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# LIGHT SCATTERING BY AQUEOUS SOLUTIONS OF ALCOHOLS NEAR THEIR SINGULAR POINTS

*The dependence of the position $x^0$ of the low-concentration peak on the curves of light scattering by aqueous solutions of alcohols on their molecular masses has been found. The relevant concentration for ethylene glycol at 20 °C is determined and compared with the literature data for the homologous series of methanol. The obtained dependence is linear to an error less than 2%.*

*Keywords*: light scattering, dilute aqueous solutions of alcohols, low-concentration peak, ethylene glycol.

It is known [1, 2] that, in the aqueous solutions of alcohols, besides the peak of light scattering by concentration fluctuations, which is observed at alcohol molar fractions $x \approx 0.3 \div 0.5$, another, the so-called low-concentration peak is observed at low alcohol molar fractions $x \approx 0.05$. The origin of the latter is most likely associated with structural reorganizations in the medium [3]. However, it has not been studied sufficiently. As a rule, the corresponding experiments on the integral light scattering are carried out at a constant temperature $T$, a constant pressure $P$, and a varying concentration. Therefore, the concentration, at which the physical properties of the solution – e.g., light scattering – demonstrate an anomalous behavior, should be called as a singular one or, in view of the constant experimental $P$, $V$, and $T$ values, as a singular point in the four-dimensional thermodynamic space $x$–$P$–$V$–$T$. It is evident that, for the varying temperature or pressure, those points will form curves on the surface, and, in the case of the simultaneous variations in the temperature and the pressure, a surface in the $x$–$P$–$T$ space.

It is of interest that the presence of singular points for alcohol solutions was discovered as long ago as by D.I. Mendeleev [4]. At the same time, the discussion in the literature concerning the nature of the low-concentration peak continues till now. Ideas were put forward that this peak is associated with the presence of microbubbles [5] or non-controllable impurities [6].

This work aimed at establishing the dependence of the low-concentration peak coordinate $x^0$ for the aqueous solution of alcohols on the molecular mass of alcohols. Experimental researches [7] were carried out on an installation, whose schematic diagram is shown in Fig. 1. Light emitted by source *1* (a helium-neon laser LGN-215) was directed with the help of system of collimators *2* onto specimen *3* located in a cylindrical cuvette. The cuvette was placed in thermostat *4*, whose temperature was stabilized to an error of ±0.1 °C. Light scattered at an angle of 90° was registered with the help of photoelectronic multiplier *5* (FEU-79) with an optical system allowing one to select the scattering volume and with PC-based electronic system *6* to calculate photopulses. Reference beam system *7* allowed the scattered light intensity to be measured with the compensation of the thermal and time drifts of the equipment.

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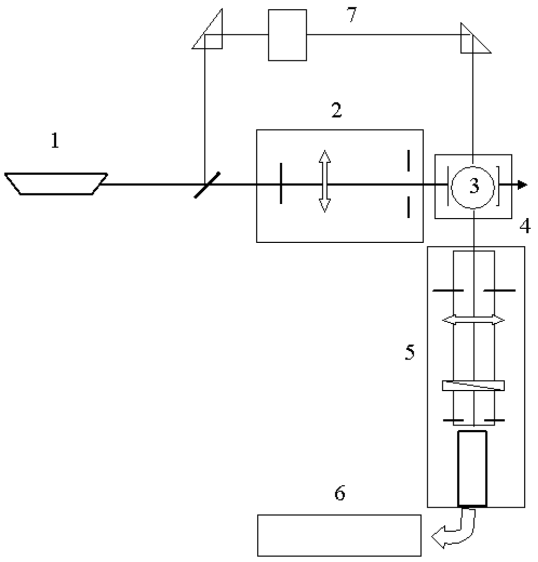

***Fig. 1.*** Schematic diagram of the installation: (*1*) light source LGN-215, (*2*) system of collimators, (*3*) specimen, (*4*) thermostat, (*5*) photodetecting unit with a photomultiplier FEU-79 operating in the single-photon regime, (*6*) PC-based registration system, (*7*) reference beam system

