



The Effect of a Hydrocarbon Fragment in a Molecule on Depressant Activity of Resins

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Abstract

The effect of resins on solidification of paraffin solutions has been studied by vibration viscosimetry. This technique was used for studies of coagulating liquids, since the sample structure is less affected by mechanical oscillations compared to traditional rotary and linear shears. The installation developed for studies of thermo-induced phase transitions and the measurement procedure are described. The viscosimetric technique allows continuous registration of rheological properties with changing temperature, and has proved to be quite sensitive to small amounts of resins in model paraffin solutions. Measurements have been performed for resins extracted from methane-naphtene crudes of various West Siberia oil deposits. Dependencies of viscosity on temperature have been measured and are presented below for various concentrations of resins (up to 3 %) in paraffin solutions. It is demonstrated that increase of resin concentration results in a shift of the inflexion point on the viscosity-temperature curve to lower temperatures. A positive correlation has been found between depressant activity and average dimensions of aliphatic fragments of the resin molecu.

Introduction

Rheological behaviour of dispersed oil systems containing paraffin, asphaltene, and resin particles in hydrocarbon matrix depends on temperature. This dependence warrants attention due to phase instabilities in such systems and a vast variety of conditions of their processing and practical utilisation.

A solidification temperature (ST) is a temperature of stopping a free liquid flow. ST of oil products depends on their hydrocarbon composition and on concentration and nature of specific additives. It is known [1] that ST of petroleum fractions decreases as any resin is incorporated into their composition. These dependencies can be analysed in detail by means of vibration viscosimetry that allows continuous registration of rheological properties of oil dispersed systems as the temperature monotonically changes. Devices of various types are used to measure viscosity. For coagulating liquids, it is difficult to interpret values of their shearing strains or flow rates measured by traditional "constant flow" viscosimeters, since a disturbance of compactness or a destruction of solid-

like bodies in samples under study becomes possible at great amplitudes of vibrations and continuously increasing deformations. The higher shearing rate results in homogenization of the sample, but in these cases the phase transition temperature (PTT) may be changed. The change of PTT may result from the phase transition itself as formation of very fine particles, or from interaction between the particles as quasi-coagulation process. The two phenomena may be considered as consecutive stages. The first stage may weakly manifest itself in relatively rough rheological experiments, and the second one depends on hydrodynamic conditions.

It follows from the above that studies of phase transitions by rheological techniques should necessarily take destructive effects of deformation into account. Results of experiments with small-amplitude mechanical oscillations approach those at zero shear, since the sample structure is less affected [2] by the mechanical oscillations than at continuous rotary or linear shears. Therefore, vibration viscosimeter represent a promising tool for studies of coagulating liquids [3-5]. With increasing vibration amplitudes, the structure degrades to a higher degree than for com-

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parable relative change in the rotary shear. Thus, the use of the high Q devices is preferable, as the amplitude of probe movements required for measurements depends strongly on the device construction and hence on its sensitivity.

Experimental

The installation «ITPT» for studies of thermo-induced phase transitions has been developed on the basis of tuning fork viscosimeter «REOKINETIKA» [6,7]. Block diagram of the installation is presented in Fig. 1. The basis of this device is a vibrator (tuning fork) fixed with a holder, and a hoister. A cylinder thermostat (jacket) is placed on the hoister; a heat-transfer liquid is circulated through the jacket during the measurements. A cell for measurement (volume 1 cm³) and a temperature sensor are placed coaxial in the thermostat. Construction of the sensor is geometrically similar to that of the cell and consists of a metal cowling and a bottom-plug. A sensitive microcircuit is soldered inside of the plug. The probe is linked to the vibrator and is submerged into the cell in the top position of the hoister.

