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CRYOSCOPIC ANALYSIS OF THE SHALE OIL

Abstract

Some problems of the cryoscopic method of the average molecular mass determination of shale oils were studied and a modification of the method is proposed. Diphenyl ether, diphenylmethane, dioxane, and benzene were compared as cryoscopic solvents. The presence of molecular complexes in the shale oil hampers an accurate determination of its molecular mass by cryoscopic methods.

Diphenyl ether is recommended as a solvent for the cryoscopic determination of the molecular mass of the shale oils and their components. It yields more accurate results, as compared to other suitable solvents; besides, it is not hygroscopic, less toxicant, has a low vapor pressure and makes measurements at ambient temperature possible.

Diphenylmethane is suitable for the determination of the molecular mass of the hydrocarbons, but cannot be applied to polar compounds.

Cryoscopic methods are usually used for the determination of the molecular mass of the shale oils. All the modifications of the cryoscopic methods are based on the measurement of the depression of the solvent freezing point that arises as a result of the sample addition to the solvent. The application of cryoscopic methods is advantageous if the samples to be measured are mixtures of volatile and nonvolatile components, or are unstable, or reactive. These methods are well developed and are applied to shale oils for many years. Nevertheless, some methodical problems may occur. Shale oils are complicated mixtures of compounds having a different chemical nature - hydrocarbons of the various types, compounds of oxygen, nitrogen, sulfur, etc. The molecular mass of these compounds may not always be determined by means of the same solvent with the required accuracy.

In most cases benzene, and sometimes dioxane, are used as solvents for the molecular mass determination of shale oil products. However, these solvents, especially benzene, have serious disadvantages. Benzene forms so called solid solutions with phenols, thiophenes, pyridine, some naphthenes, and paraffins [1—3]. This results in an increase of molecular mass during the measurements. Polar compounds, such as phenols, carboxylic acids, nitrogen compounds, when measured in benzene, also show molecular masses that are too high due to the molecular selfassociation. Benzene and dioxane are toxicant and have a high vapors pressure at ambient temperature. As dioxane gives solutions with water, this solvent must be dried carefully. Freezing points of benzene and dioxane are not convenient for the measurement at the ambient temperatures.

For these reasons we propose that solvents such as diphenylmethane and diphenyl ether will be much more suitable for measuring the molecular mass of the shale oils. These solvents have higher freezing points, as compared to benzene and dioxane, which makes measurements at ambient temperature possible. The cryoscopic constants of these solvents are high enough; this provides for a high

accuracy of the determination. Diphenylmethane and diphenyl ether are not toxic and not hygroscopic; formation of solid solutions with sulfur compounds is unknown. Some of the properties of these solvents are shown in Table 1.

Table 1. **Some Properties of the Pure Solvents [1, 4]**

Characteristics	Benzene	Dioxane	Diphenyl-methane	Diphenyl ether
Molecular mass	78.11	88.10	168.23	170.21
Freezing point, °C	5.533	11.80	25.35	26.84
Boiling point, °C	80.1	101.32	264.3	257.9
Cryoscopic constant, °C/mol/1000 g*	4.995	4.667	6.423	7.727
Vapor pressure at 20°C, mm Hg	75	27	0.02	0.03
Toxicity	+	+	-	-
Miscibility with water	-	+	-	-

*Our data.

Experimental

The 200—320 °C fraction of the Israel shale oil was the topic of the investigation by the cryoscopic method. The main components of the oil are hydrocarbons, alkyl thiophenes, phenols and nitrogen compounds [5—7]. The fraction was separated into three groups of compounds - pyridine bases extracted with the 20 % solution of sulfuric acid, phenols extracted with NaOH aqueous solution, and washed oil. The characteristics of the products of the separation are presented in Table 2.

Table 2. **Characteristics of the Products of Separation of the 200—320 °C Shale Oil Fraction**

Characteristics	Washed oil	Phenols	Pyridine bases
Elemental composition, %:			
C	78.84	72.21	78.60
H	11.53	7.85	8.58
O	1.09	12.32	3.09
N	0.64	1.17	7.80
S	7.90	5.95	1.93

The tested solvents were first used for the molecular mass determination of individual compounds of a different nature, representing main components of the shale oil: hydrocarbons and compounds of sulfur, nitrogen, and oxygen. The quality of the reagents used is shown in Table 3. The compounds' purity was determined by means of gas chromatography or by the crystallization temperature.

