

## STRUCTURE OF MECHANICAL RESISTANCE OF THE WATER-OIL CONTACT REGION

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*A scanning method for determining the rheological characteristics of two-phase liquids and the corresponding experimental technique are considered. The structure of mechanical resistance of the water-oil contact region and its relation to the interphase tension have been shown.*

**Introduction.** The rheological characteristics of the water-oil contact region largely determine the efficiency of the process of recovery, transportation, and refining of oil; however, their measurement is still a nontrivial problem.

For surface viscosity control, one usually uses devices of the type of the horizontal torsion pendulum [1–3] which create in motion a tangential shear deformation. It is believed [4] that the forces fixing particles in the surface layer and acting in the direction perpendicular to it are basic and primary, and the processes leading to tangential fixing of structure elements are secondary and are of less importance for the rheology of surfaces. This explains the anomalous stability of emulsions with low shear rheological characteristics of the interphase layer [5]. At the same time, this seems to be a convicting argument in favor of conducting experiments with the deformation direction perpendicular to the surface.

Such deformation direction is provided by a number of static measuring techniques (ring separation, sphere extension, etc.). Analogous deformation occurs also by excitation of capillary waves; however, the promising dynamic wave technique is not used for investigating water-oil contacts because of the optical opacity of samples.

At the end of the 20th Century a "scanning viscosimetry" technique for controlling the interphase region of immiscible liquids was proposed [6], in which a vibrating probe — the probe body of the viscosimeter — is moved slowly along the vertical axis of the measuring cell through the interface of the investigated liquids. In so doing, the following positions of the probe are realized sequentially: 1) in the upper liquid, 2) in the interphase region, 3) in the lower liquid. In any of these positions, the total mechanical resistance consists of two parts — the intrinsic resistance of the vibrator  $Z_0$  and the resistance contacting the probe body  $Z_c$  which is due to the characteristics of the environment:

$$Z = Z_0 + Z_c .$$

As a result of the experiment, the dependence of the contacting resistance  $Z_c$  on the probe position — the stratification curve  $Z_c = f(h)$  — was obtained. Its structure contains characteristic sections associated with the motion of the probe body in the bulks of the liquids and in the intermediate zone. On the basis of the above dependence one can calculate the viscosity values for any region of the system being controlled, including the viscosity of the intermediate emulsion layer. It is usually formed in a simultaneous flow of surface-active liquids.

Although for sufficiently concentrated emulsions the relation between the deformation rate and the arising stresses is not linear, in the region of very small deformation amplitudes ( $\leq 0.01$  mm) characteristic of scanning viscosimetry one can use for calculations the linear approximation and the equation known for Newtonian liquids [7, 8]

$$Z_{\text{liq}} = F/\xi = K\sqrt{\rho\eta} ,$$

where the coefficient  $K$  depends on the form and area of the probe. The above expression describes the mechanical resistance of a continuum. A situation is possible where the concept of the interphase region as a layer of continuous viscous liquid braking the probe body turns out to be inconsistent. It can be given as a molecular-thin, "optical" inter-

