
L.A. BULAVIN,¹ V.YA. GOTSULSKIY,¹ V.E. CHECHKO²¹ Taras Shevchenko National University of Kyiv, Faculty of Physics

(4, Academician Glushkov Ave., Kyiv 03127, Ukraine; e-mail: vygot@onu.edu.ua)

² I.I. Mechnikov National University of Odesa, Scientific and Research Institute of Physics

(27, Pasteur Str., Odesa, Ukraine)

PECULIARITIES IN THE ESTABLISHMENT OF EQUILIBRIUM STATE IN DILUTED AQUEOUS SOLUTIONS OF GLYCEROL

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The dynamics of the thermodynamic equilibrium establishment in the aqueous solutions of alcohols in a vicinity of specific points is studied on the basis of dilute aqueous solutions of glycerol. At the molar fractions of alcohol $x \sim 0.05$, the systems concerned reveal characteristic anomalies testifying to the presence of structural phase transitions. However, the unreliable reproducibility of anomalous light scattering, a phenomenon typical of aqueous alcohol solutions, makes this conclusion debatable. In this work, it was shown that the parameters of aqueous glycerol solutions, which are determined with the help of light scattering phenomenon, become stable only in a certain time interval after the solution preparation. The typical dimensions of optical non-uniformities, the coefficients of scattered light depolarization, and the asymmetry of scattering indicatrix have been found as functions of the time elapsed since the solution preparation.

Key words: anomalous light scattering, dilute alcohol aqueous solutions, glycerol, thermodynamic equilibrium.

1. Introduction

The concept of special points for solutions was introduced for the first time by D.I. Mendeleev, while analyzing the concentration dependences of the ethanol aqueous solution density [1]. In particular, a special point was found at low concentrations of the ethyl alcohol solution in water, which corresponds to the alcohol mole fraction $x^{(p)} = 0.077$ (i.e., 1 molecule of C_2H_5OH per 12 molecules of H_2O). One of the examined parameters of binary solutions is the so-called contraction, which is defined by the relation

$$\varphi(x, T) = \frac{V_{12}}{V_1 + V_2} - 1, \quad (1)$$

where V_1 and V_2 are the initial volumes of solution components, V_{12} is the solution volume, x the molar fraction of alcohol in the solution, and T the temperature. In works [2, 3], it was shown that the contraction curves corresponding to various temperatures in the interval from -5 to $+40$ °C intersect at the concentration $x = x^{(p)}$, which is just the special point determined by D.I. Mendeleev.

The available body of information in the literature contains plenty of mismatching data concerning the properties of aqueous solutions of other alcohols, in which the anomalous scattering of light was or was not revealed in a vicinity of alcohol concentrations lower than 0.1 mol/l [4–28]. Numerous researches showed that the features of light scattering in alcohol aqueous solutions depend not only on the experimental conditions, but also on the procedure of solution preparation. For instance, Vuks *et al.* [24]

observed an extra peak at low alcohol concentrations in the concentration dependence of light scattering, with the vacuum distillation of tret-butyl alcohol in water being used for the preparation of the specimen. Beer and Jolly [28] detected a similar maximum at low concentrations of tret-butyl alcohol in water only after the solution had been heated up to $+70\text{ }^{\circ}\text{C}$, with the indicated peaks of different intensities being observed depending on the purity of solution components. Note that some authors did not reveal any additional maximum in the concentration dependence of the scattered light intensity. For instance, when reproducing the procedure of solution preparation described in work [28] by Vuks' collaborators, the expected phenomenon has not been observed [25].

Such an ambiguous reproducibility of experimental results invoked some scepticism among researchers with respect to this effect. Note, however, that experimenters paid almost no attention to the procedure of specimen preparation in the majority of studies. In work [4], it was demonstrated that the procedure of solution preparation affected not only the intensity of the additional light scattering peak, but even the capability of its observation. Roschina [29] showed that the coefficient of light scattering in alcohol solutions after their preparation can monotonously decrease by a factor of 2 to 5 within several days under certain experimental conditions.

In work [26], the temperature dependences of the light scattering coefficient and the scattering indicatrix asymmetry in the aqueous solutions of tertiary butanol were determined. It was shown that the parameters of light scattering in as-prepared solutions did not coincide at the same temperature if the solutions were heated up or cooled down. The indicated dependences became reproducible only after several "heating-cooling" cycles. Unfortunately, neither the rate of temperature variation nor the number of required cycles were reported in that work.

