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**REFRACTOMETRY OF WATER–ETHANOL
SOLUTIONS NEAR THEIR CONTRACTION POINT**PACS 82.60.Lf, 61.20.Lc

The concentration dependences of the refractive index in aqueous ethanol solutions at equilibrium have been studied experimentally. Special attention was paid to their behavior in a vicinity of the peculiar point defined as the intersection point of the concentration dependences of the contraction measured at different temperatures or as a point, at which the intensity of molecular light scattering has a maximum. The refractive index is found to noticeably deviate from its reference values in a vicinity of the peculiar point, $0.05 < x < 0.1$ (x is the mole fraction of ethanol). This effect reflects the fact that the equilibrium properties of the solutions concerned are established only during a few weeks. Arguments that the system becomes microinhomogeneous in this concentration interval are presented.

Keywords: water-alcohol solutions, refractive index, microinhomogeneous structure.

1. Introduction

The analysis of the behavior of the contraction and the molecular light scattering in dilute aqueous alcohol solutions [1–4] showed that, in the interval $0.05 < x < 0.1$ of the alcohol mole fraction x , there emerges a region of special thermodynamic states. In this region, the curves describing the concentration dependences of the contraction at various temperatures intersect at the single, so-called special point. The intensity of molecular light scattering in a vicinity of this point increases by an order of magnitude and even more [5–7]. This fact testifies that the solution becomes unstable in a vicinity of the special point, so that the degree of optical inhomogeneity considerably increases. In works [8–10], it was found that the size of those inhomogeneities varies from 100 to 1000 Å. The assumption about their formation is also supported by arguments presented in works

[2, 4]. Namely, it was shown that the special point of the solution can be associated with the arrangement of water molecules around alcohol ones in the form of monomolecular layers. A solution with such a distribution of molecules has the entropy minimum, which stimulates its transition into the microinhomogeneous state. In other words, in the solution with the homogeneous distribution of water and alcohol molecules, there appear microregions with a slightly different type of the local structure or droplets of a metastable phase [11]. Their existence allows the results of experiments [8–10] and computer calculations [12] to be explained in a natural way.

In this work, the results of the research dealing with the refractive index in the aqueous ethanol solutions are reported. We proceeded from the fact that the refractive index is determined by the polarizabilities of various orders: one-particle, two-particle, and so on. As will be shown below, the account for only low-order contributions results in a regular concentration dependence of the refractive index at various tem-

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peratures. At the same time, if mesoscopic nuclei are formed in the system, the regular character of the concentration dependence of the refractive index has to be violated. As will be demonstrated below, appreciable deviations of the refractive index from its regular dependence are observed just in a vicinity of the special point.

2. Concentration Dependence of the Refractive Index

The refractometry method is traditionally classed to express methods for the analysis of a concentration in solutions, including aqueous ethanol ones [13–15]. Despite that, the available reference data are organized, as a rule, in the form of tables with a concentration step of 0.05 times the mass fraction [14]. Extrapolation dependences for the optical refractive index are also used; for example [16],

$$n_r = 1 + (0.3336 + 0.1239C_1 + 0.081C_2) \frac{\rho}{\rho_W(4^\circ\text{C})}, \quad (1)$$

where C_1 and C_2 are the ethanol and methanol, respectively, mass fractions in a ternary aqueous solution; and ρ and ρ_W are the densities of the solution and water, respectively. Note that formula (1) satisfactorily describes experimental data only at concentrations $x < 0.1$. In a wider concentration interval, the dependence of the refractive index is nonlinear.

Below, the measurements of the refractive index in aqueous ethanol solutions are confined to the concentration interval $0 < x < 0.2$. The refractive index will be designated as n_r , and the particle concentration as n . An aqueous solution of ethanol was studied, which had been stored after the preparation for not less than two weeks. In agreement with the results of work [17], this time interval is required for an equilibrium state to be established in the solution. The procedure of solution storage for a few weeks is important for the aqueous solutions of all alcohols as well. The measurements were carried out on a refractometer IRF-22 with an error of $\pm 2 \times 10^{-4}$.