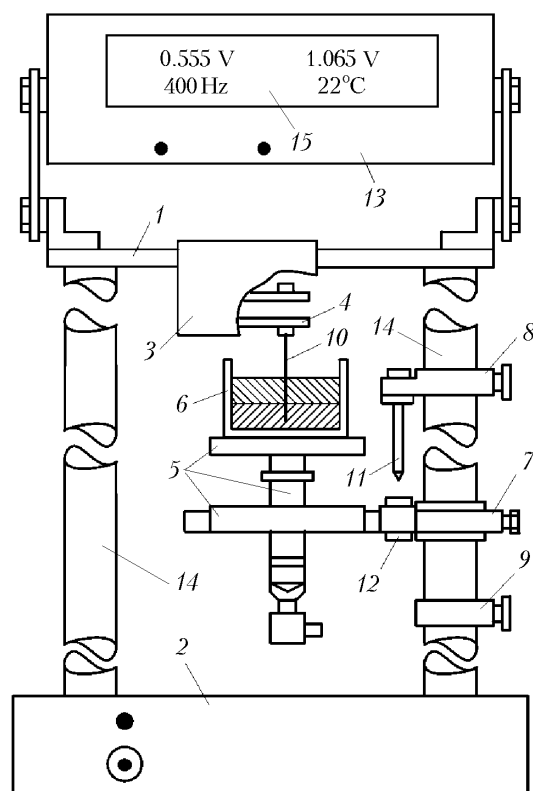


Fig. 1. Schematical representation of the facility: 1, 7) platforms; 2) tripod base; 3) sensor unit; 4) tuning fork; 5) scanning unit; 6) measuring cell; 8, 9) locks; 10) probe; 11) guide rod; 12) bush; 13) control unit; 14) tripod pin; 15) digital indicator.

face (according to Gibbs). A natural stage in the development of scanning viscosimetry seems to be the elaboration of methods for interpreting the dependences  $Z_c = f(h)$  obtained under these conditions.

To create a basis for developing methods for interpreting the above dependences, we have studied the mechanical resistance stratification in a number of model systems.

**Experimental.** We used liquids with known surface and bulk properties — heptane, diethyl ether, benzene, water, decane, cyclohexanol, technical kerosene, technical surface-active substance (SAS) AF<sub>9-12</sub> (oxyethylated nonylphenol — "Neonol") representing a mixture of oxyethylated alkylphenol [9]. Measurements were also made in kerosene solutions of the oil sample from the Strezhevsk oil field containing up to 9% of resin-asphaltene substances — weak natural SASs [10].

Two-phase models were formed in a glass rectangular vat (measuring cell) by making, by building up in layers, a 10-mm thickness of the hydrocarbon phase on a 30-mm thickness of the aqueous solution. The stratification dependences were obtained with the help of a "Vibroscan" setup. The output signal of its sensor  $U$  is proportional to the current resistance  $Z$  and is further used by us as its relative measure.  $Z$  includes  $Z_0$  corresponding to  $U_0$ .

The experimental facility (Fig. 1) consists of several function units. Its basis is a tripod. The massive base 2 contains a power supply for all assemblies. Two platforms 1, 7 are connected to the vertical rod of the tripod. Situated on the platforms are a massive slider — sensor unit (SU) 3 carrying a tuning fork 4 suspended by strings, and a piston lifter — scanner 5 which moves the measuring cell 6. The scanner is connected by a flexible hose to an external peristaltic pump PP1-05. The viscosimeter probe 10 is connected to the lower leg of the tuning fork. The control unit 13 installed in the upper part of the tripod forms analog signals  $U$  proportional to the current value of mechanical resistance  $Z$  and to the depth of immersion of the probe body  $h$ . The frequency signal corresponding to the vibration mode of the probe ( $\approx 400$  Hz) displays their values on the digital indicator and provides communication with the computer. Figure 1 shows also parts 8, 9, 11, 12 by means of which the movable platform 7 and the position of the probe