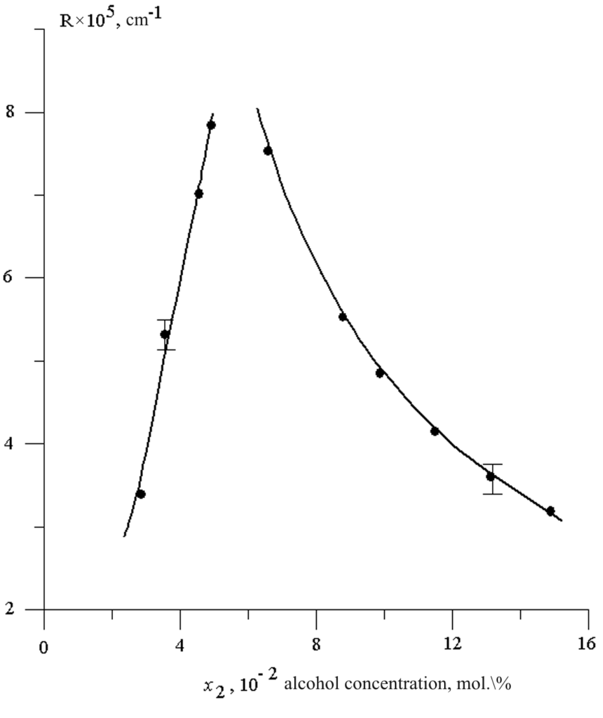

***Fig. 2.*** Light scattering coefficient for the system water–ethylene glycol at a temperature of 20 °C as a function of the alcohol molar concentration in the solution

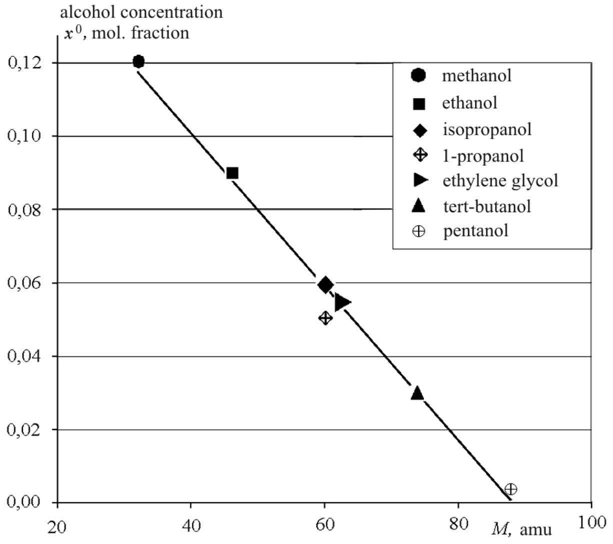

***Fig. 3.*** Dependence of the coordinate $x^0$ of the singular point for alcohol solutions on the molecular mass of dissolved alcohols: methanol [8], ethanol [1,9], isopropanol [10], tert-butanol [1,2,11], and pentanol. Points near the curve center correspond to the isomers: 1-propanol and isopropanol. All the temperatures are close to 20 °C

In order to determine the coefficient of light scattering by solutions, the installation was calibrated. For this purpose, we used benzene, for which the coefficient of light scattering is known to equal $R_\mathrm{B} = 8.2 \times 10^{-6}$ cm$^{-1}$ [1] and which is the most referenced substance. The coefficient of light scattering by the solutions was determined using the formula

$$R_x = R_\mathrm{B} \frac{I_x I_{0\mathrm{B}}}{I_{0x} I_\mathrm{B}},$$

where $I_x$, $I_{0x}$, $I_\mathrm{B}$, and $I_{0\mathrm{B}}$ are the intensities of scattered light and the reference beam (subscript 0) by the solution (subscript $x$) and benzene (subscript B).

In Fig. 2, the dependence of the light scattering coefficient for the solution water –ethylene glycol on the molar concentration of alcohol is plotted. The corresponding analysis shows that the maximum value of light scattering intensity in the solution water–ethylene glycol is observed at the molar concentration of alcohol $x^0 = 0.055$.