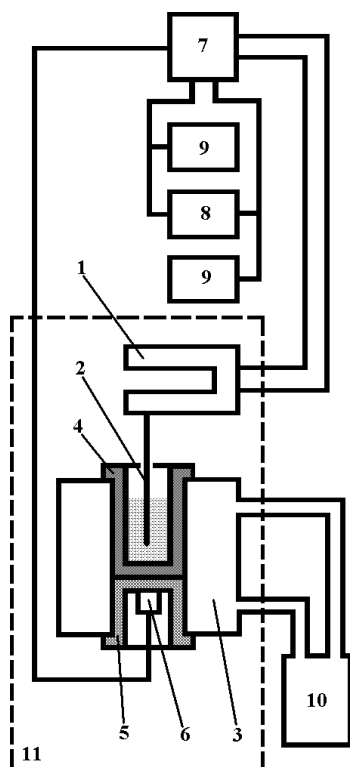


Fig. 1. Block diagram of ITPT installation. 1 - vibrator, 2 - test body, 3 - thermostat, 4 - cell, 5 - thermometer, 6 - microcircuit, 7 - control unit, 8 - dual recorder, 9 - voltmeter, 10 - cryostat, 11 - holder set.

The control block includes an electron auto-oscillator and a plate for temperature measurements. The auto-oscillator is linked to the tuning fork and operates in the mode of maintaining constant amplitude of mechanical vibrations. An output voltage corresponds to the proper electrical resistance of the sensor Z_o when the latter moves in the air. In course of a measurement the probe is vibrating in the liquid, which produces an additional mechanical resistance Z_l . It requires a greater force to be applied in order to maintain predetermined amplitude. The magnitude of the effective force is transformed into electric signal U_z proportional to the mechanical resistance

$$Z = F/\zeta = Z_o + Z_l,$$

where F is the force governing the probe movement, and ζ the velocity. For Newtonian liquids

$$Z_l = as\sqrt{\omega}\sqrt{\rho\eta}$$

where a is a coefficient depending on the shape of a probe, s surface area of a probe, ω – vibration frequency, ρ – liquid density and η – liquid viscosity. U_z value generated by the control block enters at input Y of dual recorder. Digital voltmeter is used for signal concordance and calibration.

The control block forms also the analogue signal U_t , which is proportional to the temperature in the thermostat. When the device operates in the temperature-scanning mode U_t value is recorded along a horizontal axis X of the recorder.

The viscosimetric part of the installation consists of a tuning-fork sensor with a probe and an auto-oscillator. An amplitude of probe vibrations is less than 0.01 mm. The part intended for temperature measurement includes a measuring plate and another sensor based on specific microcircuit. Using the thermostat permits us to work at a fixed temperature and to carry out kinetic investigations. Under conditions of continuous cooling (or heating), a rate of temperature change is not regulated; this rate is determined by the cooler (heater) capacity and is equal to 1°C per minute in our experiments.

The process of formation of a primary coagulation network of paraffin microparticles in hydrocarbon solutions or in real petroleum was previously shown [8] to be described by relaxation equations, which are identical in their forms. In other words, the mechanisms of network formation due to thermo-induced phase transitions at decreasing temperature are the same in both cases. It allows the paraffin solutions to be used as a model for studying the solidifi-

cation processes of actual hydrocarbon systems.

We studied viscosity-temperature characteristics of paraffin solutions containing resins extracted from methane-naphtene and methane oils from West Siberian deposits. Table 1 presents compositional characteristics of the resins extracted by Soxhlet technique [1] from preliminarily deasphaltized crudes.

Table 1

Compositional characteristics of the resins extracted from West Siberian crudes

Oil deposit	Content, wt. %			Number of C_{paraffin} atoms in the average molecule
	N	S	O	
Ust-Tegusskoye	0	1.60	0.12	10.6
Ostaninskoye	1.28	2.80	4.13	15.5
Sobolinoye	0.79	2.24	0.65	25.1
Yasnoye	0.55	0.88	1.85	25.4
Novo-Yutymyskoye	0.86	3.00	0.53	32.2

