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THE ORIGIN OF LIGHT SCATTERING BY AQUEOUS SOLUTIONS OF ALCOHOLS IN VICINITIES OF THEIR SINGULAR POINTS

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The physical nature of the anomalous peak observed in a vicinity of the singular point in molecular light scattering spectra of diluted aqueous alcohol solutions is analyzed. The singular point corresponds to an unstable state of the solution, in which water molecules are distributed in monolayers around the alcohol molecules. In a vicinity of the singular point, the solution is shown to become inhomogeneous on nano- and mesoscales. Spatial inhomogeneities are formed by two phases, which are similar by their properties, and the phases transitions between them have a fluctuation character. The process of slow establishment of the equilibrium state in aqueous alcohol solutions (for days and longer) is explained by the similarity of thermodynamic properties of those phases. Using the dynamic light scattering, it is shown that if the solution in the equilibrium state is mechanically excited, the character of relaxation has a periodic component, which corresponds to the transitions between the indicated phases. The summation of two peaks associated with independent light scattering in two mesophases makes the anomalous peak of light scattering asymmetric.

Keywords: aqueous alcohol solutions, singular point, equilibrium state, fluctuations.

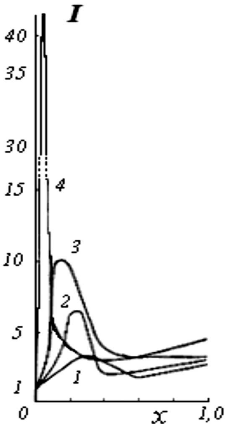
1. Introduction

Molecular scattering of light has been applied to study substances for more than hundred years. Nevertheless, the observation of an anomalous growth of the integrated intensity of molecular light scattering in diluted aqueous alcohol solutions turned out absolutely unexpected fifty years ago (Fig. 1). Such a character of the perception of this phenomenon was associated with the facts that, first, the diluted solutions were considered to possess no unexpected properties and, second – it was found out later – the result substantially depends on a set of circumstances, which were supposed by researchers to be accidental. The latter manifested itself in that experiments carried out with the same solutions in different laboratories gave rise to considerably different results.

For instance, in the works by Vuks *et al.* [1–3], the integrated intensity of light scattering in the aqueous solution of tertiary butyl alcohol was found to be an order of magnitude larger in comparison with the value calculated in the framework of the thermodynamic approach. At the same time, in the work by Beer and Jolly [4], it grew by two to three orders of magnitude for the same solution and under the same experimental conditions.

The reason for such a situation became clearer in the 1990s. As was demonstrated in works [5, 6], the character of molecular light scattering in aqueous solutions of glycerol and ethylene glycol depends on the time interval that separates the measurement moment from the solution preparation moment. Moreover, the experimental results were reliably reproduced only in several days after the preparation of a solution. This circumstance provoked an assumption that the discrepancy among the results of various authors is associated with the fact that, in their experiments, they used solutions which were in the nonequilibrium state.

Note that, in this work, we mean the term "singular points" as such points in the (x, T) phase diagram, where either the absolute maximum of the molecular light scattering intensity is observed at $x < 0.1$ or the concentration dependences of the contraction of solu-



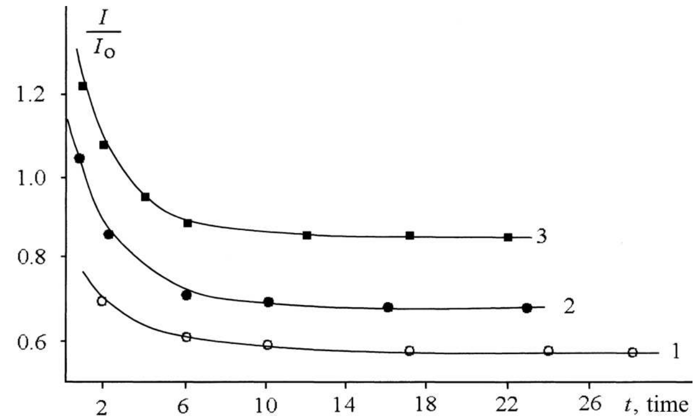


Fig. 1. Concentration dependences of the light scattering intensity in aqueous solutions of methanol (*1*), ethanol (*2*), *n*-propanol (*3*), and tret-butanol (*4*) at a temperature of 20 °C [1]

Fig. 2. Time dependences of the isotropic molecular light scattering intensity in methanol solutions of various salts: 0.15 wt.% NaCl (*1*), 13.8 wt.% NaBr (*2*), and 25 wt.% NaJ (*3*) [18]

tions measured at different temperatures intersect. In addition, singular points also manifest themselves in the heat capacity [7–9], compressibility [10–12], light refractive index [13–15], incoherent scattering of thermal neutrons, vibrational Raman spectra [16,17], and so on.

In this work, we would like, first, to present the experimental evidence for the necessity of studying aqueous solutions only in the equilibrium state and, second, to discuss comprehensively only those aspects of molecular light scattering that manifest themselves in the equilibrium state of solutions. In parallel, we will use the results obtained within the methods of dynamic light scattering and discuss the relation between the results obtained and the behavior of the refractive index in the examined solutions.

2. Peculiarities of Equilibrium Establishment in Water–Alcohol Solutions

G.P. Roshchina was the first who paid attention to the duration of the equilibrium state establishment in alcohol solutions; it amounts to several weeks. In work [18], the dependence of the integrated intensity of molecular light scattering in methanol and ethanol electrolyte solutions, which according to L.A. Bulavin's classification [19, 20] belong to ionic solutions, on the time interval between the solution preparation moment and the measurement moment was studied (see Fig. 2).

The same phenomenon was also observed by Eskin and Nesterov [21]. In the cited work, the anomalous light scattering in a diluted solution water–tret-butanol was studied. It was shown that the temperature dependences of the integrated intensity of molecular light scattering as the solution was heated up to a certain temperature and, afterward, cooled down to the initial temperature did not coincide with each other, so that a hysteresis phenomenon took place. Moreover, in the further heating–cooling cycles, those dependences were not only different from one another, but also from previous dependences. Only after a long enough time interval, those dependences started to reproduce each other (Fig. 3), and the hysteresis phenomenon disappeared. In work [7], the irreproducibility of the experimental results on molecular light scattering was hypothetically associated with the influence of nonequilibrium states of a solution.