In works [4, 24, 28], the extra peaks in the concentration dependences of the light scattering intensity were detected after a long heating of the solution. The cited authors associated them with the formation of submicronic non-uniformities in the solution. This conclusion affected the discussion of results obtained in the works carried out

within several next years. In particular, in work [30], the methods of dynamic light scattering were used to determine the correlation times at anomalous light scattering in aqueous solutions of tret-butanol. The correlation functions were shown to be characterized by two correlation times, which are different from each other by two or three orders of magnitude ($\tau_1 = 6.5 \times 10^{-5}\text{ s}$ and $\tau_2 = 2 \times 10^{-2}\text{ s}$). After the solution had been filtered out at low temperatures, large non-uniformities disappeared.

The asymmetry of a light scattering indicatrix, which results from optical non-uniformities, whose size is comparable with the incident radiation wavelength, was observed in the aqueous solutions of other non-electrolytes as well [26, 31]. The corresponding dimensions of optical non-uniformities determined with the help of correlation spectroscopy methods amounted to about 80 \AA . The authors of works [31–33] paid attention that, irrespective of the specimen preparation procedure, the anomalous light scattering is stabilized after a certain time interval, which in terms of phase transition physics can be called the latent period τ_{lat} [34]. This characteristic time considerably exceeds the characteristic molecular times and can be compared only with the dwell time of supersaturated solutions in the metastable state [35]. Note that, in the case where a new phase is formed, the parameter τ_{lat} varies from about 1 h to about 1 year depending on experimental conditions. At the same time, in our case, the period of thermodynamic stabilization amounted to about 24 h and more.

This work aimed at studying the processes of thermodynamic equilibrium establishment in glycerol aqueous solutions. For this purpose, the following characteristics were studied:

- (1) the characteristic times of processes and the characteristic dimensions of optical non-uniformities in the aqueous solutions of glycerol with the use of dynamic light scattering;
- (2) the time dependences of the scattered light depolarization coefficient in the prepared solutions;
- (3) the time dependences of the angular asymmetry of the light scattering indicatrix in glycerol aqueous solutions;
- (4) the influence of the homogenization degree in a glycerol aqueous solution on the processes of equilibrium state establishment.

2. Experimental Results

By carrying out the experiment on the dynamic light scattering [36, 37] in glycerol aqueous solutions, we studied the behavior of the correlation function for the light scattering intensity,

$$g^{(2)}(\tau) = \frac{\langle I(0)I(\tau) \rangle}{\langle I^2 \rangle} = 1 + \exp(-2Dq^2\tau) = 1 + \left| \exp\left(-\frac{\tau}{\tau_C}\right) \right|^2, \quad (2)$$

where D is the diffusion coefficient, $q = \frac{4\pi n}{\lambda_0} \sin \frac{\Theta}{2}$ is the scattering wave vector, Θ the scattering angle, λ the incident radiation wavelength, and n the refractive index of the solution. Then, using the formula [36]

$$r = \frac{8\pi n^2 \sin^2\left(\frac{\Theta}{2}\right) k_B T \tau_C}{3\eta \lambda_0^2}, \quad (3)$$

where η is the coefficient of dynamic viscosity, $\tau_C = \frac{1}{Dq^2}$ is the correlation time obtained from Eq. (2), k_B is the Boltzmann constant, and T the solution temperature, we determined the characteristic size of optical non-uniformities.

In Fig. 1, the dependences of the dimensions of optical non-uniformities in the aqueous solutions of glycerol as functions of the time elapsed since the solution preparation moment are depicted, which were determined with the use of dynamic light scattering. One can see that, at the glycerol concentration in the solution $x = 0.048$, which is close to that, at which the additional peak at the light scattering is revealed, an abnormal increase in the dimensions of optical non-uniformities is observed. In particular, the dimensions of optical non-uniformities grow in time, and, after ten hours, they are stabilized in all examined solutions.

We also studied the variation dynamics for another optical characteristic of the solutions, namely, the coefficient of scattered light depolarization, $\Delta = I_V^H/I_V^V$. In work [26], as well as in our experiments, the light scattering intensity was changed considerably during some time interval after the solution components had been mixed. In this connection, in our further experiments, we did not analyze the depolarized, I_V^H , and polarized, I_V^V , components of the integral scattered light intensity within an hour after

