

# SEPARATION OF FRACTIONS EXHIBITING VARIABLE PARAMAGNETISM FROM HEAVY OILS AND THE STUDY OF THEIR PROPERTIES

V.A. Martynova, L.N. Andreyeva, A.A. Velikov, F.G. Unger  
Institute of Petroleum Chemistry, Russian Academy of Sciences,  
634055, Tomsk, RUSSIA

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Scanty knowledge of nature of resins and asphaltenes is the main obstacle to effective and complex use of heavy oils. There are many theoretical concepts which consider the nature of supermolecular interactions in oil dispersed systems (ODS) from the positions of electrolytic dissociation, donor-acceptor interaction,  $\pi - \pi$  interactions of polyconjugated systems, exchange (quantum) interaction and etc.

In spite of different views on the nature of resins and asphaltenes the scientists have defined that just the formation and destruction conditions for supermolecular structures in oil dispersions decisively affect the processes of extraction and thermal destruction of the system components as well as predetermine the structure and physico-chemical properties of the end products of oil processing. Based on the researches carried out at the Institute of Petroleum Chemistry RAS concerned with the paramagnetic nature of oil dispersions, asphaltenes have been found to be a concentrate of paramagnetic molecules existing as associates with diamagnetic molecules. Paramagnetic molecules and reversible homolytic transformations of diamagnetic molecules into paramagnetic ones play the main role in the transformation of supermolecular structures in oil dispersed systems and are responsible for thermodynamically unstable equilibrium of the system as a whole [1-4].

Long-term studies of ODS paramagnetic nature made it possible to substantiate theoretically: i) the presence of such molecule types in ODS which under change of external effects rather easily go from diamagnetic to paramagnetic state and if the effect is removed they return to the initial state and ii) extraction of molecule concentrates from high-viscous oils exhibiting variable paramagnetic properties [5-7]. The method developed allows to divide heavy oils into fractions with different paramagnetism. The studies of fraction behaviour by ESR- and IR-spectroscopies and by microcalorimetry during dissolution and heating showed that the level and width of energy slot for a reversible diamagnetic-paramagnetic transitions depend on structure and chemical composition of molecules. Homolytic mechanism of supermolecular structure transformations has been presented based on quantum-mechanic insight into the nature of intermolecular interactions in ODS [8-10].

## EXPERIMENTAL

At the Institute of Petroleum Chemistry RAS a method has been developed to separate fractions with variable paramagnetic properties (FVP) from crude oils and heavy residues. A specially designed device was employed. The method is based on destruction of ODS supermolecular structures from the exposure to external factors (temperature, pressure, solvent type and time delay) and on the sequential selection of concentrates of FVP molecules different in the energy of reversible diamagnetic-paramagnetic transitions, i.e. in their stability to external effects.

Presented are the results on the study of initial petrol deasphaltate obtained from commercial mixture of West Siberian oils and of extracted FVP. FVP-1 and FVP-6 exhibiting different paramagnetism are characterised in Table 1.

Table 1.

Physico-chemical characteristics of ODS

Test sample	Molecular mass (oxy-accopy)	PMS, $n \times 10^{18}$ spin/cm <sup>3</sup>	Elemental composition, wt. %						
			C	H	N	S	O	$n \times 10^2$ V Ni	
Deasphaltate	751	2.76	83.40	9.66	0.65	2.52	1.78	0.90	0.40
FVP -1	693	2.11	85.16	10.00	0.54	2.43	0.96	0.49	0.21
FVP -6	1403	71.40	85.50	8.58	1.05	2.60	2.26	3.14	1.43

FVP properties dependent on external effects (temperature and solvent amount) were studied by ESR-, IR-spectroscopies and by microcalorimetry. The effect of the nature of different solvents on the change in the concentration of paramagnetic sites (PMS, spin/cm<sup>3</sup>) in ODS has been studied previously. In the present work we used chloroform as a solvent.