The processes of equilibrium state establishment in aqueous solutions of glycerol and ethylene glycol were purposefully studied in works [6, 22]. In particular, in work [22], the behavior of the integrated intensities of polarized and depolarized light scattering in water–glycerol solutions was studied; the thermodynamic properties of those solutions were studied in work [23]. In Fig. 4, a typical behavior of the intensities for depolarized, $I_V^H(t)$, and polarized, $I_V^V(t)$, light scattering at the initial stages of equilibrium state establishment are depicted for a water-glycerol solution

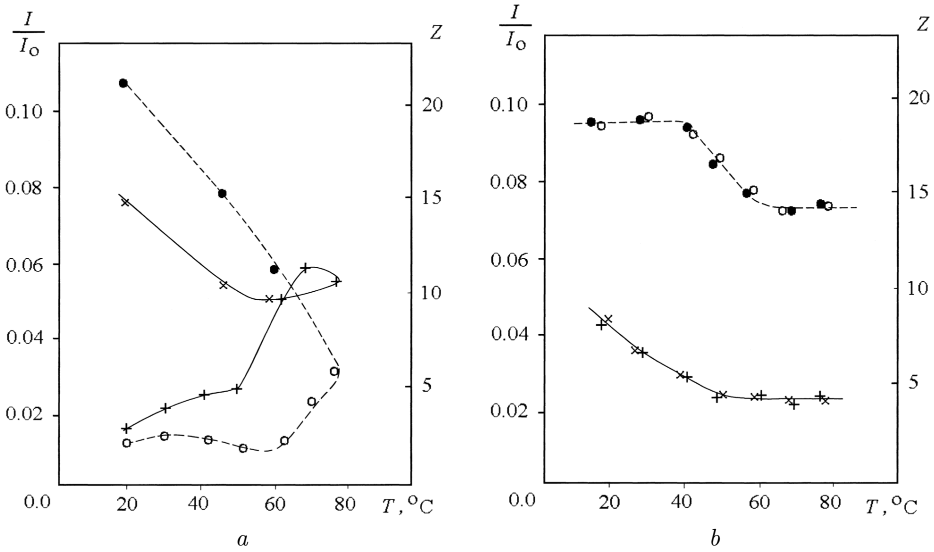


Fig. 3. Temperature dependences of the intensity I_{90° (solid curve) and the parameter of angular scattering asymmetry $Z = I_{45^\circ}/I_{135^\circ}$ (dashed curve) in the aqueous solution of tret-butanol (3 mol.% of alcohol) at its heating (○, Δ) and cooling (●, ▲) [21] (*a*). The same as in panel *a*, but for several heating–cooling cycles (*b*). Different symbols correspond to different series of measurements [21]

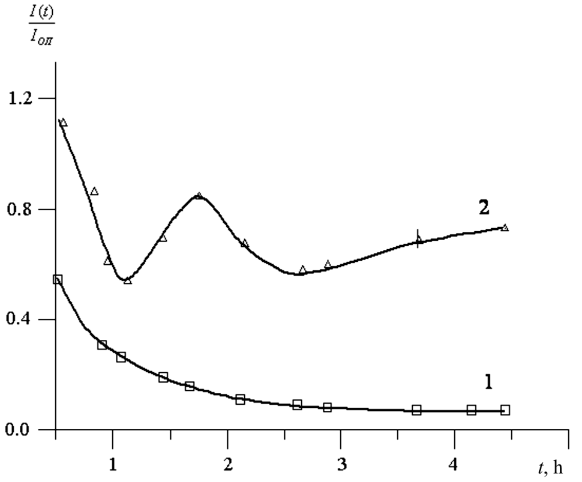


Fig. 4. Intensities of light scattering in aqueous glycerol solutions at a temperature of 10 °C [22]: anisotropic scattering I_V^H (*1*) and isotropic scattering I_V^V (*2*). The solution concentration (0.046 molar fraction) corresponds to a vicinity of the point, at which the intensity of anomalous light scattering is maximal

with a concentration corresponding to the anomalous light scattering, $x^{(p)}\,(gl) = 0.046$, and at a temperature of 10°C. In contrast to Roshchina's experiments with methanol electrolyte solutions [18], the polarized (isotropic) light scattering in the aqueous solutions of glycerol changes more substantially [22]. It was emphasized that one may say about the formation of regularities in the behavior of the intensities of polarized and depolarized light scattering only 20–30 min after the preparation of a solution, and a constant value of scattering intensity is established after a time interval of about a day. Probably, the absence of the initial stage of about 2 h in the plots taken from work [18] is a result of analogous reasons.

A substantial deviation of the molecular light scattering intensity at the initial stage is not absolutely chaotic [22]. It was found (see curve 2 in Fig. 4) that the deviation from the averaged intensity values has an oscillatory character.

Additional information concerning the establishment of a stationary state in the solution in a vicinity of the singular point can be obtained by studying the angular anisotropy of the molecular light scattering intensity. By definition, the anisotropy degree is the ratio $Z = I_{45^\circ}/I_{135^\circ}$, where I_{45° and I_{135° are the light intensities scattered at the angles of 45° and 135°, respectively. The time dependences of Z for water–glycerol solutions are exhibited in Fig. 5.