In Fig. 1, the comparative behavior of the concentration dependences of the refractive index obtained in our measurements (curve 1) and plotted using the reference data [14, 16] (curve 2) at 17 °C is shown. One can see that, at concentrations $0 < x < 0.05$ and $x > 0.1$, our results completely coincide with the reference ones. At the same time, in the concentration intervals $0.05 < x < 0.08$ and

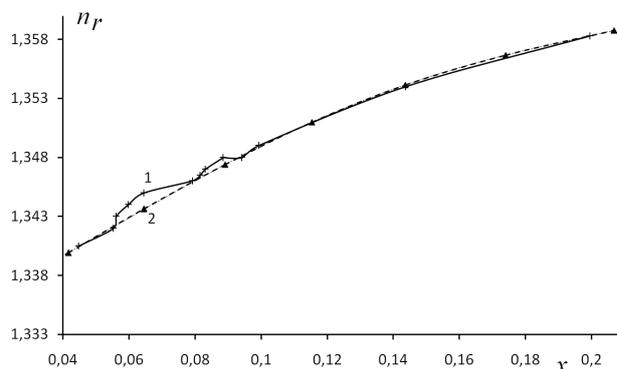


Fig. 1. Dependences of the refractive index in the aqueous ethanol solution on the alcohol mole fraction at 17 °C: (1, crosses) results of our measurements, (2, triangles) reference data [14, 16]. The cross size corresponds to the maximum measurement error

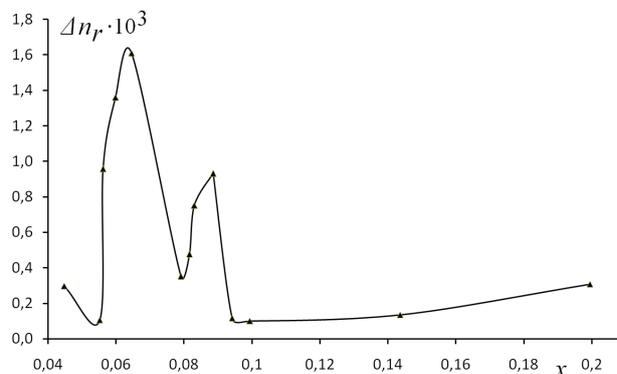


Fig. 2. Difference between the measured values of refractive index in the aqueous ethanol solutions and the reference data in a vicinity of the special point [14, 16]

$0.08 < x < 0.1$, deviations are observed with a magnitude substantially exceeding the measurement error. The character of deviations of the experimental data from the reference ones is illustrated more spectacularly in Fig. 2.

The measurements of the refractive index in solutions that were not stored for a long time revealed the same effect, but the corresponding dependences changed with the time interval passed after the solution preparation. The relevant results will be published elsewhere. It is evident that a non-trivial character of the concentration dependence of the refractive index cannot be explained in the framework of the ideas used for the description of properties of solutions homogeneous on the microscopic scale. This issue will be discussed in the next section.

3. Refraction of Light in Water–Alcohol Solutions

The dielectric permittivity ε of a homogeneous isotropic system is defined by the following general expression:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \frac{P}{E_0}, \quad (2)$$

where P is the component of the polarization vector \mathbf{P} directed along the homogeneous external field strength \mathbf{E}_0 . In homogeneous and isotropic fluids, $\mathbf{P} \parallel \mathbf{E}_0$, and the polarization vector has the structure

$$\mathbf{P} = \frac{1}{V} \left(\langle \overleftrightarrow{\alpha}_N \rangle + \frac{\beta}{3} \langle \mathbf{D}_N^2 \rangle \overleftrightarrow{I} \right) E_0, \quad (3)$$

where $\overleftrightarrow{\alpha}_N$ and \mathbf{D}_N are the polarizability and the dipole moment, respectively, of an N -particle system; V is its volume; $\beta = 1/k_B T$; \overleftrightarrow{I} is an isotropic tensor, and $\langle \dots \rangle$ means the averaging over the positions and orientations of molecules.

In the two-particle approximation, the polarizability of the system is determined by the expression

$$\overleftrightarrow{\alpha}_N = \sum_{i=1}^N \overleftrightarrow{\alpha}_i^{(1)} + \sum_{1 \leq i < j \leq N} \overleftrightarrow{\alpha}_{i,j}^{(2)} + \dots, \quad (4)$$

where the subscripts indicate the polarizability order: one-particle, two-particle, and so forth. Note that Prof. I.Z. Fisher was the first who expanded the polarizability of a system into partial contributions; however, unfortunately, his result has not been published.

