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Fig. 1 and Fig. 2: temperature dependences of dielectric constant

Figure 1: Fig. 1 and Fig. 2: temperature dependences of dielectric constant

Abstract

Full Text

PHYSICAL CHEMISTRY

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DIELECTRIC STUDY OF PHASE TRANSFORMATIONS
IN THE SYSTEM SOAP–HYDROCARBON–WATER ==========

The behavior of soaps as thickeners in consistent greases is determined to a large extent by their phase structure. Solvents and additions of hydroxyl-containing compounds to them have a noticeable effect on the temperature of phase transformations of soaps (^1). Of considerable interest is the establishment of a connection between phase transformations in soap and in a system thickened by this soap. For this purpose, various methods of investigation are used–thermal, X-ray, optical, and others–since, in order to detect different phase transitions, it is necessary to apply different independent methods.

For the study of phase transformations in the soap–hydrocarbon system, we used the method of measuring the dielectric constant, since the dielectric properties of many substances change substantially during structural transformations (^2). Doscher and Davis (^3), in studying the temperature dependence of the dielectric constant, established phase transitions in the system sodium stearate –cetane–water.

Fig. 1

Fig. 1. Temperature dependence of the dielectric constant of the system calcium oleate–xylol: *a* –1 kc, *b* –10 kc, *v* –50 kc, *g* –450 kc, *d* –1.5 Mc. Concentration 80 g per 100 ml of solvent

Fig. 2

Fig. 2. Temperature dependence of the dielectric constant of the system calcium oleate–xylol–water (semihydrate): *a* –1 kc, *b* –10 kc, *v* –450 kc, *g* – 1.5 Mc. Concentration 80 g per 100 ml of solvent

As the object of investigation we chose a system consisting of xylol and calcium oleate, distinguished by low temperatures of phase transformations. According to the data of Trapeznikov and Zakieva (^4), for the calcium oleate–water system there are transitions at 50-55° and 75-80°, and for the calcium oleate–water–velosite system, at 50 and 71.5°.

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The capacitance was measured in the range from 1 to 10 kc on an audio-

bridge and in the range from 50 kHz to 1.5 MHz on a (Q)-meter. To take into account the capacitance of the lead wires and to calculate the dielectric constant, measurements were carried out on a standard liquid ((m)-xylene). The error in measuring the dielectric constant varied, depending on the method, frequency, and magnitude of the dielectric constant. On average it was 1-5%.

The results of measuring the temperature dependence of the dielectric constant of a system consisting of 80 g of calcium oleate dissolved in 100 ml of xylene are presented in Fig. 1. The effect of additions of water is shown in Figs. 2 and 3. In all the systems studied, the dielectric constant decreases with increasing frequency. This effect is especially pronounced in systems containing water. As the frequency increases, the ( )–(t) curves level off. The noted dependence of the dielectric constant on frequency indicates Maxwell-Wagner surface polarization, which arises in the low-frequency region in the presence of two phases with different dielectric constants and conductivities ({}^{(5)}).

It is seen from Fig. 1 that, with increasing temperature, the dielectric constant of the anhydrous system increases as a result of weakening of the intermolecular interaction. This dependence is especially sharply expressed at low frequencies.

Water has a considerable influence on the dielectric properties of the system. First of all, attention is drawn to the extremal value of the dielectric constant. When water is introduced into the system at the rate of 0.5 mole per 1 mole of soap, the minimum value of the dielectric constant is observed at 55°, i.e., at the temperature of the first phase transition. With an increase in the water content to 1 mole per mole of soap, the minimum on the ( )–(t) curve shifts toward lower temperatures. An excess of water above this amount does not affect the position of the minimum. The correspondence between the temperatures of the phase transitions and the minimum of the dielectric constant in the soap–hydrocarbon–water system is noted by Doscher and Davis ({}^{(3)}).

The decrease in the dielectric constant is apparently associated with a strengthening of the interaction of the polar groups of the soap molecules during phase transformations ({}^{(3)}). The shift of the minimum of the dielectric constant observed in the system containing 1 mole of water per mole of soap indicates that calcium oleate monohydrate in the hydrocarbon has a lower transition temperature. Consequently, the addition of water to the soap leads to a lowering of the temperature of the phase transitions. Free water, which does not interact with the soap, does not affect the temperature of the phase transitions.

Fig. 3. Temperature dependence of the dielectric constant of the system calcium oleate–xylene–water (monohydrate): (a)–1 kHz, ( )–10 kHz, ( )–450 kHz, ( )–1.5 MHz. Concentration 30 g per 100 ml of solvent.

The higher values of the dielectric constant of the system containing water, in comparison with the anhydrous system, are due, first, to hydration of the soap molecules, increasing their polarity, and, second, to the peptizing action of water.

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Fig. 3. Temperature dependence of the dielectric constant of the system calcium oleate–xylene–water (monohydrate): a–1 kHz, –10 kHz, –450 kHz, –1.5 MHz. Concentration 30 g per 100 ml of solvent

Figure 2: Fig. 3. Temperature dependence of the dielectric constant of the system calcium oleate–xylene–water (monohydrate): a–1 kHz, –10 kHz, –450 kHz, –1.5 MHz. Concentration 30 g per 100 ml of solvent

The special role of water in the structure of the soap–hydrocarbon system was also noted in the study of the mechanical, thermal, and optical properties of these systems ({}^{(6)}).

It was established that, owing to supercooling of the system, the heating and cooling curves differ considerably. The dielectric properties also proved sensitive to the process of recrystallization of the system, which continued for several days.

Thus, investigation of the dielectric constant can provide valuable information on phase transformations in the soap–hydrocarbon–water system.

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CITED LITERATURE

1. G. V. Vinogradov, in: *Consistent Lubricants*, collected volume, 1951, p. 12.

2. C. P. Smyth, *Dielectric Behaviour and Structure*, Ch. V, N. Y., 1955, p. 132.

3. T. M. Doscher, S. Davis, J. Phys. and Coll. Chem., **55**, 1, 53 (1951).

4. A. A. Trapeznikov, S. Kh. Zakieva, *Proceedings of the All-Union Conference on Colloid Chemistry*, Kiev, 1952, p. 362.

5. A. Gemant, *Electrophysics of Insulating Materials*, L., 1932, p. 100.

6. A. A. Trapeznikov, in: *Low-Temperature Properties of Petroleum Products*, collected volume, M., 1949, p. 98.

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