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## ISOLATION OF NATURAL SURFACE-ACTIVE MATERIALS OF CRUDE OILS BY ADSORPTION CHROMATOGRAPHY\*

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### SUMMARY

A traditional, open-column adsorption chromatographic method has been developed to isolate natural surfactants of crude oils, using kieselguhr as column packing. The chromatographic behaviour of crudes is classified according to the interfacial activity of fractions, obtained by measuring the interfacial tension of benzene solutions against distilled water. The chemical properties of crude fractions have been evaluated by means of molecular weight measurements and infrared spectroscopy. Results for a Hungarian crude oil are given.

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### INTRODUCTION

The presence of surface-active materials in crude oils was established long ago by physicochemical, chemical and electrochemical investigations<sup>1-10</sup>. However, few studies of these materials have been published<sup>11-16</sup>. Surface-active materials contain polar components, so the natural tendency is towards isolation and investigation of these parts of crudes.

### EXPERIMENTAL

#### *Method of separation*

Kieselguhr was chosen as the column packing because silica adsorbs the interfacially active components so strongly that they could not be eluted even with the best solvents.

The crude oil sample was injected onto the dry column without any solvent, as the lower-molecular-weight fractions of crude oils can be considered the solvent for the other components.

The sequence of solvents for elution was the same as used previously, namely: propan-2-ol, methanol, water, acetone and benzene. The solvents were removed by

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distillation and evaporation using an infrared (IR) lamp under an atmosphere of nitrogen. Twelve fractions were obtained, eight of which were eluted with propan-2-ol, one with methanol, one with distilled water, one with acetone and one with benzene.

#### *Measurement of interfacial tension and mean molecular weight*

Interfacial tensions were measured in benzene solution against distilled water by the modified pendant drop method<sup>5,7</sup>. (The interfacial tension of pure benzene against distilled water was measured as 33.0 dyn/cm.) The concentration of benzene solutions was 5 g/l.

The molecular-weight measurements were carried out, also in benzene solutions, using a Hewlett-Packard Type-302 vapour pressure osmometer.

#### *Infrared investigations*

The IR investigations were carried out with a Hilger spectrophotometer, Type-H-800, in the range of NaCl prism. Samples were dissolved in CCl<sub>4</sub> or CS<sub>2</sub>, at different concentrations and using different cell thicknesses. The results were analysed by the mean group method to take account of the complexity of the fractions. The numbers of methylene and methyl groups and the percentage of aromatic carbon atoms (C<sub>A</sub>) in the fractions were calculated from the molecular extinction coefficients of peaks at 2927, 1380 and 1610 cm<sup>-1</sup>, respectively. The molecular extinction coefficients of the peaks at normal carbonyl frequencies were also calculated in order to characterize the polar groups<sup>17-24</sup>.

## RESULTS AND DISCUSSION

The quantitative results obtained following the separation of a Hungarian oil (Alg-194) are summarized in Table I. Two percentage values are presented because of partial evaporation of the lower-molecular-weight components which occurred during evaporation of the solvent.

TABLE I

DATA OBTAINED FOLLOWING THE SEPARATION OF HUNGARIAN CRUDE OIL ALG-194

<i>Number of fraction</i>	<i>Solvent</i>	<i>Concentration of eluate (g/ml)</i>	<i>Eluted material as a percentage of sample</i>	<i>Eluted material as a percentage of the whole eluted quantity</i>
1	Propan-2-ol	0.5065	35.31	52.792
2	Propan-2-ol	0.4556	12.93	19.334
3	Propan-2-ol	0.3003	8.52	12.743
4	Propan-2-ol	0.1207	3.43	5.124
5	Propan-2-ol	0.0160	1.06	1.582
6	Propan-2-ol	0.0011	0.82	1.232
7	Propan-2-ol	0.0004	0.63	0.944
8	Propan-2-ol	0.0001	0.44	0.660
9	Methanol	0.0002	0.78	1.172
10	Water	0.0001	0.34	0.512
11	Acetone	0.0002	0.87	1.302
12	Benzene	0.0004	1.74	2.603
Total			66.87	100.000

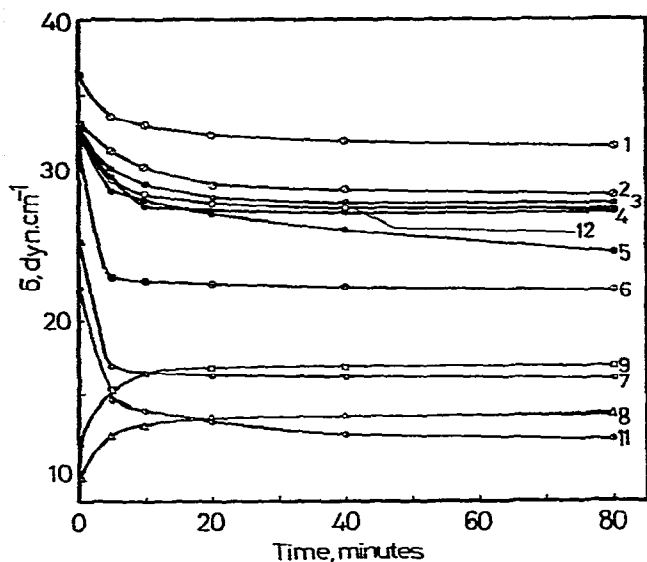


Fig. 1. Variation of interfacial tension of the 12 fractions with time.