The average one-particle contributions are identical and well-known,

$$\langle \overleftrightarrow{\alpha}_i^{(1)} \rangle \Rightarrow \alpha^{(1)} \overleftrightarrow{I}, \quad \alpha^{(1)} = \frac{1}{3} \text{Sp} \overleftrightarrow{\alpha}_1^{(1)}, \quad (5)$$

where Sp means the calculation of the matrix trace. At the same time, the behavior of two-particle contributions was practically not discussed in the literature. Therefore, let us consider, in brief, some of their important properties. The tensor of two-particle polarizability has an especially simple form for noble gases. It is possible to show that, in this case, the following estimate is valid:

$$\frac{1}{3} \text{Sp} \overleftrightarrow{\alpha}_2(r_{12}) \approx 4 \frac{\alpha^3}{r_{12}^6} \frac{1}{1 - \frac{\alpha}{r_{12}^3} - \frac{2\alpha^2}{r_{12}^6}}, \quad (6)$$

where α is the one-particle polarizability. For the distance σ for the direct contact between spherical atoms, we find

$$\frac{1}{3} \frac{\text{Sp} \overleftrightarrow{\alpha}_2(\sigma)}{\alpha^{(1)}} \equiv \frac{\alpha^{(2)}(\sigma)}{\alpha^{(1)}} \approx 0.01. \quad (7)$$

It is easy to see that the average value of two-particle contributions for a homogeneous isotropic system is determined by the expression

$$\begin{aligned} \langle \overleftrightarrow{\alpha}_2(r_{ij}) \rangle &= \langle \overleftrightarrow{\alpha}_2(r_{12}) \rangle = \gamma^{(2)} \overleftrightarrow{I}, \\ \gamma^{(2)} &= \frac{1}{3V} \int \text{Sp} \overleftrightarrow{\alpha}_2(r_{12}) g(r_{12}) d\mathbf{r}_2, \end{aligned} \quad (8)$$

where $g(r_{12})$ is the binary distribution function. According to Eq. (6),

$$\text{Sp} \overleftrightarrow{\alpha}_2(r_{12}) g(r_{12}) = \begin{cases} 0, & r_{12} < \sigma, \\ K/r_{12}^6, & r_{12} > \sigma, \end{cases} \quad K = 4\alpha^3. \quad (9)$$

Therefore,

$$\gamma^{(2)} \approx \frac{1}{V} \frac{4\pi}{3} \sigma^3 \alpha^{(2)}(\sigma). \quad (10)$$

From whence, it follows that, in the two-particle approximation,

$$\langle \overleftrightarrow{\alpha}_N \rangle = \overleftrightarrow{I} V n \left[\alpha^{(1)} + \frac{1}{2} z \alpha^{(2)} + \dots \right], \quad (11)$$

where

$$z = \frac{4\pi}{3} \sigma^3 n \quad (12)$$

is the number of the nearest neighbors. Combining Eqs. (2), (3), and (11), we obtain the following relation for the dielectric permittivity of noble gases $\varepsilon = n_r^2$:

$$\frac{n_r^2 - 1}{n_r^2 + 2} = \frac{4\pi}{3} n \left[\alpha^{(1)} + \frac{1}{2} z \alpha^{(2)} + \dots \right]. \quad (13)$$

The contributions of the electronic polarizabilities of water and alcohol molecules have the same structure and the same order of magnitude.

The contribution generated by fluctuations of the dipole moments of water and alcohol molecules can be presented in the same form. However, with an acceptable accuracy, this contribution can be neglected

at visible light frequencies. Therefore, the refractive indices of pure water and alcohols are described by formulas of type (13).

The role of two-particle contributions to the polarizability turns out considerably smaller in comparison with one-particle ones. At the same time, the former are not small enough to be neglected. For instance, in order to reproduce the experimental values for water refractive index, we have to put $\frac{1}{2}z\alpha^{(2)}(\sigma) \sim \frac{1}{70}\alpha^{(1)}$. Then, at $z = 4$, we obtain the estimate $\alpha^{(2)}(\sigma)/\alpha^{(1)} \approx 0.01$, which practically coincides with estimate (7) (it is accepted that $\alpha_w^{(1)} = 1.45 \text{ \AA}^3$ [14]).

