

# DIELECTRIC SPECTROSCOPY IN STUDYING MECHANISMS OF STRUCTURE-FORMING OILS.

D.V. Saraev<sup>a</sup>, I.V. Lunev<sup>a</sup>, T.N. Yusupova<sup>b</sup>, M.I. Tagirzyanov<sup>b</sup>,

M.R. Yakubov<sup>b</sup>, Y.A. Gusev<sup>a</sup>, G.V. Romanov<sup>b</sup>,

<sup>a</sup>*Kazan State University*

<sup>b</sup>*A.I. Arbuzov's Institute of Organic and Physical Chemistry, Russian Academy of Science.*

## Abstract

Variety and specific character of the questions appeared during study of oil dispersion systems (ODS) and anomaly in their behavior generate a need in consideration of that systems on micro- and macro-scale. The aim of this work is the application dielectric spectroscopy method for investigation of the features of the different ODS structures and consideration of the reorganization processes dynamics in that structure under the influence of the temperature. Analyzing obtained dielectric spectra of the oil dispersion structures under investigation various distinctive features in dynamics of relaxation processes were revealed. According correlation of the dielectric parameters of the ODS components and microelements composition all crude oil samples were classified on 4 major groups.

PACS codes: 77.22

---

## 1. Introduction

Characteristics of oil as a dispersion system are mainly determined by forming permolecular structures and their properties (geometry, stability, etc.) [1]. These properties influence the parameters of processes taking place during oil production in particular during oil filtration in porous media (in the oil-producing reservoir) [2]. Processes of association of oil components molecules limit oil mobility not only in the wall boundary layer (in a bounded state)

but in a free space as well. In this case the active role is played by the components of the dispersed phase. They are represented by the associated resins and asphaltene components where asphaltenes form the nucleus while the salvation sphere is composed of different resins fractions in accordance with polarity [3]. However even in case when the content of these components is not big they are able to form dispersed systems. The dispersion ability of such oils is mostly defined by the structural peculiarities of both the dispersion phase components and the content of the dispersion medium of oil dispersion systems. Its influence upon the system is ambiguous as it stipulates for a number of abnormalities in the process of oil formation under the influence of external factors.

So the purpose of this work is to study the peculiarities of oil structure with different composition and to consider the dynamics of its reformation under thermal conditions.

## 2. Experimental

The dispersion structure oil systems study was made with the help of time dielectric spectroscopy method by the reflectometer P 5-11, measuring standard line inhomogeneities. The frequency band of the device is  $10^4 - 10^9$  Hz. The temperature range during the measurements was  $20^0\text{C} - 105^0\text{C}$ . The device was calibrated with the help of the liquid reference method, as a standard we used butanol-1  $C_4H_9OH$  [4].

As samples under research we chose Tatarstan oilfields different in geological age, composition and microelements (about 40 oils). As a result we obtained dielectric spectra  $\varepsilon^* = \lg(f)$ , showing the dependence of its real component  $\varepsilon'$  and imaginary one  $\varepsilon''$  of the complex dielectric permittivity  $\varepsilon^*$  on the frequency  $f$  of the applied electric field of impulses. The estimation error in determining the parameters for  $\varepsilon'$  is 3%, for  $\varepsilon''$  is 5% [5].

### 3. Results

Fig.1 presents the experimental dielectric spectra for the two oils of Devonian formation in Abdrakhman's section in Romashkino oil field. The depositions include hard wax (1-4%), resins and asphaltene elements (18-33%). You can see an obvious maxima in the curves of dielectric permittivity  $\varepsilon''(\omega)$  that is typical for dielectric losses in the substance. They correspond to different types of molecular relaxation processes in oils. The low-frequency maximum at  $f = (10^7-10^8)$  Hz is the evidence of the presence of big particles and complexes associates in the system that have the big time relaxation  $\tau_1$ . You can refer the formation of resins and asphaltene components the structure of which in different oils has essential differences to this type of the associates.

To interpret the experimental data we used the empirical Debye's model and Cole and Davidson's one [6]

$$\varepsilon^* = \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + i\omega \tau}; \quad (1)$$

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)^\beta}; \quad (2)$$

where  $0 < \beta < 1$ .

The factor  $\beta$ , in Cole and Davidson's model (2) describes primarily not the spherical geometry of the associates and agglomerate of particles having been formed by long-time and short-time interactions. If  $\beta=1$  the formula is transformed into Debye's equation.

### 4. Discussion

The analysis of dielectric oil spectra from Abdrakhman's section with thermal changes let us reveal the distinctive peculiarities in the dynamics of relaxation processes (fig. 2, 3).