If the scattering in aqueous solutions of alcohols were a Rayleigh one, the parameter Z would be equal to 1. However, one can see that the anisotropy degree is close to 1 only for as-prepared solutions. Later, their anisotropy grew, oscillated, and finally, after the equilibrium had been established, turned out different from the Rayleigh value $Z = 1$. The emergence of such an anisotropy is characteristic of a vicinity of the stratification critical point, where a micro-sized inhomogeneous structure is formed as a result of large-scale concentration [24] or density fluctuations in single-component systems. From whence, it follows that, soon after their preparation, the water–alcohol solutions with alcohol concentrations corresponding to a vicinity of the singular point $x^{(p)}$ became micro-inhomogeneous and remained unchanged even after the establishment of an equilibrium state in them. If the concentration of alcohol considerably differs from $x^{(p)}$, the anisotropy degree of the scattered light intensity is close to 1, i.e. a large-scale micro-inhomogeneous structure does not arise, and the equilibrium is established much more rapidly. The character of inhomogeneities will be discussed in Section 4 in more details. Note that the parameter Z was used for the first time to study the properties of the water–tret-butanol system in works [21, 25].

To summarize the section, we may assert that the establishment of an equilibrium state in water–alcohol solutions occurs within a time interval that varies from one day to one week depending on the alcohol type. In particular, this time interval is about a day for the water–glycerol solution [6], and a week or even longer for the water–ethanol one. If the initial state of the solution is equilibrium, its mechanical and thermal perturbations relax following different laws.

3. Relaxation of Solutions in the Equilibrium State

We studied the character of relaxation in perturbed aqueous ethanol solutions. Researches of such states were carried out within a week after the preparation of a solution. The corresponding structures of a solution were calculated earlier in works [26, 27]. The excited solution states can be created by means of a mechanical or caloric perturbation of the solution in equilibrium. We suppose that the character of relaxation in such states does not depend on the way of their perturbation, which is natural from the viewpoint of the theory of thermal hydrodynamic fluctuations [28, 29] and finds its application in the theory of molecular light scattering [30, 31].

Relaxation in the excited solutions was studied within the laser correlation spectroscopy method.

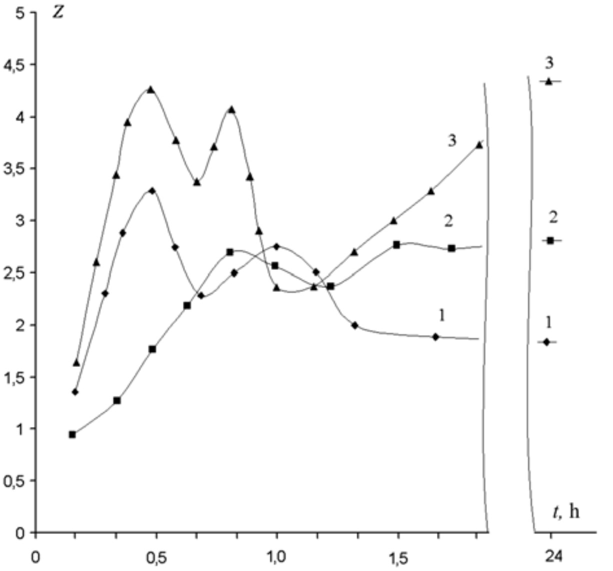


Fig. 5. Angular asymmetry of the scattered light intensity as a function of the time passed after the preparation of aqueous glycerol solutions with various molar fractions x, using the ultrasonic mixing [22]: $x = 0.047$ (*1*), 0.035 (*2*), and 0.056 (*3*). The temperature is 10 °C

The specific features of a correlatometer in use were described in work [32]. In Fig. 6, the bold curve demonstrates the dependence of the correlation time for the scattered light intensity, τ_{c}, on the time interval passed since the preparation of a solution. It was obtained by fitting the experimental data with a sixth-order polynomial in the framework of the least-squares method. One can see that, within the first 24-h interval, τ_{c} oscillates with a characteristic period of 5 h. The deviation of the correlation time from the average value $\langle\tau_{\mathrm{c}}\rangle = 25$ ms amounted to 5 ms. Next day, the period of oscillations became twice as large. In a week, the amplitude of deviations became comparable with the measurement error, which corresponded to the establishment of an equilibrium state in the solution. We should additionally note that the average correlation time $\langle\tau_{\mathrm{c}}\rangle$ in the equilibrium state gradually grew from 25 to 45 ms.

The establishment of the equilibrium state is accompanied by processes resulting in a deviation of the obtained correlation times from the approximating dependence. Those deviations are considered as accidental. In due course, they considerably diminish. For instance, for the data shown in Fig. 6, *a*, the average value was $\langle\tau_{\mathrm{c}}\rangle = 25$ ms and the root-mean-

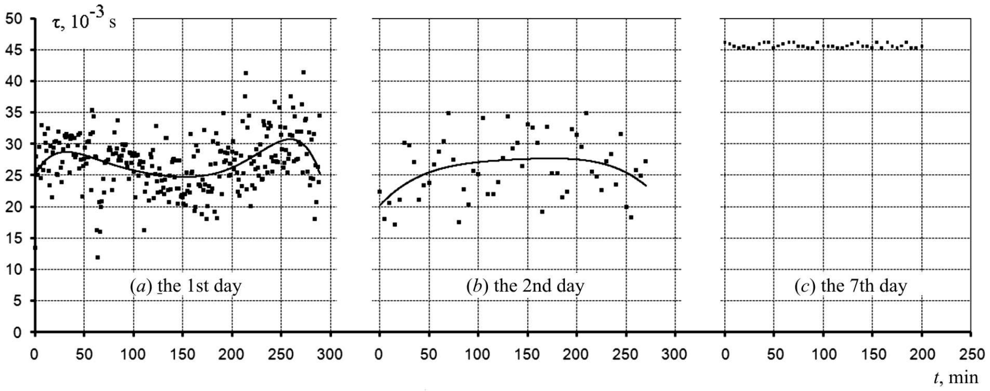


Fig. 6. Dependences of the scattered light intensity correlation time on the time interval passed after the preparation of an aqueous solution of ethanol. The concentration of ethanol (0.095 molar fraction) corresponds to the anomalous light scattering at 22°. The exposition time equals 15 min for every point in the plot