A similar expression can be written for a microhomogeneous mixture of molecules of two kinds,

$$\frac{n_r^2 - 1}{n_r^2 + 2} = \frac{n_r^2(w) - 1}{n_r^2(w) + 2} + \frac{4\pi}{3}n(x) \left[(1-x)\alpha^{(1)} + x\alpha_2^{(1)} + \frac{1}{2}z((1-x)^2\alpha_{11}^{(2)} + 2(1-x)x\alpha_{12}^{(2)} + x^2\alpha_{22}^{(2)}) + \dots \right]. \quad (14)$$

In this case, the concentration dependence of the refractive index has a regular character. At low concentrations and the neglect of two-particle effects, the refractive index is described by the expression

$$\begin{aligned} \frac{n_r^2 - 1}{n_r^2 + 2} &= \frac{n_r(w)^2 - 1}{n_r^2(w) + 2} + \frac{4\pi}{3}xn_w \left[\alpha_a^{(1)} - \alpha_w^{(1)} + \right. \\ &+ \left. \frac{b}{n_w} \left(\alpha_w^{(1)} + \frac{1}{2}z\alpha_w^{(2)} \right) + z(\alpha_{aw}^{(2)} - \alpha_w^{(2)}) \right] + \dots, \quad x \ll 1, \end{aligned} \quad (15)$$

where b is a coefficient defined by the equation $n(x) = n_w + bx + \dots$, and

$$\frac{n_r^2(w) - 1}{n_r^2(w) + 2} = \frac{4\pi}{3}n_w \left[(1-x)\alpha_w^{(1)} + z_w \frac{1}{2}\alpha_w^{(2)} + \dots \right]. \quad (16)$$

At low concentrations, n_r differs from $n_r(w)$ by the small quantity Δn_r , for which we obtain the following equation from Eqs. (11) and (12):

$$\begin{aligned} \Delta n_r(x) &= x \frac{(n_r^2(w) + 2)^2}{6n_r(w)} \left[\left(\frac{b}{n_w} - 1 \right) \frac{n_r^2(w) - 1}{n_r^2(w) + 2} + \right. \\ &+ \left. \frac{n_w}{n_a} \frac{n_r^2(a) - 1}{n_r^2(a) + 2} + z \left(\alpha_{aw}^{(2)} - \frac{1}{2}\alpha_a^{(2)} + \alpha_w^{(2)} \right) \right] + \dots \quad (17) \end{aligned}$$

The concentration dependence of the refractive index n_r in a microhomogeneous solution calculated according to formula (14) or (17) at $x < 0.1$ is shown

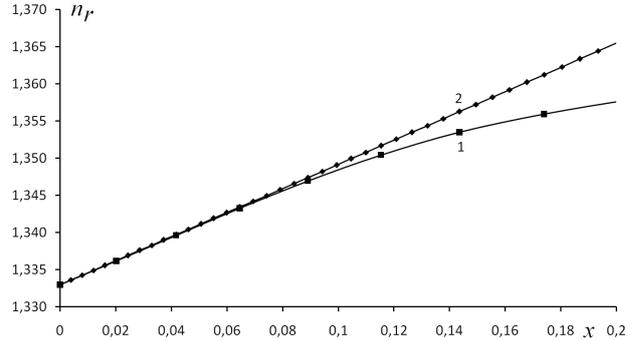


Fig. 3. Dependences of the refractive index n_r in the aqueous ethanol solution on the alcohol mole fraction at 20 °C: tabulated data from work [14] (1), calculation by formula (17) (2)

in Fig. 3. The last term in Eq. (17) gives a contribution less than 0.001 in accordance with the estimations made above. The parameter $b = -6.4 \times 10^{22} \text{ cm}^{-3}$. The comparison with experimental data presented in Fig. 1 brings us to a conclusion that the aqueous solution becomes microinhomogeneous at the concentrations $0.06 < x < 0.1$. More specifically, there emerge mesodroplets, in which the concentration of alcohol molecules differs a little from that in the surrounding solution. The effective refractive index n_{eff} in a microinhomogeneous medium is determined by the formula [19, 20]

$$\frac{n_{\text{eff}}^2(x|s) - n_r^2(x|a)}{n_{\text{eff}}^2(x|s) + 2n_r^2(x|a)} = \frac{n_r^2(d) - n_r^2(x|a)}{n_r^2(d) + 2n_r^2(x|a)}\zeta + \dots, \quad (18)$$

in which $n_r(d)$ and $n_r(x|a)$ are the refractive indices in the new-phase nuclei and in the surrounding solution, respectively; and $\zeta = \frac{V_N}{V}$ is the volume fraction occupied by the nuclei. It should be noted that the nucleation induces a redistribution of alcohol molecules and gives rise to a deviation of the alcohol concentrations from the initial values in both the nuclei and their environment.