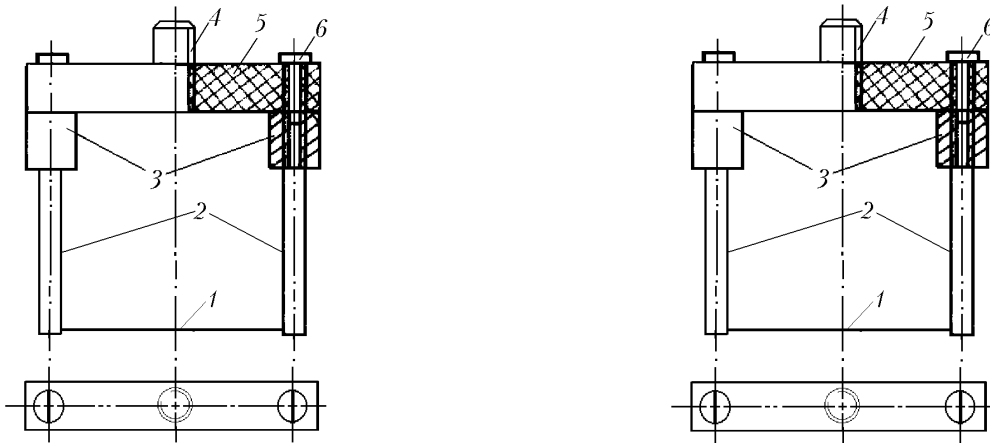


Fig. 2. Probe — sensor probe body: 1) string; 2) steel rods; 3) boss; 4) pin; 5) bar; 6) screw.

Fig. 3. Form of the dependence of mechanical resistance on the probe body position: 1) short cylinder "lying sidelong;" 2) horizontally stretched wire,  $h$ , cm.

body relative to the measuring cell are fixed. In the lower position of the platform 7 the device is in the regime of sample preparation. Moving the platform to the upper position takes the device into the measurement mode. The next stage is the switching of the scanner.

The probe body (1) (Fig. 2) represents a segment of a string of length 55 mm and diameter 0.2 mm stretched horizontally between steel rods 2.

**Results and Discussion.** The resolution of scanning viscosimetry depends on the viscosity of liquids and the ratio between the total area of the probe body and the value of its lateral parameter. Dependences of the type of curve 1 (Fig. 3) were obtained by means of a probe in the form of a short horizontally lying cylinder. By means of a probe in the form of a sufficiently long length of wire stretched on supports, we managed to reveal a latent structure in the mechanical resistance signal (curve 2, Fig. 3).

In the experimental dependences given below a horizontal section  $U_0$  is observed. It is considered further as the zero level and is subtracted from  $U$  and used as the basis for determining the value of the current contacting resistance  $Z_c$ . Then an extreme fragment connected with the movement of the probe body from air to hydrocarbon follows. Further, in the bulks of the liquids two portions with a relatively small inclination and an interposed maximum of complex form including  $\alpha$ - and  $\beta$ -fragments are observed.

In the scanning process, the probe body of the oscillatory viscosimeter executes vertical oscillations. Its contact with the considered surface may cause wave motion, and in the structure of the dependence of mechanical resistance on the probe position a section connected with the wave resistance should be present.

The first extreme fragment of the signal  $\alpha$  is observed as soon as the probe touches the interface when optimal conditions for the generation of surface waves arise. Obviously, it is just due to the wave phenomena. In the process of generation of a capillary wave, part of the probe body energy is carried away with it. To maintain the given amplitude of motion, a larger force will have to be applied.

As the probe advances, the optimal generation conditions are disturbed and a decrease in the mechanical load is registered, but in this case a meniscus begins to stretch into the depth of the lower phase. Its formation causes an apparent increase in the mass and surface of the probe body and leads to the appearance of a  $\beta$ -fragment of the output signal. The separation of the meniscus from the probe body leads to a rapid decrease in the current resistance.

The maximum of the stratification dependence associated with the radiation of the surface waves is observed in a situation where the probe touches simultaneously the two considered liquids. Evidently, it is caused by the simultaneous influence of the interface and the volumes of the contacting phases. Using the method of electromechanical analogies [11], we can propose an equivalent scheme of the situation in the form of a group of three parallel-connected resistances (Fig. 4). The  $Z_c$  value in the interphase region thereby will be equal to  $(Z_1 + Z_2)/2 + Z_s$ .

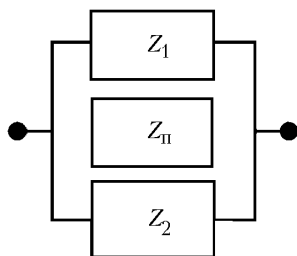


Fig. 4. Equivalent scheme.