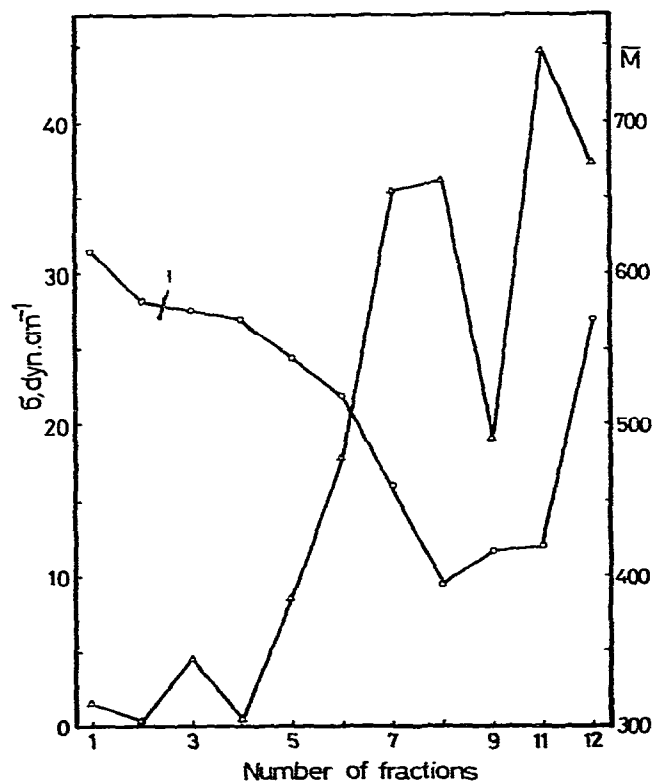


Fig. 2. Equilibrium values of interfacial tension and the mean molecular weight of the 12 fractions  
 ○, Interfacial tension; Δ, mean molecular weight.

Fig. 1 shows the variation of interfacial tension with time for the 12 fractions, and Fig. 2 plots the equilibrium interfacial tension values and the mean molecular weights. The curves for the first seven fractions all show interfacial tension decreasing with time. However, the curves for fractions 8 and 9 (Fig. 1) show a different tendency. This could be due to part of these fractions being soluble in water. These water-soluble materials, adsorbed in the monolayer at the interface, diffuse very quickly into the aqueous phase. Their concentration at the interface decreases, which results in the interfacial tension increasing with time. Therefore, the value of the interfacial tension initially measured must be considered as the true one (when the interface is rich in surface-active materials), instead of the equilibrium value.

It can be seen from Figs. 1 and 2 that the benzene fraction (12) has a relatively high interfacial tension, *i.e.*, it does not contain surface-active components. This may be due to some components being insoluble in polar solvents, but soluble in benzene. Fig. 3 shows the numbers of methylene and methyl groups and the percentage of aromatic carbon atoms in each fraction, as calculated from the IR spectra. The methanolic fraction (9) conspicuously does not follow the trend of an increasing number of methylene groups, but contains a relatively low number, and also shows a maximum value for  $C_A$ .