Table 3. **Characteristics of the Used Reagents**

Compound	Density at 20 °C, g/cm^3	Temperature of crystallization, °C	Content of the principal compound, %
Benzene	-	5.50	99.9
Dioxane	-	11.50	99.6
Diphenyl	-	69.10	99.1
Diphenyl ether	-	26.77	99.8
Diphenylmethane	-	25.14	99.6
Heptane	0.6839	-	99.8
Phenol	-	40.65	99.3
Quinoline	1.0935	-	99.4
Thiophene	1.0652	-	99.5
Toluene	0.8670	-	99.9

The molecular mass determination was carried out according to the method described in [1]. Standard solvent quantity was 25 ml. The bath temperature was maintained by 5 °C lower than the solution freezing point. The solution was supercooled at 0.2—0.3 °C. The temperature depression was measured by means of a Beckman thermometer.

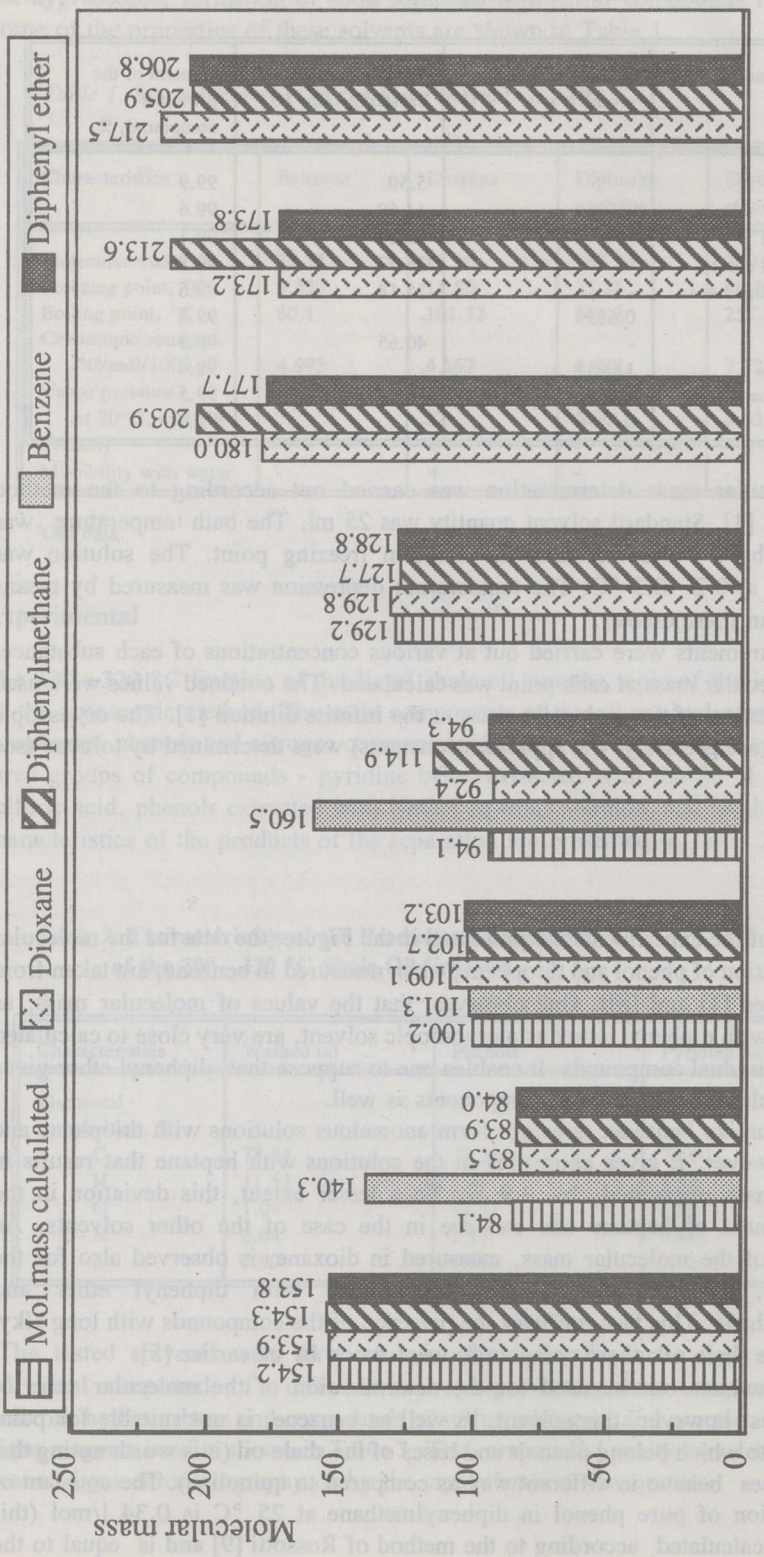
The measurements were carried out at various concentrations of each substance, and the molecular mass at each point was calculated. The obtained values were used in the calculation of the molecular mass at the infinite dilution [1]. The cryoscopic constants (more precisely, the apparatus constants) were determined by toluene (see Table 1).

