The structure of dilute solutions of certain ethers of ethylene glycol and alcohols was investigated by the ultrasonic method. A calculation was carried out of the number of bonded and stabilized water molecules. It was established that the stabilizing effect increases with increasing number of methyl groups in the hydrocarbon radical of the ethoxylates. A qualitative mechanism was proposed for association of the dissolved molecules.

Compounds containing an aliphatic or cyclic hydrocarbon radical and a polyethylene glycol chain find wide use in various branches of industry due to their ability to form associates, micelles, under certain conditions. To date, the mechanism of formation of associates of dissolved molecules remains unclear because knowledge of dilute solutions of these materials is extraordinarily sparse. The purpose of this research was the investigation of the structure of dilute aqueous solutions of certain oxyethylated alcohols and alkylphenols.

Materials. Oxyethylated alcohols were obtained by the method of [1]. Oxyethylated alkylphenols were industrial samples OP-7 and OP-10. All materials were subjected to purification from impurities, and some of them were fractionated by the method of [2]. Analysis for content of the average number of glycol residues in the molecules was carried out by IR and UV spectroscopic methods. In this work we used CH₃(CH₂)₇(OCH₂CH₃)ₓOH(CₓPₓ), where x = 4, 6, 7; CH₃(CH₂)₉(OCH₂CH₂)₇OH(C₁₀P₇); CH₃(CH₂)₁₀(OCH₂CH₂)₆OH(C₁₁P₆); OP-7; OP-14.4.

Water was distilled two times from potassium permanganate from a quartz vessel.

Method. The ultrasonic method of investigating structure of solutions was used in this work. Velocity of sound was determined on a differential ultrasonic interferometer [3] with an accuracy of ± 5 cm/sec. Values of velocity of sound were used to calculate compressibility by the Laplace equation \( \beta = 1/u^2p \). Solution densities were measured on an apparatus constructed on the principle of a magnetic float balance having two solenoids [4]. The accuracy of measuring density was ± 5 · 10⁻⁶ g/ml. During measurements of velocity of sound the temperature was maintained with an accuracy of ± 0.02°C and with an accuracy of ± 0.005°C during determination of density.

EXPERIMENTAL RESULTS AND DISCUSSION

The dependence of compressibility of solutions of the investigated materials on concentration at 25-30°C is shown in Figs. 1 and 2. It can be noted that the greater the glycol residues in molecules of dissolved material at an identical length of the hydrocarbon radical, the more intensely occurs a decrease in compressibility of solutions. At an identical number of glycol groups, materials in which the hydrocarbon radical is longer have a larger effect on compressibility. It is also interesting to note that the effect of the methyl group of the hydrocarbon radical is analogous to the effect of the glycol residue, since the dependence of compressibility of C₁₀P₇ and C₁₁P₆ solutions on concentration is identical (Fig. 2, curve 3). Increasing the temperature from 25 to 30°C decreases the effect of all materials on the compressibility of solutions.

Aqueous solutions of diphilic materials containing a hydrophobic hydrocarbon radical and hydrophilic chain can be represented as a combination of phase regions, in which molecules of solvent and water can be found in one
of the following states: 1) unperturbed molecules, forming a structure typical for water at the given temperature; 2) water molecules, associated with the ether oxygen of the glycol groups, i.e., solvate portion of the solvent; 3) molecules of structural formations around hydrophobic hydrocarbon radicals. Drawing in the original model of Samoilov [5], we can consider that solution of diphilic molecules occurs by an insertion-substitution mechanism, when the hydrocarbon radical is situated in large cavities of the prepared structural formation, partially occupying vacant sites, partially displacing "hydrophobic" cavity-type water molecules, and the formation of hydrogen bonds between the ether oxygen atoms of glycol groups and water molecules leads to formation of new structure formations, differing in their properties only insignificantly from ice-like structure.

The ability of hydrocarbons to stabilize the water structure, proposed for the first time in the paper of Frank and Evans [6] and subsequently developed in the paper of Scheraga [7], does not now raise any doubts. The theoretical development of this question was presented in [8].

It was established in [9] that introduction of diphilic materials, having a hydrocarbon radical, leads to a sharper appearance of the absorption band, characteristic for ice. According to spectroscopic data the effect of additions of such materials is analogous to a decrease in temperature and disappears upon transition of the system from a molecular state to an associative state, micellar, i.e., when contact between the hydrocarbon radical and water disappears.

Starting from the premise that water, stabilized by hydrocarbon radicals and bonded with glycol groups, has an ice-like structure, we carried out a calculation of the number of bonded and stabilized water molecules, going for one molecule of dissolved material. Calculation was carried out by the equation [10]

\[ \frac{d\beta}{dc} = h_1 V_1 \Delta \beta_1 \cdot 10^{-3} + V_2 \Delta \beta_2 \cdot 10^{-4}, \]

where \( \frac{d\beta}{dc} \) is the slope of the concentration dependence of compressibility of solutions; \( h_1 \) is the number of water molecules bonded and stabilized by one molecule of dissolved material; \( V_1 \) is the molar volume of bonded water (18.094 ml/mole); \( \Delta \beta_1 - \beta_0 \) is the difference in compressibility of bonded (11 \( \cdot \) \( 10^{-12} \) cm\(^2\)/dyn) and free water; \( V_2 = M/\rho_0 (1 - dp/dc) \) is the partial molar volume of dissolved materials (ml/mole); \( M \) is the molecular weight of dissolved material; \( \rho_0 \) is the density of solvent (g/ml); \( dp/dc \) is the concentration coefficient of density of solutions; \( \Delta \beta_2 = \beta_2 - \beta_0 \) is the difference in compressibility of dissolved material and solvent. Before formation of associates it is considered that \( \beta_2 = 0 \); after formation \( \beta_2 = 70.1 \cdot 10^{-12} \) cm\(^2\)/dyn, while \( \beta_3 = \beta_0, \) i.e., compressibility of solution at the critical concentration of association. Calculation results are presented in Table 1.

Data presented in Figs. 1 and 2 and in Table 1 make it possible to trace a series of interesting regularities.

1. The linearity of the dependence of compressibility on concentration indicates the absence of interaction between molecules of dissolved materials and associates, micelles, in dilute solutions, which can probably be ex-