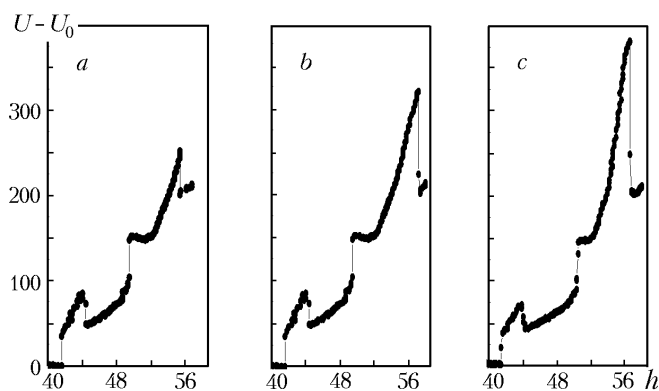


Fig. 5. Dependence of the signal of mechanical resistance on the depth of immersion of the probe into the cell with a two-phase liquid in the systems: a) ether/water; b) benzene/water; c) heptane/water.  $h$ , cm.

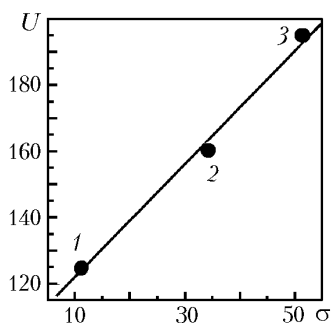


Fig. 6. Dependence of the output signal on the value of interphase tension in the systems: 1) ether/water; 2) benzene/water; 3) heptane/water.  $U$ , mV;  $\sigma$ , mN/m.

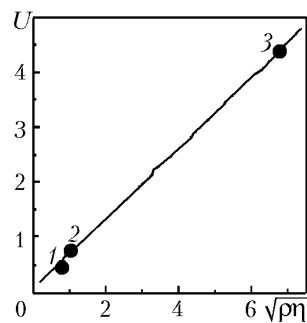


Fig. 7. Dependence of the output signal of the sensor on the probe position in the bulk of the liquid on  $\sqrt{\rho\eta}$ : 1) decane; 2) water; 3) cyclohexanol.  $U$ , mV.

Figure 5 presents the measurement data obtained in pure low-viscosity binary liquids. The left gentle slope of the  $\beta$  peak corresponds to the relatively slow process of meniscus formation, and the right vertical slope represents the fast process of its "collapse" as soon as the moving probe breaks the surface.

In accordance with the proposed equivalent scheme,  $U_{\beta} \sim Z_{\beta}$  was determined on the diagrams obtained. We measured the distance between the level corresponding to the mean viscosity of the contacting liquids and the amplitude of the extreme right peak. Figure 6 demonstrates the symbatic change in the value of interphase tension  $\sigma$  and the value of the  $\beta$ -fragment of the signal obtained in the above manner. In so doing, both the liquid viscosities and the interphase tension were varied from sample to sample. Figure 7 presents the measurement data obtained for the same depth of immersion of the probe into the bulks of liquids with known and reproduced viscosities. The figure points to the linearity of the sensor used.

Analogous measurements were made with solutions of SASs, which, in small concentrations, decrease considerably the surface tension practically without changing therewith the medium viscosity. As a hydrocarbon liquid, decane was used. The interphase tension was determined independently by the ring separation method. In so doing, the correlation coefficient between  $Z$  and  $\sigma$  turns out to be very close to unity (Fig. 8).

Distilled water was covered with layers of technical kerosene and oil from the Strezhevsk oil field. The curves obtained thereby are given in Fig. 9. The  $U_0$  level was not subtracted from the current value of the signal.

