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THEORETICAL ANALYSIS OF THE INTENSITY OF ULTRASOUND ABSORPTION IN AQUEOUS ALCOHOLIC SOLUTIONS

Ultrasound absorption in aqueous alcoholic solutions has been studied in the vicinity of their singular points. The abnormal ultrasound absorption is assumed to occur due to the formation of unstable nuclei of a new phase. A model for the time evolution of those nuclei is proposed. The model makes it possible to explain the emergence of the resonance ultrasound absorption in the vicinity of the singular point of the 2-propanol solution. The dependences of the absorption intensity on the nucleus parameters, temperature, and ultrasound frequency are analyzed. A contribution of the ultrasound radiation from the nuclei to the effective shear viscosity of the solutions is estimated. The results of theoretical calculations are compared with available experimental data.

Keywords: ultrasound absorption coefficient, ultrasound absorption maximum, aqueous alcoholic solutions, Lagrange–Rayleigh function, new phase nuclei, interaction with the acoustic field.

1. Introduction

The analysis of the behavior of aqueous alcoholic solutions at relatively low molar alcohol concentrations ($x < 0.1$) revealed a number of anomalous properties in them [1–5, 9, 10, 15, 16]. The latter are observed near the so-called singular points of the solution [1–3]. In particular, an anomalous growth in the intensity of molecular light scattering and the intersection of the contraction concentration dependences measured at different temperatures take place in the aqueous solution of ethanol near the solution concentration $x_s \approx 0.077$ [2]. Furthermore, in work [3], it was shown that the value of the ethanol diffusion coefficient is minimum at the singular point.

Similar peculiarities in the behavior of various physical quantities are also observed at the singular points of other aqueous alcoholic solutions. As a rule, the relevant differences manifest themselves in the magnitude of the corresponding effect that is observed experimentally. It should be noted that such deviations can only be observed in a day after the solution has been prepared [4], which is associated with the formation of mesoscopic inhomogeneities [5–8].

Note that the solution singular points also manifest themselves in ultrasound measurements [9, 10]. For instance, the interaction of an ultrasonic wave with the aqueous solution of 2-propanol was studied in work [10], and it was shown that (i) the curves describing the concentration dependences of the longitudinal sound velocity measured at different temperatures mutually intersect at the solution concentration $x_s \approx 0.03$ and (ii) the ultrasound absorption curves have a pronounced maximum in the vicinity of this singular point. The latter is illustrated in Fig. 1. It should be noted here that the properties of the aqueous solutions of 1- and 2-propanol are similar, because their molecular configurations differ from each other only in the hydroxyl group position.

As one can see from Fig. 1, the maximum in the ultrasound absorption is observed at the solution concentration $x_s \approx 0.1$ and the ultrasound frequency $\omega_0 \approx 0.63 \times 10^8$ s^{-1}. The maximum location practically does not depend on the temperature. It is clear that the origin of the absorption coefficient maximum goes beyond the framework of the classical theory of ultrasound absorption, where the magnitude of the effect is proportional to the shear viscosity of the medium, η, and inversely proportional to the cube of the sound wave propagation velocity in the medium, C: $\alpha_f \sim \eta/C^3$. This behavior of the absorption coefficient is observed only at frequencies $\omega > 4 \times 10^8$ s^{-1} [10, 11].

Each of the concentration dependences for the ultrasound absorption coefficient that are depicted in Fig. 1 can be represented as the sum of two components: one of them corresponds to classical absorption [12, 13] and the other to an additional resonance absorption, which occurs when the system approaches its singular point (see below and works [12, 14]):

$$\alpha = \frac{\omega^2}{2\rho C^3}\left[\frac{4}{3}\eta + \kappa\left(\frac{1}{C_V} - \frac{1}{C_p}\right)\right] + \\ + \frac{\xi\tau\omega^2}{\tau^2\left(\omega_0^2 - \omega^2\right)^2 + \omega^2}, \quad (1)$$

where α is the ultrasound absorption coefficient of the solution, ω the incident wave frequency, ω_0 the characteristic frequency of elastic vibrations in the system, C the velocity of sound propagation in the medium, ρ the medium density, η the shear viscosity of the medium, κ the coefficient of thermal conductivity, ξ a parameter related to the bulk viscosity of the system, τ the relaxation time (in particular, the lifetime of bound water-alcohol molecular complexes), and C_V and C_p are the isochoric and isobaric, respectively, heat capacities of the system. The resonant character of the additional contribution cannot be explained, in principle, from the viewpoint of the classical absorption theory.

Really, in the framework of the classical relaxation theory [13], the addition of small amounts of alcohol can be described by introducing an internal relaxation parameter. This parameter describes the formation of water-alcohol clusters whose properties change in time. The relaxation of this internal parameter results in an additional frequency dispersion of all viscoelastic moduli. But its contribution is not crucial.