The fall in the time of relaxation  $\tau_1$  (fig.2 b) with the corresponding decrease in static dielectric permittivity informing us about the oil system polarity (fig.3 b) is a result of the decay of the oil dispersed phase aggregated complex from hole 714 D

The result of such decay is a phase transition with the transfiguration of the system into the molecular solution. The dynamics of the time relaxation  $\tau_1$  behavior and dielectric permittivity for oils from hole 13948 (fig. 2a, 3a) shows that with the temperature increase it has a reverse character that is the evidence of the associate structuring in the dispersed phase ending in forming the agglomerate that transforms the system into the fine-dispersated state.

Thus, with temperatures  $T > 40^\circ\text{C}$  the given oils endure phase transitions resulting in changing its aggregative state. Such behavior is caused by the high molecular alkanes acting either as combining the associate 'mediators' melting of which promotes the aggregated combinations destruction or as a phase of crystallization that is the associate nucleus where the temperature increase leads to further associating of the corresponding aggregated complex. Unlike crude oils from Devonian period that are the dispersed systems with light or average concentration oils with high viscosity from Carbon formations are dispersed systems with high concentration.

Due to the character of dielectric spectra and the dynamics of changing dielectric parameters  $\tau_1$ ,  $\epsilon_s$  oils with high viscosity were divided into groups. (Tab. 1)

Group 1 is represented by the light-gravity oils from Podgorny field. It has relatively small content of high-molecular components. The process of association in this group of oils is impulsive in the temperature range of  $36-50^\circ\text{C}$ . The time relaxation increase  $\tau_1$  of the most volumetric part of the dispersed phase and statistic dielectric permittivity  $\epsilon_s$  responsible for the general system polarity makes it obvious (fig. 4a, 5a).

The formation of big asphaltene aggregations takes place in the case of resins molecular 'desorption' from the asphaltene surface. The energy of activation of the relaxation process for the first group oils is characterized by the smallest values. Such oils behavior can be explained

by the weak intermolecular bonds in asphaltenes with the low concentration of structures containing vanadium. Similar association processes with the temperature increase leading to the time relaxation  $\tau_1$  increase (fig. 4b) are mentioned for oils of group 2 and 3 (Northern field). However, dielectric permittivity  $\epsilon_s$  dependence on temperature for oils of group 2 (fig 5 b) has the extreme character. You can observe the monotonous growth of  $\epsilon_s$  up to 50<sup>0</sup>C and afterwards up to 100<sup>0</sup>C - its fall. The general polarity decrease of the system can be stipulated for the dispersed phase dipole moment decrease due to the asphaltene molecules structuring into aggregations primarily with spherical form. Such geometry of a macromolecule forms the low dipole moment of the associate in total due to the fact that the asphaltene and resins components dipole moments have the opposite directions. The oil system polarity decreases in result. The energy of activation in forming the associates of spherical forms is the highest.

The mixture in the dispersed phase of the oils from group 2 has the highest asphaltene content with the average values of vanadium. The increasing value of the ratio V/A in oils from group 3 with less asphaltene content leads to the formation of the associates with higher permittivity (fig.5b), weaker structure, broken sphericity.

The analysis of dielectric parameters of oils from group 4 (Northern and Summer fields) characterized by the highest asphaltene and vanadium content (Tab.1) showed the presence of volumetric structures in a dispersed phase having the constant relaxation time  $\tau_1$  in the temperature interval under research. Probably the high concentration of vanadium and vanadyl and porphyrinic complexes including the asphaltene associates determine the impossibility of the phase transition that is responsible for changes in solvation.

## 5. Conclusion

Thus, the study of oils with different compositions by the dielectric spectroscopy method let us reveal the distinctive peculiarities of the associates –forming processes in a dispersed phase with thermal changes. The obtained data proved the elaboration of differential best conditions of external action (temperature, physical influence, chemical reagents) for oils with different structures in technological processes of oil production, transportation and refining.

## References

1. Tumanyan B.P. Scientific and applied aspects by theory of oil dispersion systems.-M.: «Engineering», 2000 – 336p.
2. Ratov A.N. Russian chemistry journal. 1995, v.39, №5, p.106
3. Safieva R.Z. Physical chemistry of oil. M.: Химия, 1998 - 448с.
4. Ahadov Y.Y. Dielectrical parametrs of pure liquids: Reference book.-M.: Publishers MAI, 1999
5. Feldman Y.D., Zuev Y.F., Valitov V.M. Time dielectric spectroscopy PTE, №3, 1979.
6. H. Frohlich, Theory of Dielectrics. Dielectrical permittivity and dielectrical waste.- M.1960.