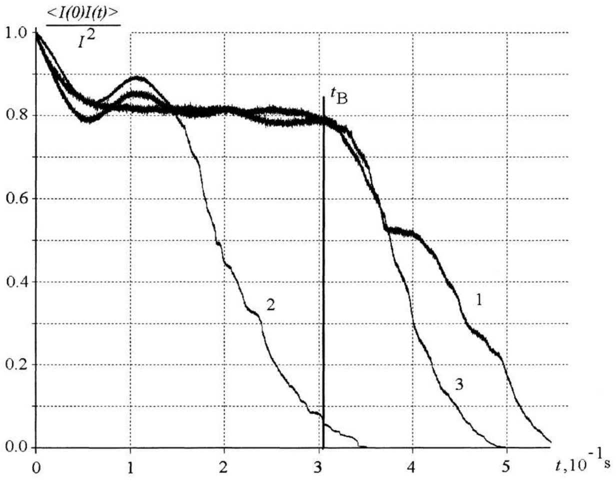


Fig. 7. Time dependences of the scattered light intensity correlation functions for the mechanically perturbed water–ethanol solution with an alcohol concentration of 0.095 molar fraction: in the equilibrium state (*1*), in 1 min after the perturbation (*2*), and in 5 min after the excitation (*3*)

square deviation $\sigma = \sqrt{D(\tau_c)} = 4.3$ ms or 17%. After the 24-h interval (see Fig. 6, *b*), the corresponding values amounted to $\tau_c = 27$ ms and $\sigma = 3.8$ ms or 14%. In a week (Fig. 6, *c*), accidental deviations from the average value were practically absent: $\tau_c = 45$ ms and $\sigma = 0.33$ ms or 0.7%.

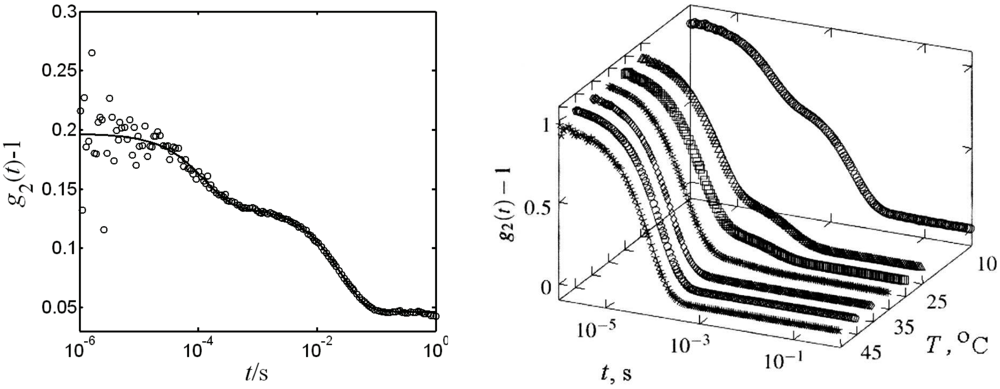
The analysis (Fig. 7) testifies that, when the equilibrium state is excited, there emerge new components in the relaxation process. Curve *1* corresponds to the light scattering in the nonperturbed solution. Curves *2* and *3* correspond to the correlation functions of the scattered light intensity in the solutions 1 min (curve *2*) and 5 min (curve *3*) after their perturbation. From works [33–35], it is known that the correlation function of the scattered light intensity, which changes following the harmonic law with a stochastic deviation of the frequency in a vicinity of the fundamental harmonic, looks like

$$g^{(2)}(\tau) = a + c\exp(-\gamma\tau)\cos(2\pi\nu\tau), \tag{1}$$

where the parameter γ is determined by the set of frequencies, and a and c are constants. The fundamental harmonic is associated with the dominating oscillation process occurring in the system. As will be shown below, there are transitions between two states of the system, which are close by parameters, but the cluster orderings in which are a little different. In both cases, the fundamental frequency equals $\nu \sim 10$ Hz.

Note that, after the solution has been excited, the scattered light intensity changes owing to the scattering by thermal fluctuations in the equilibrium state (the corresponding characteristic time of the intensity correlation is of an order of 10 ms) and the scattering by spatial inhomogeneities formed as a result of a mechanical or thermal perturbation of the solution (their characteristic time is determined as $1/\nu \sim 0.1$ s). The simultaneous action of both indicated factors gives rise to the correlation function

$$g^{(2)}(\tau) = a + \left[b\exp\left(-2\frac{\tau}{\tau_c}\right) + c\exp(-\gamma\tau)\cos(2\pi\nu\tau)\right]. \tag{2}$$



a *b*

Fig. 8. Temporal correlation function of the light intensity scattered at the angle $\theta = 3°$ (hollow circles) for the aqueous solution to tret-butanol with an alcohol concentration of 0.083 molar fraction at $T = 22.8$ °C (*a*). The solid curve approximates the data by formula (3). The exponential contributions correspond to the molecular diffusion with $D = 1.5 \times 10^{-6}$ cm^2/s and mesodiffusion with $D = 4.2 \times 10^{-9}$ cm^2/s [36]. Normalized autocorrelation functions for the scattered light intensity obtained for the ternary solution 3-methylpyridine–D$_2$O–NaBPh$_4$ at a scattering angle of 90° (*b*). The concentration of 3-methylpyridine is 0.0755 molar fraction, and the concentration of NaBPh$_4$ salt is 7.07 mmol/l [38]

The first term in the brackets corresponds to thermal fluctuations.

The same structure of the correlation function $g^{(2)}(t)$ was observed in works [36–39] devoted to the research of the dynamic light scattering in water–tret-butanol solutions at $x = 0.083$ (see Fig. 8). Note that the anomalous peak of light scattering in those solutions is observed at the different concentration, $x^{(p)} = 0.03$ [2–4]. The basic result of work [38] consists in that the time dependence of the function $g^{(2)}(t)$ has a simple exponential form at $T > 35$ °C, whereas two exponential contributions are observed at $T < 35$ °C:

$$g^{(2)}(\tau) = a + \left[b \exp\left(-2\frac{\tau}{\tau_1}\right) + c \exp\left(-\frac{\tau}{\tau_2}\right)\right]. \tag{3}$$

Numerically, the relaxation times are different from each other by three orders of magnitude: $\tau_1 \sim 10^{-5}$ s and $\tau_2 \sim 10^{-2}$ s. This formula practically coincides with Eq. (2) if the fundamental frequency is close to zero.

