DISPERSE STRUCTURES AND SURFACE PHENOMENA IN OIL SYSTEMS RESEARCHED BY MODERN PHYSICIAN METHODS

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Surface phenomena and disperse states of oil systems define their numerous macroscopic properties, such as viscosity, surface tension, aggregative stability, etc. The researches of microscopic structure is important for understanding and prognosis the behavior of oil systems.

The investigations of disperse particles at model, real asphaltene solutions and oil products were made by dielectric frequency-domain spectroscopy methods. The sizes of asphaltene particles were measured by Debye formulae at wide region of pressures (up to 1.0 GPa) and different temperatures. It was found that they changes sharply near the regions of phase transitions of the pure solvents —benzene and toluene. In spite of the similarity of chemical structures that solvents differ considerably on their physical properties.

The pressure dependencies of the relaxation times (log τ_r) and solvent relative viscosity (long η/η_0) are shown at Figure 1. The presented dependencies are similar for benzene and toluene asphaltene solutions. An increase in τ_r value with an increase in pressure is mainly due to an increase in the viscosity. Near the phase transition region (below P_{cr} = 0.058 GPa for benzene and 0.9 GPa for toluene) the rapid growth of τ_r should be explained by sharp increase in the asphaltene particle sizes to the maximum values. On a further increase in pressure the clusters become "frozen" and lose the capacity for free rotation. At higher pressures the movement of the cluster segments is responsible for the relaxation due to asphaltene porosity in the considered models. The further increase in pressure also suppress dipole-segmental movements and later the dielectric relaxation proceeds via the movement of the individual polar groups — via dipole-grouping losses.

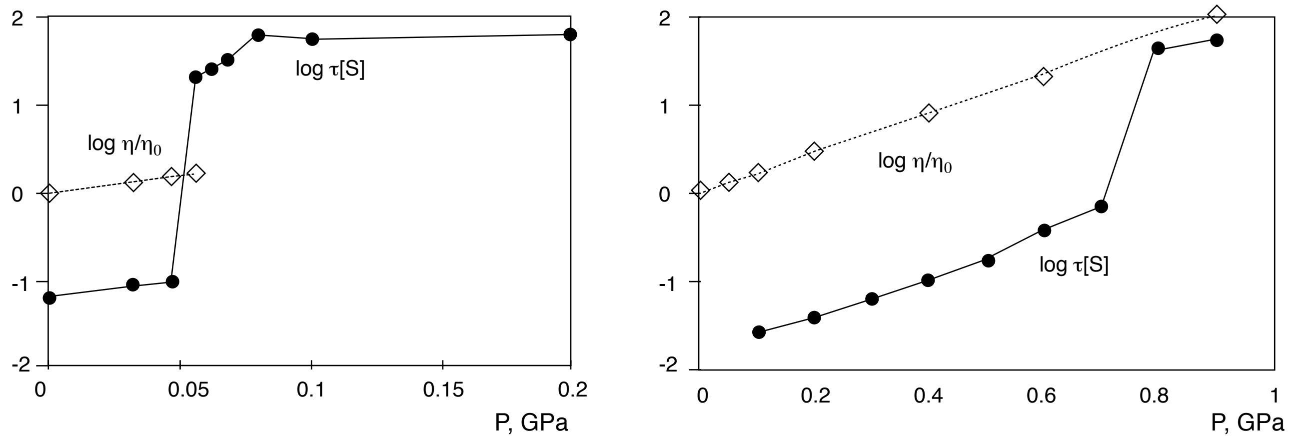

Figure 1a and 1b

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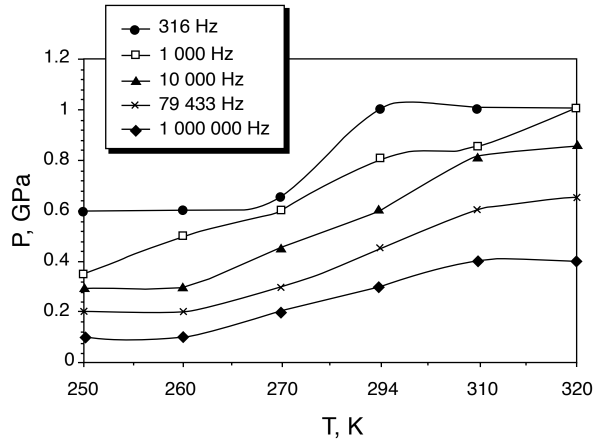