The solution samples were prepared by weighing appropriate amounts of the components. 5 % paraffin and the resin were placed into titanium vessels, which were filled with kerosene, hermetically sealed, and held in the cabinet drier at the temperature above 80°C until full dissolution was attained. Then the sample of the solution was carried into the cell of the ITPT installation and cooled using laboratory circulation thermostat MK-70. At the moment when the temperature reached up to 30°C, a probe (a test body of the viscometer) was placed into the cell, and the dual recorder was switched on. With further decrease of temperature changes in viscosity due to solution solidification were recorded. On each graph sheet, there were indicated signal levels corresponding to probe oscillations in air (U_o) and in calibration liquid (U_{cal} , glycerine) [9]. The curves obtained were digitized, and the values of relative resistances $Z_{rel} = Z_{liq} / Z_{cal}$ were used subsequently on the graphs without foot-indices (i.e. $Z_{rel} = Z$).

Results and Discussion

Studies of paraffin solutions containing 1, 2 or 3 % of resins extracted from various oils (Table 1) demonstrated that increase of resin concentration results in a shift of the inflexion point on the $Z = f(T)$ curve to lower temperatures. None of the resin samples changed noticeably the initial viscosity of the solu-

tion, though the resins differ significantly both in heteroatomic composition and in the mean number C_p of carbon atoms in molecular paraffin fragments (C_p). Coinciding at higher temperatures, the curves for various samples diverge as temperature decreases, and their slopes continuously change (Fig. 2).

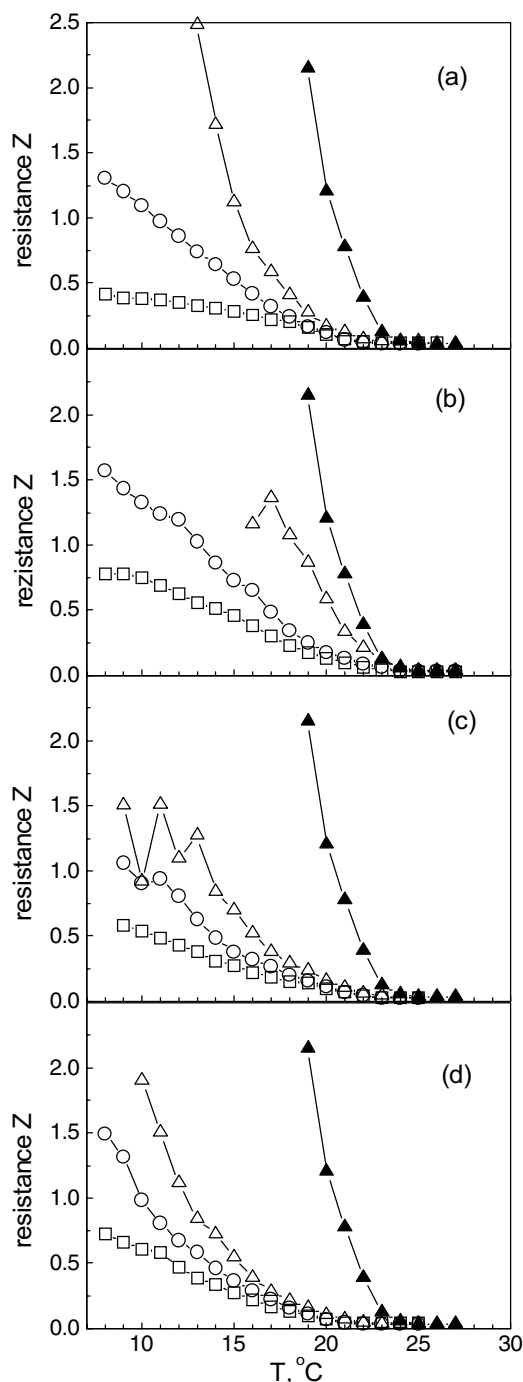


Fig. 2. The dependence of a mechanical resistance on the temperature for paraffin solutions containing the resins from oils extracted from Novo-Yutymyskoye (a), Ostaninskoye (b), Sobolinoye (c) and Yasnoye (d) oil deposits (\blacktriangle - 0 %, \triangle - 1 %, \circ - 2 %, \square - 3 %).