4. Main Properties of Anomalous Light Scattering Peak Parameters

A shortcoming that is inherent to the majority of works dealing with the molecular light scattering in a vicinity of the singular point in aqueous alcohol solutions, as well as in similar ones, is the fact that only one of the molecular light scattering parameters was analyzed. On the contrary, the following important parameters were studied in work [40] for the aqueous solutions of ethylene glycol and glycerol: the integrated intensity of molecular light scattering as a function of the temperature and the concentration, angular dependence of the scattered intensity, polarization, and correlation times of long- and short-term relaxation processes.

In Fig. 9, the dependences of the light scattering coefficient R in water–ethylene glycol solutions at $T = 20$ °C on the molar fraction of the dissolved component are depicted [5]. In work [5], the attention was paid for the first time to that the shape of the anomalous peak of light scattering in aqueous solutions is considerably asymmetric. Unfortunately, this important circumstance was overlooked in previous publications.

An interesting result was obtained in work [41] for the dependence of the position of the anomalous light scattering peak on the molecular mass of alcohols in aqueous alcohol solutions. The corresponding illustration is shown in Fig. 10. Experimental data obtained by various authors correspond to the same temperature and are well fitted by a straight line. Using the least-squares method, it was found that this dependence can be described by the empirical formula

$$x^{(p)} = 0.002(88 - M), \tag{4}$$

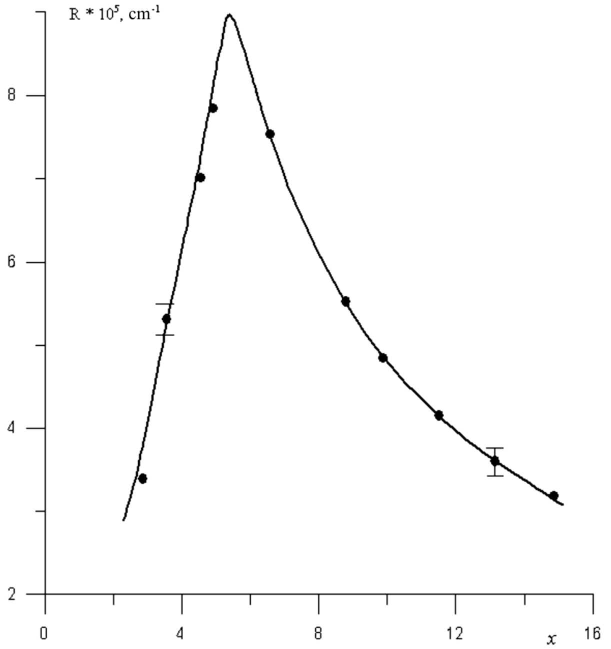


Fig. 9. Dependence of the scattering coefficient for the aqueous ethylene glycol solution on the molar fraction of the dissolved component at $T = 20^\circ$ [5]

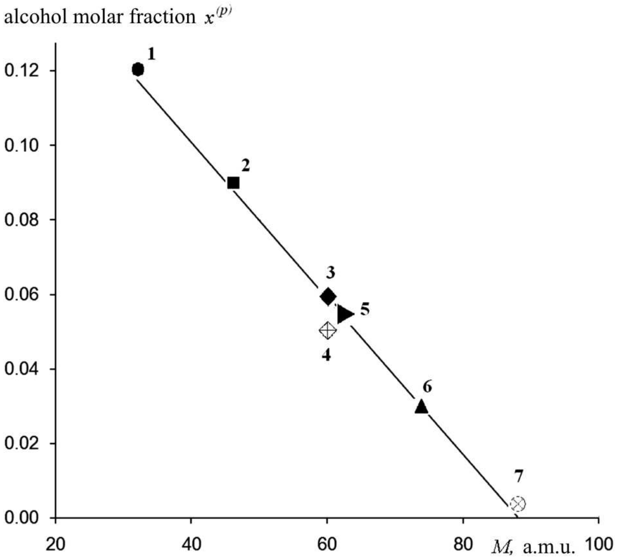


Fig. 10. Dependence of the singular point coordinate $x^{(p)}$ on the molecular mass of a dissolved alcohol: methanol (*1*) [18], ethanol (*2*) [30, 42], isopropanol (*3*) [43], *n*-propanol (*4*) [3], ethylene glycol (*5*) [5], tret-butanol (*6*) [3,4], and pentanol (*7*)

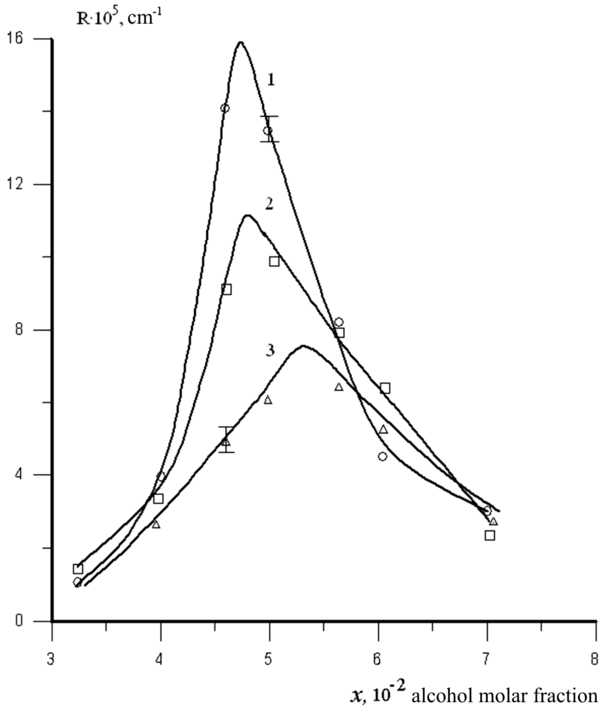


Fig. 11. Concentration dependences of the light scattering coefficient, $R(x)$, for aqueous glycerol solutions at various temperatures $T = 3$ (*1*), 5 (*2*), and 10° (*3*) [45]

where M is the molecular mass of alcohol, with an error less than 2%. This dependence testifies that the emergence of the anomalous light scattering peak is associated neither with admixtures [7,30] nor with the influence of nanobubbles [44], because those factors generate an irregular behavior of the peak position.