Since the properties of nuclei and their environment are close to those of the equilibrium (microhomogeneous) phase, formula (14) can be substantially simplified. Let

$$\begin{aligned} n_{\text{eff}}(x|s) &= n_R(x) + \Delta n_{\text{eff}}(x|s), \\ n_r(d) &= n_R(x) + \Delta n_d(x_2), \\ n_r(x|a) &= n_R(x) + \Delta n_r(x_1), \end{aligned} \quad (19)$$

where $n_R(x)$ is a refractive index value found for the given concentration, by using the approxima-

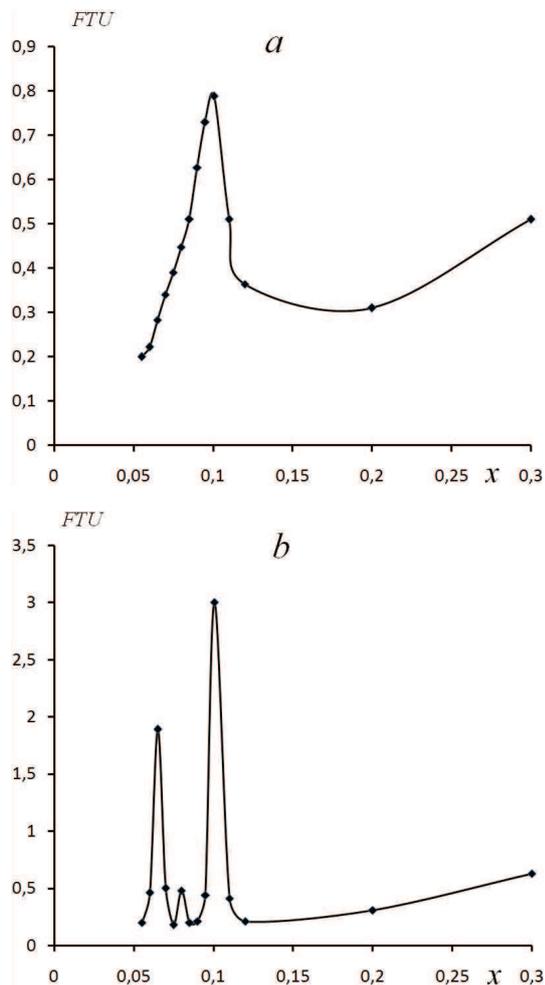


Fig. 4. Dependences of the turbidity of aqueous ethanol solutions on the ethanol mole fraction obtained by the relative method: in a day (a) and in a week after solution preparation (b)

tion curve (1), $\Delta n_{\text{eff}}(x|s)$ is the experimentally determined deviation from $n_R(x)$, $\Delta n_d(x_2) = n_R(x + x_2) - n_R(x)$, and $\Delta n_r(x_1) = n_R(x + x_1) - n_R(x)$. Here, the refractive indices of the solution inside and outside the nuclei are determined by the approximation curve (1) with shifted concentration values (the shift magnitudes x_1 and x_2 depend on x). It is easy to be convinced that $\Delta n_{\text{eff}}(x|s)$ is determined by the equation

$$\Delta n_{\text{eff}}(x|s) = A[x_1(x) + \zeta(x)(x_2(x) - x_1(x))] + \dots, \tag{20}$$

where $A = \frac{dn_r(x)}{dx}$ is a constant at low concentrations.