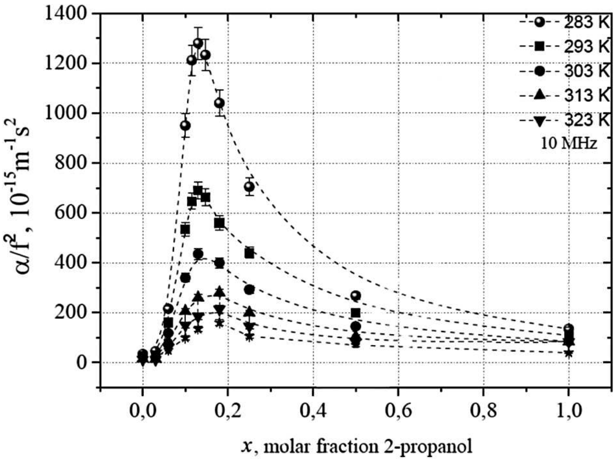

Fig. 1. Concentration dependences of the ultrasound absorption in the aqueous solutions of 2-propanol at the frequency $f \approx 10$ MHz and various temperatures (according to the results of work [10])

At the same time, as was marked in works [1–3, 15], in solutions whose concentrations are close to the corresponding concentration at the singular point, the formation of structures that are inhomogeneous at the micronic level – in other words, unstable nuclei of a new phase – takes place. It is clear that the influence of the nuclei on the system properties cannot be taken into account in the framework of the quasithermodynamic perturbation theory. Instead, it requires a different approach.

In this work, a model of ultrasound absorption owing to radial vibrations of nuclei of the new phase that are formed in aqueous alcoholic solutions is considered. According to this model, a planar sound wave falls on a system containing the nuclei of a metastable phase. This wave induces pressure oscillations, which result in the resonance absorption of ultrasound. Special attention is paid to the study of the intensity of ultrasound radiation and its dependences on the temperature and the solution concentration at various incident wave frequencies. The vibration frequencies of the nuclei were also determined.

2. The Lagrange–Rayleigh Function for a Single Nucleus

While constructing the Lagrange–Rayleigh function, we proceeded from the hypothesis that ultrasound is absorbed by the nuclei of a metastable phase, which are formed in the aqueous alcoholic solutions. The nuclei are assumed to be elastic, and their size varies under the influence of the external oscillating sound field. The medium inside and outside a nucleus is considered to be liquid with a definite shear viscosity. At the first step, our main task is to construct the Lagrange–Rayleigh function for a single nucleus.

2.1. Kinetic energy

The kinetic energy of the nucleus-solution system is determined by the velocity of the fluid at the surface of the nucleus during its vibration. The velocity field created in a liquid by spherical surface vibrations is well known and satisfies to the following conditions: (i) the velocity oscillations vanish at infinity, and (ii) the velocity potential must be finite inside the nucleus [14]. Using our notations, we obtain

$$\begin{aligned} u_{\mathrm{n}}(r) &= \dot{r}_s \frac{r}{r_0}, \\ u_{\mathrm{m}}(r) &= \dot{r}_s \frac{r_0}{r}, \end{aligned} \tag{2}$$

where $u_{\mathrm{n}}(r)$ and $u_{\mathrm{m}}(r)$ are the velocities of the molecules located inside the nucleus and in the medium, respectively, at the distance r from the nucleus center.

The kinetic energy is an additive quantity. Therefore, it is equal to the sum of kinetic energies inside and outside the nucleus,

$$T = \int\limits_{V_{\mathrm{n}}} \frac{\rho_{\mathrm{n}}}{2} u_{\mathrm{n}}^2(r) dV + \int\limits_{V_{\mathrm{m}}} \frac{\rho_{\mathrm{m}}}{2} u_{\mathrm{m}}^2(r) dV. \tag{3}$$

By substituting the velocities from Eqs. (2) into Eq. (3), we obtain

$$T = 2\pi \left(\frac{\rho_{\mathrm{n}}}{3} + \rho_{\mathrm{m}}\right) r_0^3 \, \delta\dot{r}^2. \tag{4}$$

2.2. Potential energy

The potential energy of the system is the sum of two components,

$$U = U_\sigma + U_{\mathrm{el}}.$$

The componrent U_σ describes the effect of the nucleus surface tension σ, and the component U_{el} the elastic response of the system, which corresponds to radial vibrations. According to the results of works [16, 17], the component U_σ equals

$$U_\sigma = 4\pi\sigma\delta r^2 + \frac{1}{2}\sigma \sum_{mn} (n-1)(n+2)|\lambda_{mn}|^2, \tag{5}$$

where λ_{mn} are generalized coordinates that determine the angular dependence of the nucleus radius change,

$$\delta r(\theta, \alpha) = \sum_{mn} \lambda_{mn} \Upsilon_{mn}(\theta, \alpha),$$

and $\Upsilon_{mn}(\theta, \alpha)$ are spherical functions. The summation in formula (5) is carried out from $n \geq 2$.