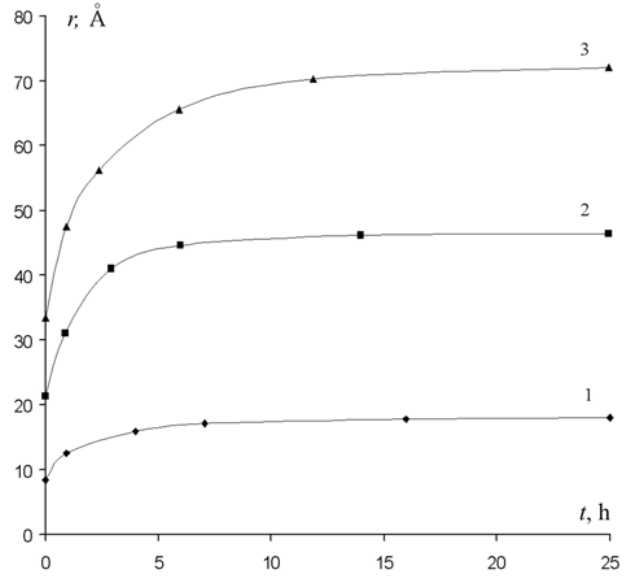


Fig. 1. Dependences of the optical non-uniformity dimensions in aqueous solutions of glycerol on the time elapsed since the solution preparation at a temperature of 20 °C for various molar fractions of glycerol $x = 0.031$ (1), 0.055 (2), and 0.048 (3). The non-uniformity sizes were calculated using Eq. (2)

the specimen preparation. Note that work [39] contains no optical data for a time period of 2 h after the specimen preparation.

The obtained dependences of the scattered light depolarization coefficient in the glycerol aqueous solutions on the time elapsed since their preparation are exhibited in Fig. 2. It should be noted that the solution concentration, at which the coefficient of light depolarization is maximum, does not coincide with the concentration, at which the anomalous light scattering is maximum. Really, at a temperature of 10 °C, the maximum of the depolarization coefficient $\Delta = I_V^H/I_V^V$ is observed at the mole fraction of glycerol in the solution $x = 0.035$, whereas the maximum of the anomalous light scattering occurs at the concentration $x^{(p)} = 0.046$.

From Fig. 2, it is evident that, if the mole fraction of glycerol in the water-glycerol system is low, the equilibrium state is attained slowly. The stable value of depolarization coefficient was reached in about ten hours after the solution had been prepared. Solid curves in Fig. 2 demonstrate the results of experimental data smoothing. Although the spread of intensity values is considerable, we shall demonstrate below that it reveals certain regularities. The

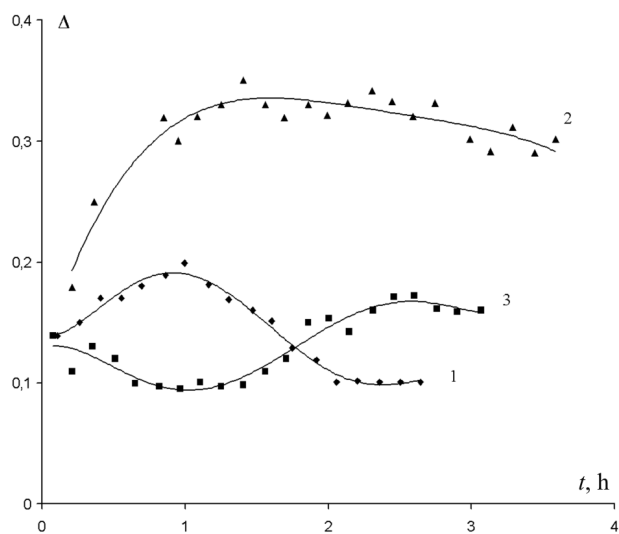


Fig. 2. Dependences of the scattered light depolarization coefficient in an aqueous solution of glycerol on the time elapsed since the solution preparation at a temperature of 10 °C for various molar fractions of glycerol in the solution: $x = 0.031$ (1), 0.035 (2), and 0.046 (3). Solid curves demonstrate the results of the mathematical smoothing of the data. Curve 3 corresponds to the anomalous light scattering