The complete solution of the problem concerned is rather laborious. It includes the calculation of thermodynamic potentials in the competing phases and the analysis of conditions for their equilibrium at various concentrations. At the same time, the character of solutions, as follows from experimental data, is simple. With the accepted accuracy, the surplus $\Delta n_{\text{eff}}(x|s)$ to the effective refractive index equals zero at the points p_i and q_i ($i = 1, 2, \dots$), and the functions $x_1(x)$, $x_2(x)$, and $\zeta_i(x)$ can be approximated by simple polynomials:

$$\begin{aligned} x_i(x) &= r_i(x - p)(x - q_i), \\ \zeta_i(x) &= s_i(x - p_i)(x - q_i), \end{aligned} \tag{21} \quad i = 1, 2.$$

The values for r_i and s_i can be determined, by using the least-squares method.

It should be noted that, for the conservation law of particle number to be not violated, there must be $r_1 < 0$ and $r_2 > 0$.

4. Discussion of the Obtained Results

Let us compare the experimentally obtained peculiarity in the refractive index behavior with the peculiarities in the intensity of molecular light scattering [21, 22] and the contraction behavior [1–4]. As one can see, the center of the concentration interval, in which the behavior of the refractive index is unusual, coincides with the position of the special point for the aqueous ethanol solution. We recall that this point is defined as the intersection point of curves describing the concentration dependences of the contraction at various temperatures [1] or as a location point of the anomalous maximum in the intensity of molecular light scattering [6]. According to the results of work [4], in a vicinity of the special point, the microhomogeneous state of the solution is thermodynamically unstable and prone to the stratification. At the same time, the microinhomogeneous state, into which the system transits, is close to the microhomogeneous one, so that fluctuation-induced transitions between them take place. The formation of the microinhomogeneous phase is confirmed by the abnormal, but confined, growth of the molecular light scattering intensity. The fluctuation character of the transition is also confirmed by the results of the dynamic light scattering [8–10], which al-

low the size of microinhomogeneities to be estimated (10^3 Å).

Small deviations of the refractive index from its regular values also point to the close proximity of properties in the microhomogeneous and microinhomogeneous phases. However, the results obtained in this work do not allow one to unambiguously determine the relative volume ζ occupied by nuclei, as well as the alcohol concentrations in the nuclei and in their environment. This issue will be studied separately.

We would like to emphasize that the results are reproduced only if the solution has been stored for a long time after its preparation. This circumstance also testifies that the redistribution of alcohol molecules in the solution is not governed by a simple diffusive mechanism, but has a more complicated character associated with the emergence and the destruction of metastable phase nuclei.

The results obtained in this work are also confirmed by nephelometry data, which are depicted in Fig. 4. The initial concentration dependence of the turbidity had a single maximum (Fig. 4, *a*). In two weeks, it is transformed into a number of peaks (Fig. 4, *b*), whose positions completely agree with the positions of regions, where the refractive index of the solution deviated from its reference values.

5. Conclusions

Our experimental researches of aqueous ethanol solutions near the special contraction point confirmed the necessity to store the prepared solution for a long time. The specific feature in the behavior of the refractive index in a vicinity of the special point of aqueous ethanol solutions testifies to the instability of their thermodynamic states. In our opinion, this can be explained by the presence of nuclei of the metastable phase in the solution, whose properties are close to the properties of the homogeneous phase. Similar anomalies in the concentration dependences of the refractive index at various temperatures should be expected in other water–alcohol solutions. The model proposed for the calculation of the refractive index in a vicinity of the special point of aqueous ethanol solutions is based on exact expansions of the N -particle polarization in irreducible one-, two-, three-, etc. particle contributions.

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Received 28.02.15.

Translated from Ukrainian by O.I. Voitenko

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РЕФРАКТОМЕТРІЯ ВОДНИХ
РОЗЧИНІВ ЕТАНОЛУ ПОБЛИЗУ ОСОБЛИВОЇ
ТОЧКИ КОНТРАКЦІЇ

Резюме

Робота присвячена експериментальному дослідженню концентраційної залежності показника заломлення в рівноважних водних розчинах етанолу. Увага приділяється околу

особливої точки, яка визначається як точка перетину кривих концентраційних залежностей контракції при різних температурах або як точка, в якій спостерігається максимум інтенсивності молекулярного розсіяння світла. Показано, що в околі особливої точки $0,05 < x < 0,1$ спостерігається помітне відхилення показника заломлення від його довідкових значень (x – мольна частка етанолу у розчині). Цей ефект відображає той факт, що рівноважні властивості розчинів встановлюються за декілька тижнів. Представлено аргументи на користь того, що при зазначених концентраціях система стає мікронеоднорідною.