## I. ESR-SPECTROSCOPY

The changes in PMS concentrations (spin/cm<sup>3</sup>) in ODS dependent on external factors were studied by ESR-spectrometer "SEX-2544" (Poland). Detailed procedure features are described in [4,8]. The results of ESR-studies of the three ODS samples (deasphaltate, FVP-1 and FVP-6) are presented in Figs. 1-4.

Fig. 1 presents the change in paramagnetic properties of the test samples versus the temperature. The test samples were vacuum pretreated and sealed in quartz ampoules. The change in ODS paramagnetism versus the solvent concentrations in chloroform is shown in Fig. 2. The change in FVP-1 paramagnetic properties versus solvent and temperature is given in Fig. 3. As is seen from ESR-spectra presented in Fig. 4, the quantitative view of the spectrum varies because of temperature and solvent effects.

Relative change in the intensity of ESR-signal for ODS versus the temperature

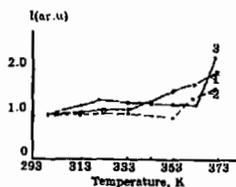


Fig. 1.  
1. desophtalinate  
2. FVP-1  
3. FVP-6

Relative change in the intensity of ESR signal for ODS in chloroform versus the concentration

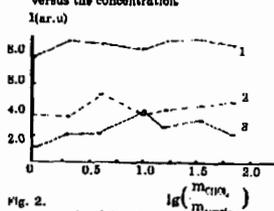


Fig. 2.  
1. desophtalinate  
2. FVP-1  
3. FVP-6

Relative change in the intensity of ESR-signal for FVP-1 in chloroform versus the concentration and temperature

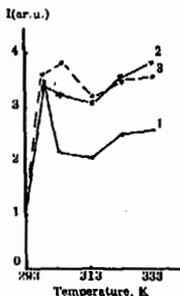


Fig. 3.  
1. FVP-1 : CHCl<sub>3</sub> wt. ratio 1:1  
2. " " " 1:2  
3. " " " 1:10

The results of ESR-studies are expressed in arbitrary units (ar.u.). PMS concentration (spin/cm<sup>3</sup>) of vacuum-treated ODS samples at 298 K is taken as a unit.

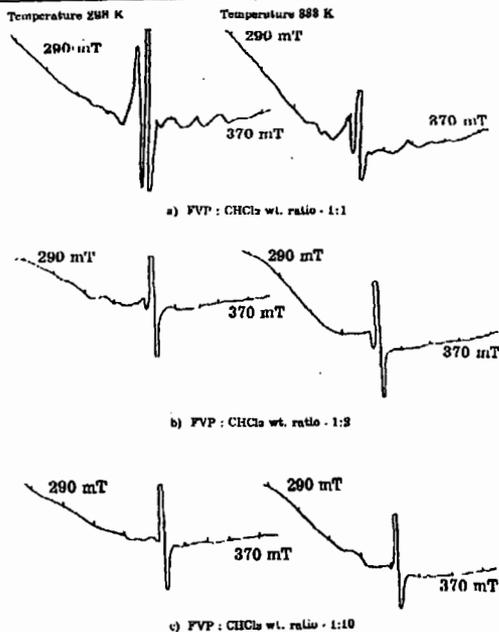


Fig. 4 (a,b,c). ESR-spectra for FVP-1 in chloroform obtained at different concentrations and temperatures

## II. IR-SPECTROSCOPY

IR-spectra were registered by "SPECORD" M-80 (Germany) in sodium chloride cells. Recorded were review solution spectra in chloroform relative to chloroform as well as film spectra of the test samples obtained from chloroform solutions in KBr window relative to air. Detailed procedure features of IR-spectra recording are given in [6,9]. The aims of IR-studies were: i) to reveal structural fragments of the molecules included in FVP and responsible for their behaviour and ii) to study the changes in  $D_{opt}$  characteristic absorption bands under dilution in chloroform.