In Fig. 11, the concentration dependences of the light scattering coefficient, $R(x)$, are shown for water–glycerol solutions measured at various temperatures $T = 3$ (curve *1*), *5* (curve *2*), and 10 °C (curve *3*). One can see that the peak height decreases with the temperature growth, and the peak itself shifts toward high concentrations. The same behavior is also typical of aqueous tret-butanol solutions [30]. If the scattering occurred at concentration fluctuations, the height of the scattered light peak would grow with the temperature. This is a basis to call this peak as the peak of anomalous light scattering.

In Fig. 12, the coefficient of light scattering R as a function of the solution temperature is depicted for various solution concentrations [40]. In the cited work, the specimens were cooled down to the crystallization temperature. The maximum of the coefficient R was observed for the solution with the glycerol molar fraction $x^{(p)} = 0.046$ at a temperature of 3 °C (curve *4*). For the solutions with other concentrations, the positions of the light scattering maximum were shifted toward higher temperatures (curves *5* and *6*), whereas the corresponding R-values decreased.

Hence, in the case of aqueous glycerol solutions, we may assert that the maximum positions of the anomalous light scattering intensity depend on the temperature, and this scattering can be observed only in a narrow interval of alcohol molar concentrations $0.03 < x < 0.06$. Outside of this interval, the properties of a solution are described in the framework of the standard fluctuation theory.

An important circumstance, which has been overlooked for a long time, is the asymmetry of anomalous light scattering peaks (see Fig. 1). The parameters of these peaks, namely, their height and width, as well as the asymmetry degree, are exhibited in Fig. 13 as functions of the molecular masses of alcohols. The asymmetry degree /A is defined as the ratio $\Delta x_r/\Delta x_l$, where Δx_r and Δx_l are the shoulders of the peak width Δx_P reckoned from the peak height H_P. Note that the ratio $A/\Delta x_P$ reproduces the dependence of H_P on the molecular masses of alcohols.

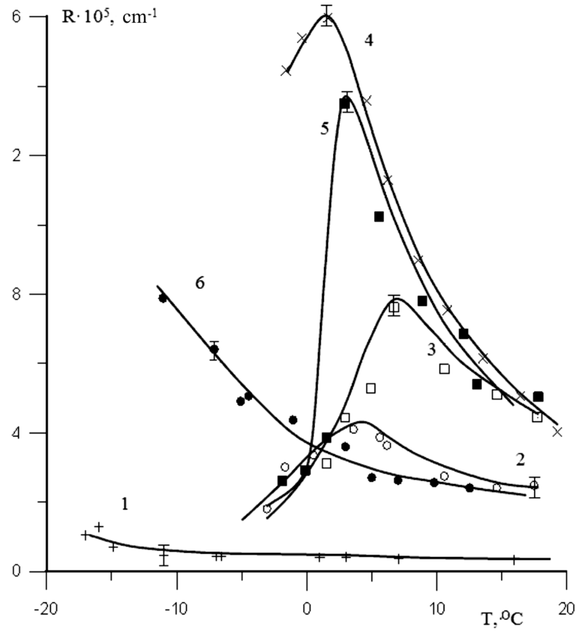


Fig. 12. Temperature dependences of the light scattering coefficient for aqueous glycerol solutions at various glycerol concentrations: 0.032 (*1*), 0.037 (*2*), 0.040 (*3*), 0.046 (*4*), 0.052 (*5*), and 0.070 mol;ar fraction (*6*) [40]

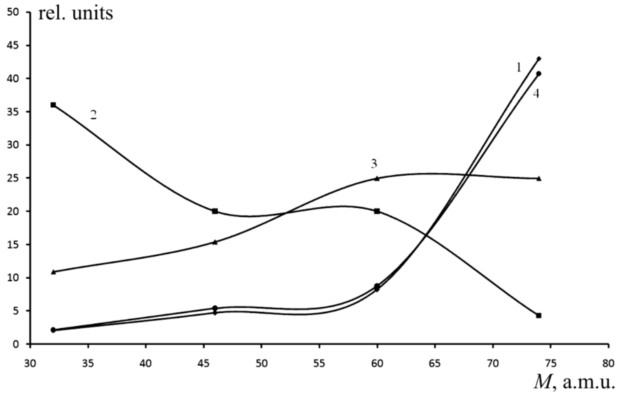


Fig. 13. Dependences of the parameters of the low-concentration peak of light scattering in the aqueous solutions of alcohols from the homologous series of methanol on the alcohol atomic mass [1]: the peak height H_P (*1*), the peak width Δx_P (*2*), the asymmetry degree $A = \Delta x_r/\Delta x_l$ (*3*), where Δx_r and Δx_l are the peak width shoulders Δx_P, and the ratio between the asymmetry degree and the width (*4*)

5. Anomalous Growth of Molecular Light Scattering Intensity in Diluted Solutions. Qualitative Model

Our results together with available literature data allow a conclusion to be drawn that the aqueous solutions of alcohols have a micro-sized inhomogeneous structure in vicinities of their singular points. This conclusion is based on the following facts.

1. The behavior of the integrated intensities of polarized and depolarized molecular light scatterings. In particular, it follows from Fig. 4 that those components of the molecular light scattering are essentially different. Namely, the depolarized light scattering smoothly diminishes as the solution approaches the equilibrium state, whereas the polarized component of the light scattering intensity grows and tends to its equilibrium value in an oscillatory manner. In our opinion, this fact testifies to the emergence of nano- and mesoscopic spatial inhomogeneities in the system, which are, to some extent, similar to nuclei of a new phase.