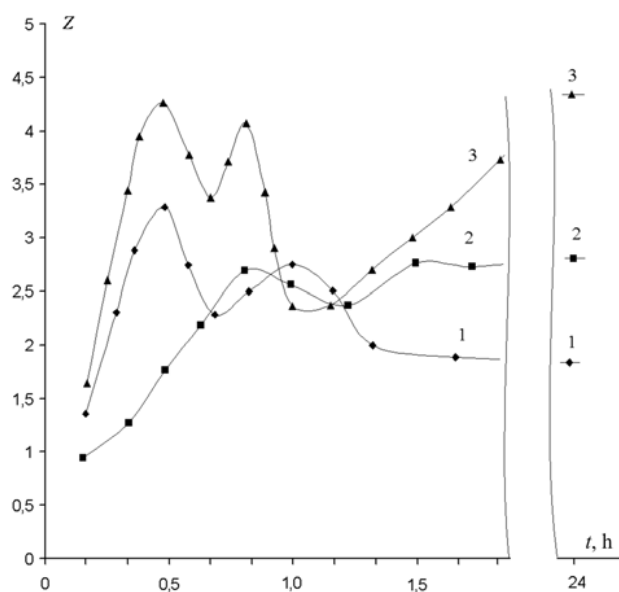


Fig. 3. Angular asymmetry of the light scattering indicatrix as a function of the time elapsed since the preparation of glycerol aqueous solutions by the ultrasonic mixing for various molar fractions of glycerol in the solution: $x = 0.047$ (1), 0.035 (2), and 0.056 (3)

figure also testifies that, if the experiment is carried out after a substantial time interval and a subsequent averaging is done, some processes can be overlooked and the experiment errors can be overestimated.

It should be noted that the determination of non-uniformity dimensions using formula 2 can turn out incorrect, to some extent. Really, if the scattering occurs at structural fluctuations in the solution, it is not quite correct to estimate the size of non-uniformities as the size of Brownian particles, which is typical of the dynamic light scattering method. It is so because, in this case, the correlation time can be governed by the lifetime of such fluctuations.

As was done in work [26], in order to estimate the time of the stationary state establishment in the solution in a vicinity of the special point, we used the Debye theory [38], which was proposed for the description of critical phenomena in the solutions of low-molecular liquids and polymers. When approaching the critical stratification temperature, the light scattering has to be accompanied by an angular asymmetry of the scattering indicatrix, which can be evaluated with the help of the parameter $Z = I_{45^\circ}/I_{135^\circ}$, where I_{45° and I_{135° are the intensities of light scattered at angles of 45° and 135°, respectively. The applicability of the Debye theory, while studying the anomalous light scattering, was proved in work [26].

The values obtained for the coefficients of light scattering angular asymmetry in the concentration interval of the anomalous light scattering really showed that the growth of the scattering intensity is connected with the transformation of the Rayleigh scattering to the scattering with the angular indicatrix strongly elongated forward. Since it was earlier demonstrated that the transition of the solutions into the thermodynamic equilibrium state is rather long, we measured the angular asymmetry of the light scattering, $Z = I_{45^\circ}/I_{135^\circ}$, as a function of the time t elapsed since the solution preparation. In Fig. 3, the corresponding dependences are shown for three aqueous solutions of glycerol with different concentrations in vicinities of their special points.

The calculation of the characteristic size L of light scatterers at the angles of 45° and 135° carried out, following the method of work [38], gave rise to a maximum non-uniformity size of about 400 nm. This value

is comparable with the radiation wavelength of a He–Ne laser (632.8 nm) used in our experiment.

The constant value of parameter Z was established within 24 h. In Fig. 3, those equilibrium values are shown by points to the right from the discontinuities of curves. The analysis of this figure shows that, at the first stage after the solution preparation, the angular asymmetry of the scattering indicatrix substantially depends on both the solution concentration and the time t . However, every curve demonstrates maxima, the magnitudes and time positions of which are different. In our opinion, such a complicated behavior of $Z(t)$ can be explained as a manifestation of the diffusion mixing processes, which take place after the dispersion of the solution at its preparation. Therefore, we made additional experiments to study the time dependences of the light scattering parameters at various methods of solution dispersion.

3. Influence of Solution Homogenization on the Processes of Equilibrium Establishment

When preparing the solutions, we used both the ordinary mechanical mixing and the ultrasonic dispersion. For the ultrasonic-assisted mixing, an UP-1 apparatus with a frequency of 40 kHz and a power of 200 W was used. When dispersing, hermetically sealed specimens were embedded into a water bath in the working chamber of a device, arranged there at the standing-wave antinode, and held for 2 min. The degree of solution dispersion was monitored with the help of a similar chamber filled with a two-phase water–oil mixture. Two minutes of the ultrasonic treatment turned out enough for both the direct and inverse water–oil emulsions with non-uniformity dimensions of $1\ \mu\text{m}$ to be formed in the reference specimen. The dispersion sizes were monitored using the dynamic light scattering [36, 37].