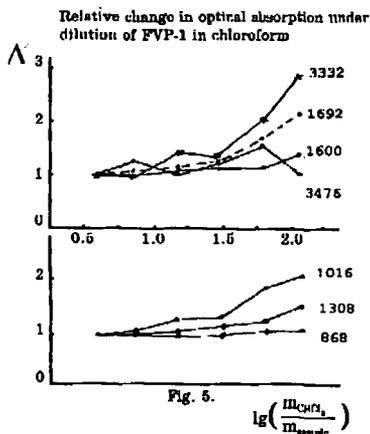
Table 2 and Figure 5 present the results of IR-spectroscopic studies. The analyses of IR-spectra made it possible the observations in the following range of wave numbers: 3600-3200; 1900-1500; 1400-1300 and 1100-800  $\text{cm}^{-1}$ , respectively.

## II. IR - SPECTROSCOPY

Table 2.

Reference of characteristic absorption bands for ODS solutions in chloroform studied by IR-spectroscopy

Wave number, $\text{cm}^{-1}$	Vibrations	Possible structures
3476	$>\text{N} - \text{H}$	pyrrol cycle
3332	$-\text{OH}$	hydroxyl group
1692	$\text{C} = \text{O}$	carbonyl group
1600	$\text{C} = \text{C} (\text{arom})$	benzene rings
1308	$\text{S} = \text{O}$	sulfones, sulfonamides
1016	$\text{R} - \text{O} - \text{C} - \text{O} - \text{R}'$	acetoxy-group
868	$\nu \text{C} - \text{N}$ $\sigma \text{C} - \text{H}$ arom	nitro-, amino-groups



## III. MICROCALORIMETRY

Thermodynamic characteristics ( $Q$ ,  $J$  and  $\Delta H$ ,  $\text{kJ/mol}$ ) of ODS samples dilution in chloroform were studied by differential microcalorimeter MKDP-2, designed at the Institute of Petroleum Chemistry RAS. The sensitivity of the device is  $2 \times 10^{-3} \text{ J}$ . Detailed procedure of ODS microcalorimetric studies is given in [4,10]. The results of ODS microcalorimetric studies are given in Figs. 6-7 and in Tables 3-4. They were carried out under the conditions similar to those observed in ESR- and IR-spectroscopies.

### III. MICROCALORIMETRY

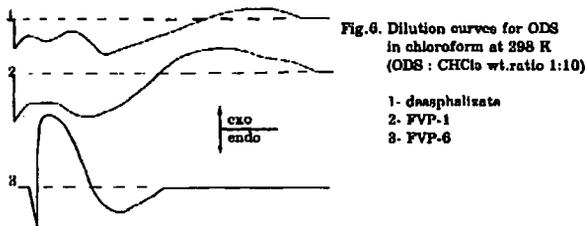


Table 3.

Enthalpies of ODS dilution in chloroform at different concentrations (298 K)

ODS : solvent wt. ratio	ΔH, kJ / mol		
	desasphaltate	FVP-1	FVP-6
1 : 10	{ + 4.35 - 0.59	{ + 4.59 - 1.16	{ - 6.07 + 2.24
1 : 20	{ + 4.70 - 0.25	{ 4.21	{ - 6.75 + 0.20
1 : 30	{ + 5.66 - 0.59	{ + 3.45	{ - 2.29 + 3.20
1 : 40	{ 5.85	{ + 5.87	{ - 3.35 + 0.54
1 : 100	{ 12.35	{ + 4.28	{ - 4.28 + 1.94

the " + " sign - endothermic process  
the " - " sign - exothermic process

### III. MICROCALORIMETRY

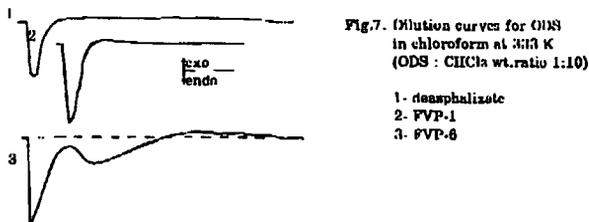


Table 4.