Figure 9a pertaining to the sample with a zero concentration of oil is very similar to the above-considered dependences obtained in pure binary liquids. In Fig. 9b pertaining to the sample with a 100% content of oil, the structure of the left part of the graph, which follows the movement of the probe body from air to the hydrocarbon phase,

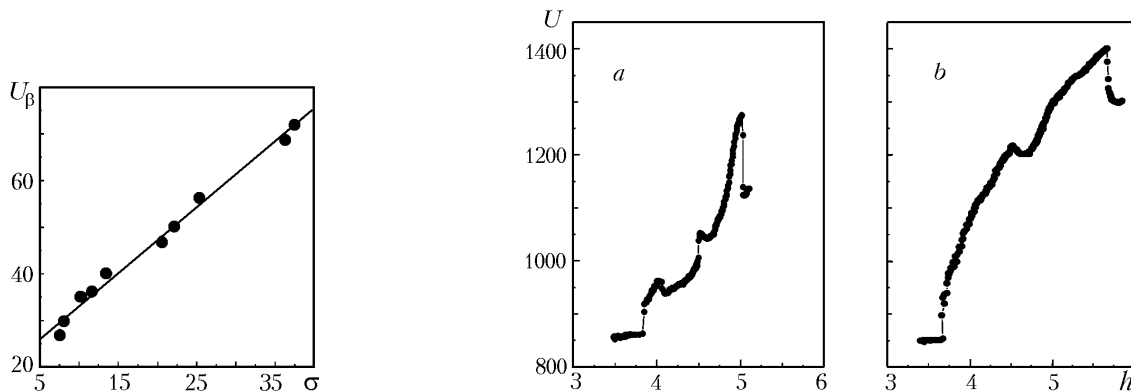


Fig. 8. Interrelationship between the  $U_{\beta}$ -fragment of the signal and the value of the interphase tension in the system decane–AF<sub>9–12</sub> solution (dots show the experiment).  $R = 0.996$ .  $U_{\beta}$ , mV;  $\sigma$ , mN/m.

Fig. 9. Dependence of the mechanical resistance on the depth of immersion of the probe body in the systems: a) kerosene–water; b) oil–water.  $U$ , mV;  $h$ , cm.

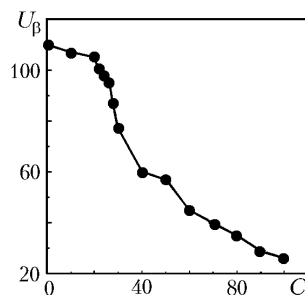


Fig. 10. Dependence of the mechanical resistance of the interphase region on the oil content in the sample (dots show the experiment).  $C$ , %;  $U_{\beta}$ , mV.

does not show up. Evidently, the masking influence of the oil viscosity, which is higher compared to the considered liquids, takes place. The structure of the  $\alpha$ - and  $\beta$ -signals therewith is seen fairly clearly.

Diluting sequentially oil with water, we obtained 13 samples with a lower viscosity of the hydrocarbon phase. A gradual change in the corresponding stratification dependences from the form of Fig. 9b to the form of Fig. 9a was observed.

We did not manage to get a clearly defined level of mechanical resistance intermediate between the two phases on the graphs obtained for samples with a large content of oil. As a base for counting off the  $U_{\beta}$  value of the whole group of models indicated above, we used the straight line connecting the beginning and end of the  $\alpha$ -fragment of the signal. Figure 10 shows the dependence of the thus obtained  $U_{\beta}$  value on the content of oil in the sample. The curve has a left extreme section with a relatively small slope and is, in general, similar to the smoothed interphase tension isotherm — the dependence of  $\sigma$  on the concentration  $C$  of colloidal SASs in the bulk phases [12]. Such a form is a consequence of the change in the degree of association of the above solutions with the concentration. In accordance with the mass action law  $C_{\text{mic}} = K_{\text{mic}}(C_m)^m$  [13], the chemical potential of the SASs in the system increases weakly upon reaching the critical concentration of micelle formation (CCM) — the region of the right knee of the considered curve.