2. The behavior and the numerical values of angular anisotropy coefficient Z for the integrated intensity of the molecular light scattering (Fig. 5). In the as-prepared solution, the parameter Z is close to 1, which is typical of spatially homogeneous systems. The value of Z grows and oscillates in the course of time. Such a behavior is possible only pro-

vided the emergence of spatial inhomogeneities (nuclei of a new phase) in the system. The average size of those inhomogeneities was evaluated with the help of the Debye formula [46, 47]

$$r^2 = \frac{3\lambda^2}{8\pi^2}(Z-1), \tag{5}$$

where λ is the wavelength of scattered light, and the value of Z was approximated by the ratio $Z = I_{45^\circ}/I_{135^\circ}$. The concentration dependence of the characteristic inhomogeneity size is actaully governed by the behavior of Z (see Fig. 5). With an acceptable accuracy, it is possible to put $r \approx \sqrt{Z/5}\lambda$, i.e. the size of inhomogeneities in the aqueous solution of glycerol reaches half the wavelength of scattered light [40]. According to the results of works [7, 21], the size of inhomogeneities in the aqueous solution of tret-butanol is considerably larger: $r \approx \lambda$.

3. The behavior of the refractive index of the aqueous ethanol solution (see work [15]). In the cited work, it was shown that the monotonic concentration dependence of the refractive index is violated in a narrow concentration interval near the singular point $x^{(p)} = 0.08$. To be more accurate, within the concentration intervals $0.06 < x \leq 0.08$ and $0.08 < x < 0.1$, the corresponding deviations look like small peaks, which points to the formation of either inhomogeneities (nuclei of a new phase) of two types or two close states of the system. Transitions between the latter occur owing to thermal fluctuations.

4. Outside of a narrow concentration interval ($0.06 < x < 0.1$ for ethanol), the examined solution remains microhomogeneous and demonstrates a behavior that can be described in the framework of the standard thermodynamic approach.

5. The instability of the system at the concentration $x^{(p)}$ is a result of the characteristic distribution of water molecules [48]. At the singular point of the solution, water molecules are arranged in monolayers around ethanol molecules. The entropy of the system is minimum at that, so that the system tries to pass into another state with a higher entropy.

6. The formation of two states in the system is also confirmed by the results of researches concerning the turbidity of an aqueous ethanol solution (see work [15]). In particular, 16 specimens of the aqueous ethanol solution with concentrations varied in the interval $0.045 < x \leqslant 0.15$ were prepared simultaneously. The solution with the ethanol molar fraction $x = 0.1$ was found to be the most turbid at the beginning of the experiment. After holding the specimens for a week, the situation changed drastically. The specimens with the concentrations $x_1 = 0.065$ and $x_2 = 0.95$, which are "symmetric" with respect to $x^{(p)} = 0.08$, turned out the most turbid. No further redistribution of turbidity was observed.

7. In some sense, similar conclusions were made in work [49] for the aqueous solution of n-propanol. Using the methods of positron spectroscopy and light absorption by solvated electrons, the authors of the cited work drew conclusion that nanobubbles of alcohol are formed in the solution within the concentration interval $0.1 < x < 0.3$. However, this result can hardly be regarded as ultimate, because there is no consistent theory for the interaction of positrons and solvated electrons with water.

Hence, there emerge two states in vicinities of the singular points of solutions (at least, the aqueous ethanol solution). Those states are more stable in comparison with the homogeneous solution. The close similarity of the properties of those states means that nuclei with the structure of one state are formed in the other state and *vice versa*. Transitions between the states occur owing to thermal fluctuations. The mechanical or thermal perturbation of such a system results in the appearance of a damped periodic process, which can be registered using the correlation spectroscopy methods. From this viewpoint, the frequency ν and the damping factor γ in formula (2) should be considered as parameters of this periodic process.

Another phenomenon, which the model concerned can explain, is the asymmetry of the anomalous light scattering peak. We associate the appearance of asymmetry with the fact that thermal fluctuations in each of those states generate a peak in the scattered light intensity. The resulting peak is their sum (see Fig. 14).

Note that the parameters of both states of the system have values that are close to one another in a vicinity of the singular point. Therefore, the transition from one state into another one can be characterized both from the viewpoint of the mentioned nucleation model and with the help of a simple diffusion mechanism, as was done in works [33–36].

First, let us consider some results obtained, while applying the diffusion approach to the analysis of properties of an aqueous glycerol solution [6]. In this case, the correlation function of the scattering light intensity is approximated by the formula

$$G^{(2)}(\tau) = \frac{\langle I(0)I(\tau)\rangle}{\langle I^2\rangle} =$$

$$= a + b\exp(-2Dq^2\tau) = a + b\left|\exp\left(-2\frac{\tau}{\tau_\mathrm{c}}\right)\right|^2, \tag{6}$$

where $q = \frac{4\pi n}{\lambda_0}\sin\frac{\theta}{2}$ is the absolute value of scattering wave vector, θ the scattering angle, and n the refractive index of the solution. We suppose that the diffusion coefficient is described by the Einstein formula $D = \frac{kT}{6\pi\eta r}$. From whence, it follows that the characteristic size of spatial inhomogeneities satisfies the equation [49]

$$r = \frac{8\pi n^2 \sin^2\left(\frac{\theta}{2}\right) k_\mathrm{B} T \tau_\mathrm{c}}{3\eta\lambda_0^2}, \tag{7}$$

where η is the dynamic viscosity coefficient of the solution. The diffusion coefficient and the relaxation time are related by the formula $D = \frac{1}{\tau_\mathrm{c} q^2}$. The time dependence of the characteristic inhomogeneity size is depicted in Fig. 15. Note that the plotted curves correspond to a temperature of 20 °C, which is considerably higher in comparison with a temperature of 3 °C, at which the anomalous light scattering in aqueous glycerol solutions has an absolute maximum.