Figure 2

Crude oil demonstrate the nonlinear extremal behavior of imaginary part of the dielectric permeability —ε" upon pressure and temperature. It is connected with the internal restructuring of the object and the existence of phase transition regions for the components. The structural organization is defined by supermolecular scale. Really it is possible to describe oil behavior as the polymer solutions with significant degree of disorder. Usually such systems are called as organic glasses. The dielectric relaxation processes of different nature could be observed in complex systems. The nature of that processes is universal and not depends on the chemical structure of the substances. Near the phase transition regions relaxation times are of the same order and it is possible to registrate only summarized dielectric response. That behavior is specific feature of the glass phase transition. Dielectric spectra of researched oil are significantly wide. It is impossible to fix the peaks of losses. On that reason the dependencies of imaginary part of the dielectric penetrability ε" upon pressure and temperature for the fixed frequencies were searched. At isobaric conditions the dependencies ε" passes through maximal value at some temperature. At constant temperature the situation repeats for the some value of pressure. The values of that specific temperatures and pressures are different for the different frequencies. Every region of ε" maximal values is connected with definite kind of the heat movement on that thermodynamic parameters and structural rebuilding of oil system. The polymer systems demonstrates similar behavior. The curves of phase equilibrium at pressure-temperature coordinates were plotted for different used frequencies and are shown at Figure 2. The curves divide the regions of existence or absence different kind of movement which are specific for fixed frequency. The region where that movement is absent is in the upper part of the plot. The existence of frequency domain of "the movement freezing" shows that oil could be described as glass object. The phase state of oil does not change at the observed glass transition. The change of thermodynamic parameters leads to slow "freezing" of different kind of movement.

The investigation of asphaltene solutions in model and technological systems by luminescence polarized method is very perspective. Asphaltene molecules fluoresce in visible spectra region. The degree of polarization of fluorescence is a measurable parameter. This one is connected with the rotation diffusion coefficient. The definition of asphaltene particle sizes was executed by using Levshin-Perrine formula :

$$\frac{1}{P}=\frac{1}{P_0}+\left(\frac{1}{P_0}-\frac{1}{3}\right)\frac{\tau kT}{\eta V}$$

where:

P : the polarization degree
P_0 : the ultimate polarization degree
τ : middle lifetime of excited state
T : temperature

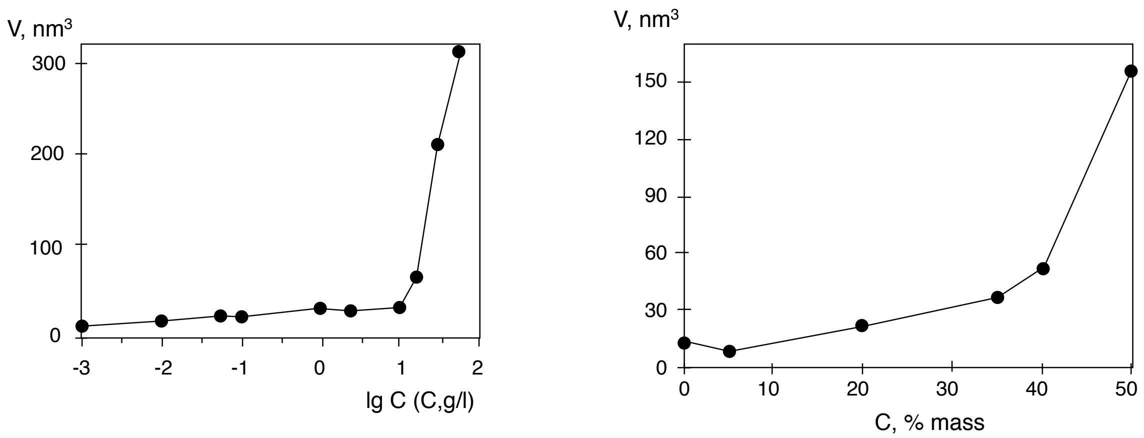

Figure 3a and 3b

η : solvent viscosity
V : volume of particles
k : Boltzmann constant.

The point of sharp changes of the rate of asphaltene association was determined at the benzene solution (Fig. 3a). Two different mechanisms are responsible for slow growth before concentration 1 g/l and fast increase after. At first region it could be Witten-Sander aggregation and later cluster-cluster aggregation. The asphaltene particle volume dependence in the industrial 2-component mixture upon concentration of heavy residue component (HRC) is presented at Figure 3b. The asphaltene particle sizes change nonmonotoneus upon temperature. The temperature when maximum of sizes is observed varies with concentration of HRC. The maximal phase stability and minimal temperature when maximum size volumes is achieved relate to the same concentration of HRC. The complicated character of internal organization this system is underlined by temperature hysteresis.

The thickness of surface layers for model systems and real diesel fuels under the influence of additives was searched by ellipsometry method. The growth of the thickness at optimal concentration of additive is connected with the increase of the molecule amount at surface layer and, sequentially, the decrease of evaporation energy. In both cases the boiling temperature decreases in presence of the additives. The fractional composition changes significantly. The redistribution of the hydrocarbons between volume and surface phases leads to the improvement of the exploitation parameters.

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