The surface tension of solutions is determined by the substance concentration in the molecular form. Therefore, the slope of the  $\sigma$ – $C$  dependence of the right part of the curve upon reaching the CCM decreases and practically disappears for pure synthetic SASs. The definition of the above knee depends on the aggregation number, surface activity, and polydispersity of the composition. If the surface-active composition represents a mixture of substances, then the surface tension isotherm has the form of a smooth S-shaped curve not divided into clear sections.

Since the  $\beta$ -fragment of mechanical resistance turns out to be associated with the surface tension (see, e.g., Fig. 8), we can also attempt to interpret the concentration dependence  $U_{\beta}$ - $C$  from the point of view of the associative character of the corresponding solutions.

The nearly horizontal section of the curve in the region with a small concentration of oil corresponds to a small quantity of the SASs present. Relatively high values of interphase tension and mechanical resistance are observed. In the region with a content of oil over 20%, the presence of natural SASs is already noticeable. The value of  $U_{\beta}$  strongly depends on the degree of dilution. At a concentration of oil over 50% the slope of the considered graph changes. Some of the composition components appear to be included in the structure of the aggregates; however, the adsorption layer on the flat surface of the interface is still not filled. The slope of the extreme right section of the S-shaped interphase tension isotherm with respect to the abscissa axis is typical of the solution of a mixture of substances and points to the presence of some of them in the molecular form.

**Conclusions.** The structure of the mechanical resistance of immiscible liquids, including the region of the water-oil contact, has a complex character. As the probe body moves through the interface surface, two extreme fragments are observed sequentially: the  $\alpha$ -fragment of the signal arises from the generation of capillary waves and is connected with the dynamic properties of the considered interface; the  $\beta$ -fragment appears in the process of meniscus stretching. A similar situation takes place in measuring  $\sigma$  by the ring separation method. The  $\beta$ -fragment is connected with the interphase tension and can be interpreted from the point of view of the surface activity of the composition of samples. Evidently, the concentration dependence of  $Z_{\beta}$  obtained by diluting oil can be used as an integral characteristic of the association of its heteroatomic components.

## NOTATION

$C$ , solution concentration, vol. %;  $C_{mic}$ , micelle concentration;  $C_m$ , concentration of molecular-dissolved substances;  $F$ , force exciting oscillatory motion, dyn;  $h$ , depth of immersion of the probe body, cm;  $K_{mic}$ , equilibrium constant of the aggregation-micelle formation process;  $m$ , aggregation number;  $R$ , correlation coefficient;  $U_0$ , value of the sensor output signal when the probe body moves in air, mV;  $U$ , current value of the output signal of the tensor, mV;  $U_{\beta}$ , value of the signal corresponding to the  $\beta$ -fragment of the dependence, mV;  $Z$ , current value of mechanical resistance, dyn·sec/cm, rel. units;  $Z_0$ , intrinsic mechanical resistance of the vibrator, rel. units;  $Z_c$ , contacting resistance, rel. units;  $Z_{liq}$ , liquid resistance, rel. units;  $Z_1$ ,  $Z_2$ , mechanical resistance of the upper and lower liquids, rel. units;  $Z_s$ , interface resistance, rel. units;  $Z_{\beta}$ , mechanical resistance corresponding to the  $\beta$ -fragment of the dependence, rel. units;  $\alpha$ ,  $\beta$ , markings of the extreme fragments of the stratification dependence;  $\eta$ , liquid viscosity, mPa·sec;  $\xi$ , velocity of vibrational motion, cm/sec;  $\rho$ , liquid density, g/cm<sup>3</sup>;  $\sigma$ , interphase tension, mN/m. Subscripts: 0, initial value; liq, liquid; mic, micelle; m, molecular; c, contacting; 1 and 2, upper and lower liquids; s, surface.

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