In order to illustrate the variation of concentration $x^0$ as the molecular masses of dissolved alcohols change, we analyzed the literature data taken from works [1, 2, 8–11] and compared them with our results. In Fig. 3, the obtained dependence of the singular point coordinate $x^0$ for the solutions of alcohols from the homologous series of methanol on the molecular mass of a dissolved alcohol is depicted. One can see that the experimental points fall well on a straight line. The processing of experimental data using the least-squares method enabled us to describe this dependence with an error less than 2% by the formula

$$x^0 = 0.002(88 - M),$$

where $M$ is the molecular mass of the corresponding alcohol.

Hence, in our opinion, the revealed linear relation between the concentration coordinate of singular points in the solutions of alcohols from the homologous series of methanol and the molecular masses of the corresponding alcohols proves that the low-concentration peak on the light scattering curve is associated neither with impurities in the series of mutually independent experiments nor with the influence of nanobubbles on the light scattering. Really, it is difficult to imagine a situation when identical conditions for the emergence of nanobubbles would be created in different experiments, or when the solutions of different alcohols in those experiments would contain the same impurities at the same concentrations.

In our opinion, the issue of whether the coordinates of singular points for alcohol solutions will coincide if they are determined by analyzing various physical properties, e.g., acoustic, thermal, and rheological ones, remains open. Nevertheless, as was shown in work [12], nine of twelve mentioned methods for the determination of singular point parameters in aqueous solutions of alcohols give identical coordinates for the position of the low-concentration light scattering maximum. The following issue also remains open: What is the form of curves circumscribed by the singular points in the three-dimensional thermodynamic space when the thermodynamic parameters vary? To answer this question, a series of experiments on molecular light scattering in the indicated solutions with the varying temperature and pressure has to be done.

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1. M.F. Vuks, *Light Scattering in Gases, Liquids, and Solutions* (Leningrad State Univ., Leningrad, 1977) (in Russian).
2. G.W. Beer and D.J. Jolly, Opt. Commun. **11**, 150 (1974).
3. M.A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, Philadelphia, 1991).
4. D.I. Mendeleev, *Solutions* (Izd. Akad. Nauk SSSR, Moscow, 1956) (in Russian).
5. N.F. Bunkin and F.V. Bunkin, Zh. Eksp. Teor. Fiz. **101**, 512 (1992).
6. D. Subramanian and M.A. Anisimov, J. Phys. Chem. B **115**, 9179 (2011).
7. V.E. Chechko and V.G. Zaremba, Khim. Fiz. **12**, 1036 (1993).
8. G.P. Roshchina and A.S. Kaurova, Ukr. Fiz. Zh. **9**, 512 (1964).
9. H. Tonaka, K. Nakanishi, and H. Tonhara, J. Chem. Phys. **81**, 4065 (1983).
10. M.F. Vuks, L.I. Lisnyanskii, and L.V. Shurupova, in *Structure and Role of Water in a Living Organism* (Leningrad State Univ., Leningrad, 1968), Issue 2, p. 39 (in Russian).
11. M.F. Vuks and L.V. Shurupova, Zh. Strukt. Khim. **12**, 712 (1971).
12. V.M. Byakov, L.V. Lanshina, O.P. Stepanova, and S.V. Stepanov, Zh. Fiz. Khim. **83**, 280 (2009).

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## РОЗСІЯННЯ СВІТЛА ВОДНИМИ РОЗЧИНАМИ СПИРТІВ ПОБЛИЗУ ЇХ ОСОБЛИВИХ ТОЧОК

Резюме

Робота присвячена встановленню залежності положення низькоконцентраційного піка розсіяння світла водними розчинами спиртів $x^0$ мольної частки спирту від їх молекулярної маси. Знайдена відповідна концентрація особливої точки $x^0$ для етиленгліколю при 20 °C і порівняна з літературними даними для гомологічного ряду метанол. Отримана залежність є лінійною з похибкою <2%.