*Kazan State University      Address: 18, Kremsevsкая str., Kazan, Russia, 420008.*

*A.I.Arbutov's Institute of Organic and Physical Chemistry, Russian Academy of Science.*

*Address: 8, Arbuzova str., Kazan, Russia, 420088.*

*e-mail: [denisay@mail.ru](mailto:denisay@mail.ru) , [Ivan.Lunev@ksu.ru](mailto:Ivan.Lunev@ksu.ru)*

**Figure captions:**

Fig.1 The experimental dielectric oils spectra:

- a) Abdrakhman's section, hole 13948
- b) Abdrakhman's section, hole 714D

Fig.2 The dependence of the relaxation times  $\tau_1$  and  $\tau_2$  as well as statistical dielectric permittivity  $\varepsilon_s$  on temperature.

- a) Abdrakhman's section, hole 13948
- b) Abdrakhman's section, hole 714D

Fig.3 The dependence of the statistical dielectric permittivity  $\varepsilon_s$  on temperature:

- a) Abdrakhman's section, hole 13948
- b) Abdrakhman's section, hole 714D

Fig.4 The temperature dependences of times relaxations for oils:

- a) Podgorny field, hole 25
- b) Northern field, hole 3186

Fig.5 The temperature dependencies of the statistical dielectric permittivity for oils:

- a) Podgorny field, hole 25
- b) Northern field, hole 3186

Table 1. Composition characteristics in the groups of high-viscosity oils in Tatarstan fields from Carbon formations:

Group number	Rel.content of samples in the group	Contents, macc. %		V/A *10 <sup>-3</sup>	E <sub>a</sub> , kilojoule/mole
		Asphaltenes (A)	Vanadium (V)		
1	12%	(0,4-5)	(0,0071-0,02)	(1,54-1,9)	(16-25)
2	32%	(6,4-13,6)	(0,022-0,048)	(1,92-3,77)	(45-108)
3	29%	(5,5-6,6)	(0,02-0,028)	(4,0-4,8)	(40-68)
4	27%	(6,8-16,6)	(0,048-0,08)	>4.2	-----