The duration of the equilibrium state establishment, which is determined in the framework of the diffusion mechanism model, completely coincides with the value calculated from the behavior of the integrated scattered light intensity. At the same time, the typical size of spatial inhomogeneities is an order of magnitude smaller than that predicted by the Debye formula. This discrepancy of results can be explained by the fact that the Debye formula was applied to the curves obtained in a temperature interval from 3 to 10 °C, whereas the radius of optical inhomogeneities shown in Fig. 15 corresponds to a temperature of 20 °C. As one can see from Fig. 15, the inhomogeneity sizes gradually increase in time from the values typical of elementary clusters [45], which arise in the as-prepared solution, to a characteristic size of nano-nuclei available in the equilibrium state. The closer the concentration of a solution to that at the singular point, the larger is the size of nuclei.

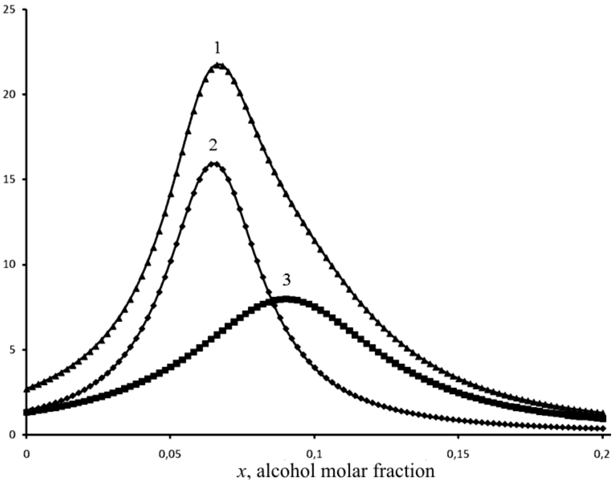


Fig. 14. Resolution of the asymmetric light scattering peak (*1*) into two symmetric partial components (*2* and *3*) corresponding to two different thermodynamic states of the solution

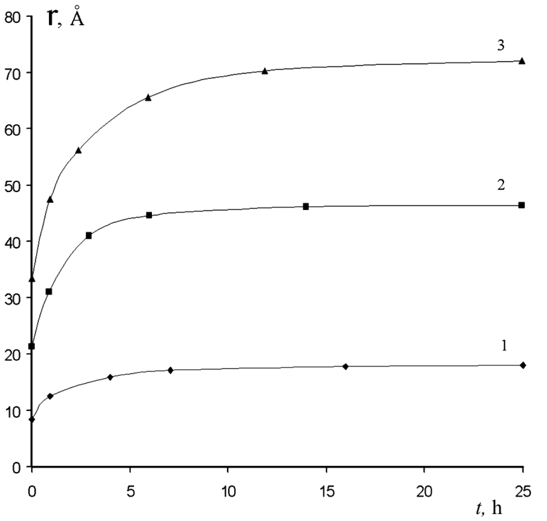


Fig. 15. Dependences of the sizes of optical inhomogeneities in water–glycerol solutions on the time interval passed after the preparation of a solution at a temperature 20° for various molar fractions of glycerol: 0.031 (*1*), 0.055 (*2*), and 0.048 molar fraction (*3*). The sizes were calculated by formula (7) [6]

Experimental results on molecular light scattering in the aqueous solution of tret-butanol, which were reported in work [38], encompassed a broader temperature interval. In particular, it was shown that the correlation functions of the scattered light intensity can be approximated by exponential dependences of the form (1) at temperatures $T > T^*$, where $T^* = 30$ °C (this value is close to the characteristic water temperature [51–53]), and by the sum of two exponential functions at $T < T^*$. The corresponding diffusion coefficients for those exponential contributions equal

$$D/(\mathrm{cm}^2/\mathrm{c}) \sim \begin{cases} 10^{-5}, & T > T^*, \\ 10^{-9}, & T < T^*. \end{cases}$$

Hence, light is scattered by a weakly clustered medium at $T > T^*$ and by a medium with meso-sized inhomogeneities at $T < T^*$, which agrees well with the scenario of the new phase nucleation in aqueous solutions of tret-butanol.

6. Conclusions

The main result of the work consists in proving the existence of inhomogeneous structure in aqueous alcohol solutions, when the latter are in the equilibrium state. It is shown that these nano- and meso-sized inhomogeneities are formed only at alcohol concentrations close to that at the singular point of a solution, $x^{(p)}$. The aqueous alcohol solution with concentration $x^{(p)}$ is found to be thermodynamically unstable and decaying into two states with similar physical properties. The spatial distribution of those states is governed by the appearance of nuclei with a new structure in the solution. Each of those states makes its contribution to the molecular light scattering. As a consequence, the peak of the anomalous light scattering, which is a sum of those contributions, becomes asymmetric.

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ПРИРОДА РОЗСІЯННЯ СВІТЛА ВОДНИМИ РОЗЧИНАМИ СПИРТІВ В ОКОЛІ ЇХ ОСОБЛИВИХ ТОЧОК

Резюме

Робота присвячена дослідженню фізичної природи аномального піка молекулярного розсіяння світла, який спостерігається в околі особливої точки розбавлених водних розчинів спиртів. Зазначено, що особлива точка відповідає нестійкому стану розчину, в якому молекули води розподілені у моношарах навколо молекул спирту. Показано, що в околі особливої точки розчин стає мікронеоднорідним на нано- та мезомасштабах. Просторові неоднорідності утворюються двома близькими за властивостями фазами, переходи між якими мають флуктуаційний характер. Процес повільного встановлення рівноважного стану водноспиртових розчинів (доба та більше) пояснюється близькістю термодинамічних властивостей цих фаз. За допомогою динамічного розсіяння світла показано, що при механічному збудженні рівноважного стану характер релаксації має періодичну складову, яка відповідає переходам між зазначеними фазами. Складання двох піків, які відповідають незалежному розсіянню світла на обох мезомасштабних фазах, приводить до асиметрії аномального піка розсіяння світла.