Irrespective of the method used to mix the solution components, the optical parameters of the anomalous light scattering in glycerol aqueous solutions measured in about 24 h after their preparation had approximately identical values. In Fig. 4, the time dependences of the depolarization coefficient L for light scattered in the glycerol aqueous solutions at the concentration and the temperature correspond-

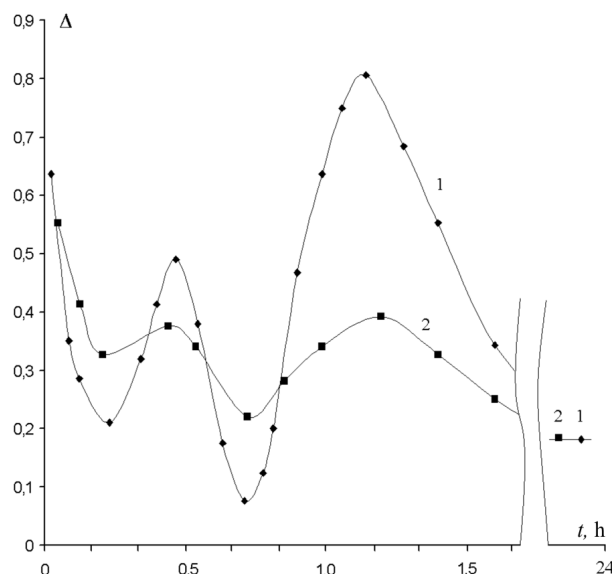


Fig. 4. Time dependences of the scattered light depolarization coefficient in water–glycerol solutions prepared by the ultrasonic dispersion (1) and the mechanical mixing (2). In both cases, the glycerol mole fraction is $x = 0.046$, and the temperature equals $10\ ^\circ\text{C}$

ing to the anomalous light scattering are depicted for various methods of mixing of the specimen. One can see that the oscillatory behavior of $L(t)$, especially at the initial stages of equilibrium establishment, are considerably enhanced in the case of ultrasonic dispersion, with the corresponding size of spatial non-uniformities being equal to approximately $1\ \mu\text{m}$.

In our opinion, the processes of equilibrium state establishment in the solutions in the interval of special points of a solution can be associated with both the diffusion homogenization of solutions and the establishment of structure in the indicated solutions. In the case of the ultrasonic mixing of solution phases, the size spread is much smaller, which is evidently responsible for a sharper shape of curve 1 in comparison with that of curve 2 in Fig. 4. The equilibrium value of parameter L is attained in 24 h both at the ultrasonic and mechanical mixings of the specimen.

4. Conclusions

1. With the help of two optical methods – namely, the dynamic light scattering and the scattered light depo-

larization – the dimensions of optical non-uniformities in glycerol aqueous solutions are determined. It is shown that those dimensions substantially differ from one another. In particular, according to the results of researches of the scattered light angular anisotropy, the characteristic dimension reaches 400 nm, whereas the hydrodynamic radius of optical non-uniformities determined from the results of the dynamic light scattering amounts to 80 nm.

2. Optical non-uniformities and the resulting anomalous light scattering are formed during a long time interval (of an order of 24 h) and do not depend on the homogenization degree of the solution at the initial stage after the preparation.

3. The behavior of the time dependences of the light scattering optical characteristics can be explained by the simultaneous action of several physical processes: the diffusion homogenization of the solution and its structuring on the nano- and, at the anomalous light scattering, submicron scales.

4. The ambiguity in the literature data concerning the optical properties of alcohol aqueous solutions can be explained by rather a long process of thermodynamic equilibrium establishment in the examined solutions.

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Л.А. Булавін, В.Я. Гоцульський, В.Є. Чечко

ОСОБЛИВОСТІ ВСТАНОВЛЕННЯ
РІВНОВАЖНОГО СТАНУ В РОЗБАВЛЕНИХ
ВОДНИХ РОЗЧИНАХ ГЛІЦЕРИНУ

Резюме

Робота присвячена дослідженню динаміки встановлення термодинамічної рівноваги у водних розчинах спиртів в околі особливих точок на прикладі розбавлених водних розчинів гліцерину. При концентраціях $x \sim 0,05$ мольної частки спирту в таких системах виявляються характерні аномалії, що дозволяє говорити про наявність структурних фазових переходів. Проте, недостатня відтворюваність одного з характерних явищ у водних розчинах спиртів, а саме – аномального розсіювання світла, стимулювала численні дискусії. В роботі показано, що параметри водних розчинів гліцерину, які визначаються за допомогою розсіювання світла, набувають сталого значення лише через певний проміжок часу після виготовлення розчину. Знайдені характерні розміри оптичних неоднорідностей, коефіцієнти деполяризації розсіяного світла, асиметрія індикатрисы розсіювання як функції часу, що пройшов після виготовлення розчину.