Fig. 1

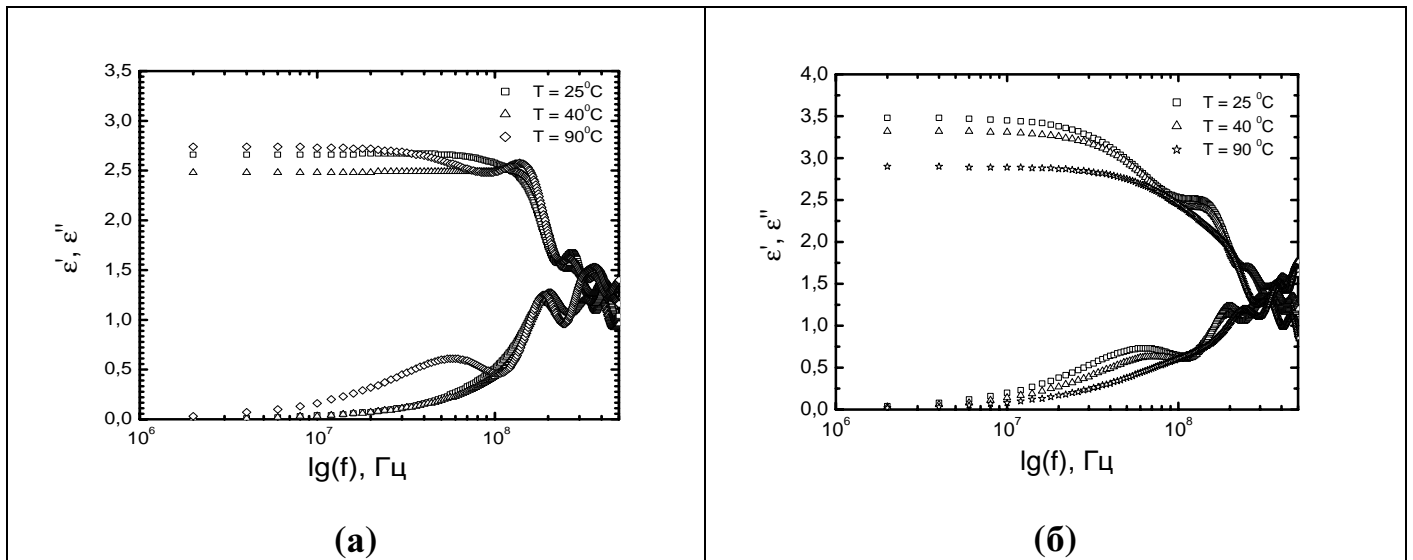


Fig. 2

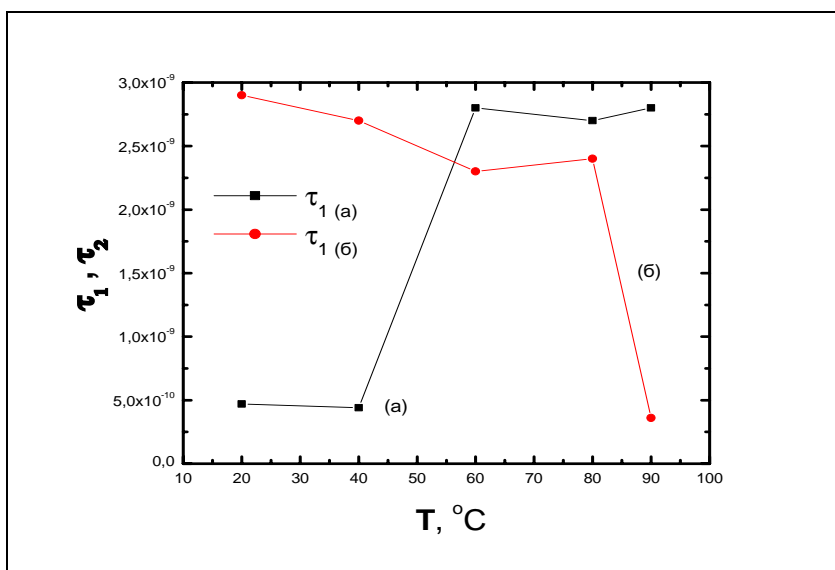


Fig. 3

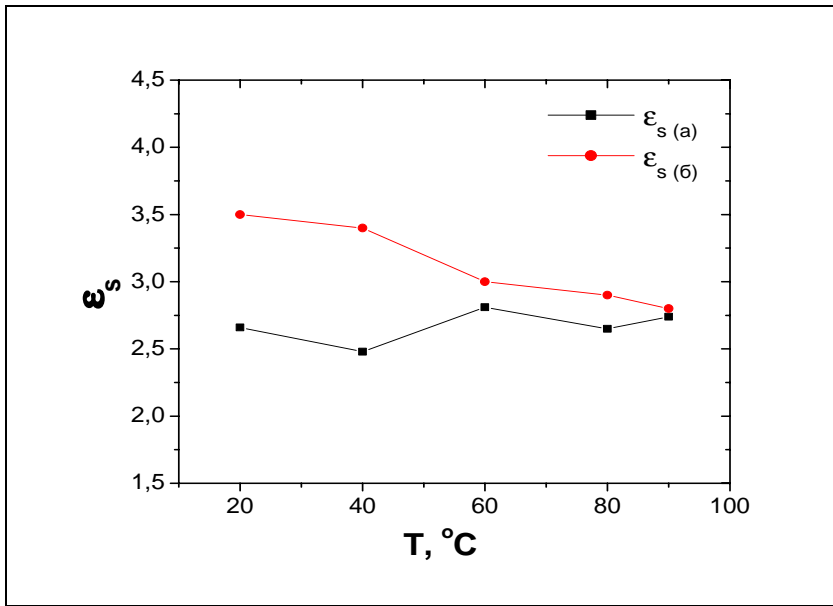


Fig. 4

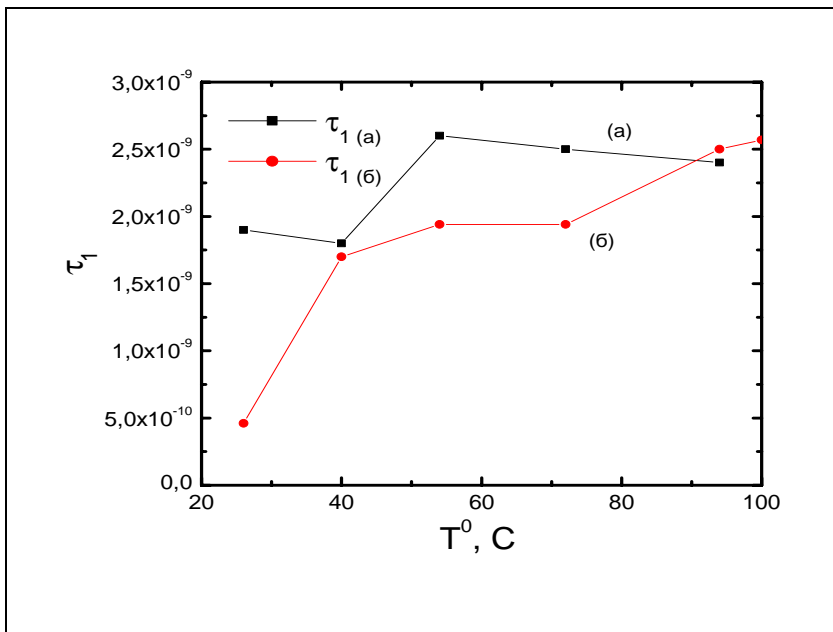


Fig. 5