Discussion

The results of the experiments are presented in the Figure (the data for the molecular mass calculation of phenol and thiophene, when measured in benzene, are taken from the references [1] and [8]). One observes, that the values of molecular mass, as determined with diphenyl ether as a cryoscopic solvent, are very close to calculated ones for individual compounds. It enables one to suppose that diphenyl ether gives the best results for the shale oil components as well.

Dioxane, unlike benzene, does not form anomalous solutions with thiophene and phenol. However, it gives anomalies in the solutions with heptane that results in molecular mass overstated by ~9 %. To a lesser extent, this deviation in the molecular mass of heptane one can see in the case of the other solvents. An overstating of the molecular mass, measured in dioxane, is observed also for the washed oil, as compared to that determined with diphenyl ether and diphenylmethane. This fact confirms the presence of the compounds with long alkyl chains in the shale oil; these compounds were found by us earlier [5].

Diphenylmethane can be used for the determination of the molecular mass of hydrocarbons; however, this solvent, as well as benzene, is not suitable for polar substances, to which belong phenols and bases of the shale oil (it is worth noting that shale oil bases behave in different way as compared to quinoline). The constant of the association of pure phenol in diphenylmethane at 25 °C is 0.34 l/mol (this constant is calculated according to the method of Rossotti [9] and is equal to the


Molecular mass determined with different solvents
Molecular mass
250
200
150
100
50
0
Mol.mass calculated
Dioxane
Diphenylmethane
Benzene
Diphenyl ether
Diphenyl
154.2
153.9
154.3
153.8
Thiophene
84.1
140.3
83.5
83.9
84.0
n-Heptane
100.2
101.3
109.1
102.7
103.2
Phenol
94.1
160.5
92.4
114.9
94.3
Quinoline
129.2
129.8
127.7
128.8
Oil shale phenols
180.0
203.9
177.7
Pyridine bases
173.2
213.6
173.8
Washed oil
217.5
205.9
206.8

slope of the curve B/S = f(S), where B - analytical, and S - measured concentrations of phenol). It is less than the constant of the phenol association in benzene, which is 0.57 l/mol at 25 °C [10]. This explains a lesser overstating of molecular mass of phenol when measured in diphenylmethane as compared to that measured in benzene. The constant of the association of shale oil phenols in diphenylmethane calculated according to the same method is 0.76 l/mol, i.e., more than in the case of phenol itself. This indicates that shale oil phenols contain compounds which may form additional H-bonds. It was shown [11] that phenols form high polar associates with other oxygen compounds and with compounds of nitrogen and sulfur. Thus, a higher value of the association constant of shale oil phenols as compared to that of the individual phenol may be explained by the presence of molecular complexes in the shale oil.

Conclusion

Some problems of the cryoscopic method of the average molecular mass determination of shale oils were studied. The presence of molecular complexes and polar compounds in the shale oil hampers an accurate determination of its molecular mass by cryoscopic methods.

Diphenyl ether is recommended as a solvent for the cryoscopic determination of the molecular mass of the shale oils and their components. It gives more accurate results, as compared to other suitable solvents; besides, it is not hygroscopic, less toxic, has a low vapor pressure and makes measurement at ambient temperature possible.

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КРИОСКОПИЧЕСКИЙ АНАЛИЗ СЛАНЦЕВОЙ СМОЛЫ

Резюме

Рассмотрены некоторые проблемы криоскопического анализа сланцевых смол и подобных им сложных смесей. Проведено сравнение дифенилового эфира, дифенилметана, диоксана и бензола как криоскопических растворителей. Присутствие молекулярных комплексов в сланцевой смоле препятствует точному определению ее средней молекулярной массы.

Определение молекулярной массы индивидуальных веществ и сланцевой смолы в различных растворителях (см. рисунок) показывает, что наиболее точные результаты дает дифениловый эфир. Кроме того, этот растворитель негигроскопичен, имеет низкое давление паров, нетоксичен и позволяет проводить измерения при комнатной температуре. Дифениловый эфир рекомендован для определения среднего молекулярного веса сланцевых смол криоскопическим методом.

Дифениловый метан пригоден для определения молекулярных весов углеводородов, но дает неточные результаты для полярных соединений.

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