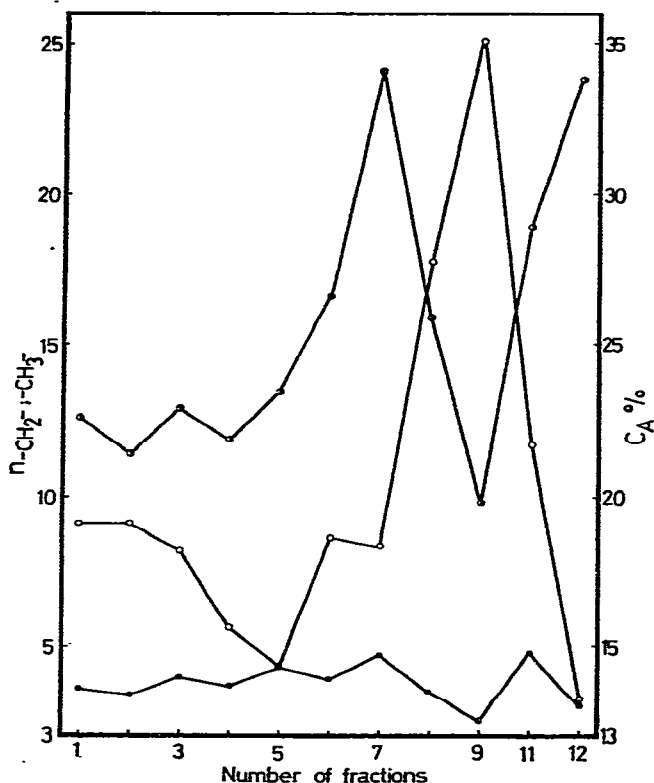


Fig. 3. Numbers of methylene (○) and methyl (●) groups and the percentage of aromatic carbon atoms (○) in the 12 fractions.

Fig. 4 plots the interfacial tension values and the molecular extinction coefficients at the carbonyl absorption frequencies (1700–1800  $\text{cm}^{-1}$ ). As interfacial tension decreases so an increase in the extinction coefficients of the peaks at 1740 and 1705  $\text{cm}^{-1}$  occurs, revealing a close connection between the interfacial activity at the liquid–liquid interface and the polar groups containing oxygen. No such relationship with other polar groups or heteroatoms has been established.

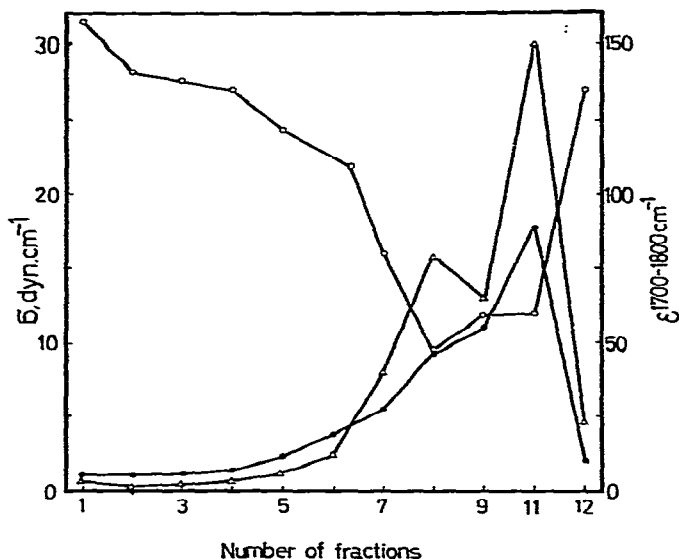


Fig. 4. Comparison of interfacial tension and molecular extinction coefficient at the carbonyl absorption frequencies.  $\circ$ , Interfacial tension;  $\bullet$ , molecular extinction at 1705  $\text{cm}^{-1}$ ;  $\triangle$ , molecular extinction coefficient at 1740  $\text{cm}^{-1}$ .

The figures do not show data for the aqueous fraction (10); although it is partially soluble in water, its low solubility and the small amount of it present preclude the preparation of solutions of the same concentrations as are possible for the other fractions. Measurement of the molecular weight is very difficult for the same reasons. The IR spectrum of this fraction shows no hydrocarbon or carbonyl peaks.

Five Hungarian crude oils were separated and tested by this method. The chromatographic and physicochemical behaviour, as well as chemical features, of the fractions of different oils were easily distinguished. Quantitative separation data are in Table II.

## CONCLUSIONS

The surface-active fractions are complex mixtures of polar components. From the IR data these polar groups seem to be esters, or acids, or a mixture. The number of methylene groups and the  $C_A$  values show that fractions 7, 8 and 11 are mainly saturated, whereas fraction 9 is mainly aromatic. The surface-active fractions have relatively high average molecular weights, except fraction 9. The amount and quality

TABLE II  
QUANTITATIVE SEPARATION DATA FOR FIVE HUNGARIAN CRUDE OILS

Oil	Percentage of material eluted with									
	Propanol		Methanol		Water		Acetone		Benzene	
	A*	B**	A	B	A	B	A	B	A	B
Alg-3	63.96	97.30	0.60	0.91	0.20	0.30	—	—	0.97	1.48
Alg-194	63.11	94.41	0.78	1.17	0.34	0.51	0.87	1.30	1.74	2.60
Alg-233	61.42	95.24	0.65	1.01	0.31	0.48	0.89	1.40	1.20	1.86
NI-187	67.16	77.54	0.10	0.12	0.02	0.03	4.59	5.30	14.69	16.96
B-92	49.8	97.36	0.25	0.49	0.60	1.18	0.12	0.24	0.38	0.74

\* A = Eluted material as a percentage of sample.

\*\* B = Eluted material as a percentage of whole eluted quantity.

of surface-active fractions of different crude oils are characteristic of the given oil. More detailed information about the composition of surface-active materials would be obtained from further separation of surface-active fractions.

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