For the resins from the Novo-Yutymyskoye, Yasnoe, Sobolinoye, and Ostaninskoye oil deposits, a positive correlation was observed between depressant activity and average number of paraffin carbon atoms per molecule. Fig. 3 presents the dependence of slope angles of viscosity-temperature curves at temperature 15°C on C_p in added resins. Within the present range of component concentrations (paraffin – 5 %, resin – up to 3 %), the curve is well approximated by a straight line.

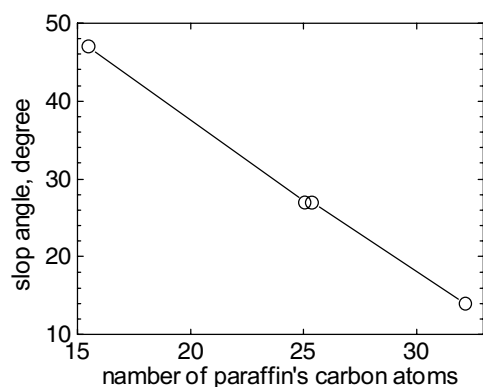


Fig. 3. The dependence of slope angles of viscosity-temperature curves at the point corresponding 15 °C, on average size of paraffin fragments in resin molecules.

Viscosity-temperature curves are close to each other for resins from Yasnoe and Sobolinoye oils; these resins only slightly differ as regards composition of hydrocarbon parts of their molecules. For solutions containing the resins from Novo-Yutymyskoye and Ostaninskoye oils, the slope angles of the curves differ by a factor of two. It is probable that in this petroleum series the size of aliphatic chains in resin molecules has a decisive effect on depressant activity, since an adsorbability of the molecules on the paraffin microcrystals and germs rises with lengthening these chains. Heteroatomic fragments of the resin molecules provide only non-specific protective action.

Preliminary data for the resins from petroleum of the Ust-Tegusskoe oil deposit are shown in Fig. 4. These resins are poor in the paraffin carbon atoms and all heteroelements, especially nitrogen. The general behaviour and relative positions of the obtained curves remained unchanged. However, the gross depressant activity of these resins was higher than that of other resin samples containing a larger amount of paraffin carbon atoms (Table 1). This is not in accord with the adsorption hypothesis [10]. It is possible that, once C_p has decreased to sufficiently small values, the ratio of hydrocarbon and heteroatomic

fragments in resin molecules dominates their depressant activity.

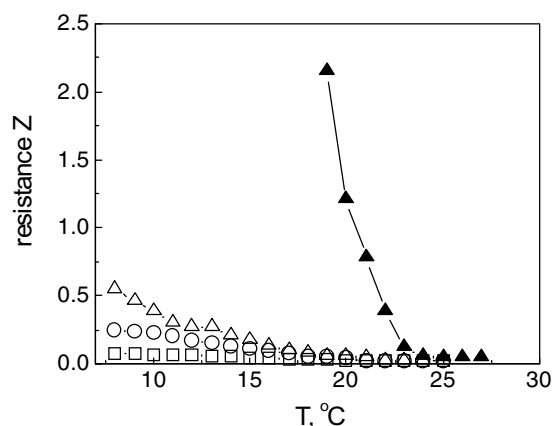


Fig. 4. The dependence of a mechanical resistance on the temperature for paraffin solutions containing the resins from the oil extracted from Ust-Tegusskoye oil deposit. (▲- 0 %, △- 1 %, ○- 2 %, □- 3 %).

Conclusions

Technique and procedure of measurement developed in this experiment are sufficiently sensitive to small concentrations of resins in the model paraffin solutions.

A positive correlation between depressant activity of petroleum resins and the average size of aliphatic chains in the molecules was established.

For small size of aliphatic part and low content of heteroelements, the depressant activity may depend on the ratio of hydrocarbon and heteroatomic fragments in resin molecules.

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