Enthalpies of ODS dilution in chloroform at different temperatures (ODS : CHCl<sub>3</sub> wt.ratio 1:10)

Test sample	Δ H, kJ / mol		
	Temperature, K		
	298	313	333
Desasphaltate	{ + 4.35 - 0.59	{ + 4.28 - 0.36	{ + 1.13 - 1.04
FVP-1	{ + 4.59 - 1.15	{ + 2.72 - 0.46	{ + 1.08
FVP-6	{ 6.07 + 2.24	{ - 5.08 + 3.37	{ + 10.20 - 2.08

the " + " sign - endothermic process  
the " - " sign - exothermic process

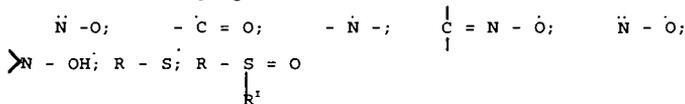
## CONCLUSION

Thus the results of ESR-studies allow to conclude that FVP really differ in their paramagnetism and under external effects exhibit variable paramagnetic properties, i.e. their components are the carriers of ODS labile properties. FVP-1 was found to be the most susceptible to external changes. Under the conditions of separation this fraction had to contain compounds with low energy of diamagnetic-paramagnetic transitions. Biradicals are known to exhibit such paramagnetic properties in the initial state and in the solutions. They are likely included in a concentrate of separated molecules (FVP) and are responsible for their variable paramagnetism as well as for unstable thermodynamic equilibrium of ODS.

IR-studies were carried out to reveal structural fragments responsible for such FVP behaviour. Seven characteristic absorption bands have been identified for all the separated FVP fractions. They differ only in their intensities. The lowest  $D_{osc}$  values were obtained for FVP-1 while the highest ones - for FVP-6. Based on elemental analysis and IR-spectroscopy it has been determined that the presence of cyclic and aromatic compounds of a polyconjugated type with S, N and O-containing fragments is typical for FVP. IR-spectra of FVP are similar and the differences in the elemental compositions are insignificant. Based only on these data it was difficult to explain a great difference in fraction behaviours determined by ESR-spectroscopy. Therefore we carried out IR-studies of FVP relative to solution concentration in chloroform.

The comparison of data obtained by ESR- and IR-spectroscopies allowed: i) to define that for ODS solutions Lambert-Buger-Beer law becomes invalid and ii) to conclude that increasing solvent portion (by  $kT$  change) in the system intensifies intermolecular interactions between solvent molecules and the components of supermolecular ODS structures. It results in the strengthened vibrations of atoms in structural fragments up to the break of separate bonds and/or to transition of a part of ODS molecules into a triple state. ESR- and IR-spectroscopies data indicate the proceeding of homolytic processes in ODS. The specific features of FVP behaviour are caused by biradical state of individual ODS components.

At present nitrite, hydrazile, phenoxy, hydrocarbon and mixed bi- and polyradicals are well known. They include the following fragments:



and etc. corroborated by our studies.

Stable biradicals with similar fragments may be attributed to a group of "biradicals with heteroatoms", the non-paired electron of which is to a great extent located on S, N and O atoms. The presence of biradicals of "metal ketyls" group is also possible.

Microcalorimetric measurements of enthalpies of ODS dilution dependent on external factors (solvent amount, temperature) indicate that these processes proceed at low energies (1-15 kJ/mol). Dilution curves have complex profile of thermal effects of dilution, which can be explained by different rate of dilution for individual ODS components as well as by transformations of supermolecular structures in the solution after a complete dilution. Sign inversion (exo-, endo-) indicates deep character of the phenomena. Comparison of the data on the relative change in PMS concentration in the system and the data on the change in dilution enthalpies ( $\Delta H$ , kJ/mol), obtained under similar conditions, indicates that the processes of dilution associate formation in ODS have a predominant-radical nature (endo-effects), which intensify under external effects (change of  $kT$  system), i.e. depend on the initial concentration of PMS in ODS, different capacity of concentrates of FVP molecules to singlet-triplet changes, on the solvent type and solvent amount and on temperatures.

The authors consider the search for mechanisms intended to control homolytic processes proceeding in ODS to be a key to solve many problems of technological preparation, transportation and processing of high-viscous crude oil and heavy oil residues.

## REFERENCES