properties of oils obtained in the standard Fischer retort from four different oil shale (Mandra, Sysola, Jarenga and Perelyub deposits) were studied. Twenty three test compounds (alkanes, alkenes, ketones, etc.) were used as test compounds.

2. The specific retention volumes V_g^0 of test compounds in oils at different temperatures (303-366 K) were determined. The temperature dependence of specific retention volumes V_g^0 of test compounds (i.e., dependence of natural logarithm of V_g^0 on reciprocal temperature) was examined. The dependence is linear. The partial excess enthalpies of mixing at $\overline{H}^E$ 298.2 K were calculated.

3. The obtained data can be used for characterization of shale oils of different origin.

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