The elastic potential energy of the nucleus is determined as the increment of the Gibbs energy for the system with the new phase nucleus,

$$U_{\mathrm{el}} = \frac{1}{2} \frac{\partial^2 F}{\partial V^2}\bigg|_0 \delta V^2 + ..., \tag{6}$$

where $F = F_{\mathrm{n}} + F_{\mathrm{m}}$; F_{n} and F_{m} are the free energies of the nucleus and medium, respectively; and $\delta V = 4\pi r_0^2 \delta r$ is the variation of the nucleus volume. The growth of the nucleus volume is accompanied by a volume decrease of the external medium, $\delta V_n = -\delta V_m$. With the help of thermodynamic identities, it is easy to find that

$$U_{\mathrm{el}} = \frac{1}{2}\left(\frac{1}{V_{\mathrm{n}}}\frac{1}{\beta_T^{(\mathrm{n})}} - \frac{1}{V_{\mathrm{m}}}\frac{1}{\beta_T^{(\mathrm{m})}}\right)\delta V_{\mathrm{n}}^2 + \dots .$$

Taking into account additionally that the isothermal compressibility and the isothermal velocity of the sound are coupled by the relation $\beta_T = \left(\rho C_T^2\right)^{-1}$, we obtain the ultimate expression for the potential energy,

$$U_{\mathrm{el}} \approx 6\pi r_0 \left(\rho_{\mathrm{n}} C_T^{(\mathrm{n})2} - \rho_m C_T^{(m)2}\right) \delta r^2. \tag{7}$$

2.3. Interaction of the nucleus with the external sound field of an incident wave

Let us consider the case where a flat sound wave falls on the nucleus. The pressure variation in this wave is described by the expression

$$\delta p(r, t) = \delta p_0 e^{i\mathbf{kr}}, \tag{8}$$

where the value of δp_0 is determined by the sound generator power.

For further calculations, the expansion of the plane wave in a series of spherical functions is used:

$$e^{i\mathbf{kr}} = \sum_{l=0}^{\infty} i^l \, (2l+1) \, P_l(\cos\,\theta) j_l(kr), \tag{9}$$

where $P_l(\cos\,\theta)$ are the Legendre polynomials, and $j_l(kr)$ the spherical Bessel functions [18]. According to work [18], the first terms in the asymptotic expansion for the radial component of the sound wave pressure at the nucleus surface equal

$$\begin{aligned} &\delta p\,(r_0, t) = \delta p_0\,(1 + ikr_0 \cos\theta + ...), \\ &kr_0 \ll 1, \\ &\delta p\,(r_0, t) = -i\delta p_0 \frac{e^{ikr_0}}{kr_0}\,(1 + 3\cos\theta + ...), \\ &kr_0 \gg 1. \end{aligned} \tag{10}$$

The energy of interaction between the nucleus and the field of the external sound wave is determined by the minimum work ($R_{\min} = \delta p \; \delta V$ [19]) that is required to change the nucleus radius r_0 by δr,

$$U_{\rm int} = -4\pi r_0^2 \, \delta p(r_{0,} t) \, \delta r. \tag{11}$$

Note that, in experiments [10], the ultrasound radiation with the frequency varying from 10 to 2500 MHz was used. Such frequency values correspond to the wave vector magnitudes $k = \omega/C$ within the interval 3×10^{-2} cm^{-1} $< k <$ 8 cm^{-1}. The characteristic size of the nucleus r_0 is determined by evaluating the size of the micro-sized inhomogeneities. According to works [1, 4, 15], it has an order of $r_0 \sim \sim (10^{-6} \div 10^{-4})$ cm. From whence, it follows that the product kr_0 changes from about 3×10^{-6} to about 8×10^{-4}.

2.4. Dissipation function

Dissipative forces are governed by the viscous friction forces emerging as a result of the fluid motion induced by vibrations, as well as by energy losses taking place owing to the sound emission to infinity. The contribution of the first type to the dissipation function R is the sum of two components corresponding to the nucleus, R_1, and to the surrounding medium, R_2. Each i-th ($i = 1, 2$) component is determined by the equation of the same type,

$$R_i = \frac{\eta_i}{2} \int_{V_i} \left(\frac{\partial u_n^{(i)}}{\partial x_k} + \frac{\partial u_k^{(i)}}{\partial x_n} - \frac{2}{3}\delta_{nk} \frac{\partial u_l^{(i)}}{\partial x_l} \right)^2 dV,$$

$$i = 1, 2. \tag{12}$$

Making allowance for only the radial velocity components, we obtain

$$R_i = 8\pi \eta_i r_0^2 \left(\frac{\partial}{\partial r} u_i^2 \right) \Bigg|_{r=r_0} \qquad (i = 1, 2). \tag{13}$$

Besides the viscous frictional forces, the energy dissipation in the medium also takes place owing to energy losses as a result of the propagation of the sound waves generated by the nucleus surface vibrations toward infinity. The flow of the sound wave energy through a spherical surface located at a definite distance from the nucleus is determined by the relation

$$J_E = \oint_s \varepsilon C_T^{(m)} \; dS = 2\pi \delta p_0^2 \frac{1}{\rho C_T^{(m)}} \frac{1}{k^2}, \tag{14}$$

where $\varepsilon = \frac{1}{2} \beta_T^{(C)} \delta p_0^2$ is the mean value of the sound energy density over a period. By definition, the effective viscosity of the medium associated with the sound energy losses is determined from the relation

$$J_E \approx R_{\rm us}, \tag{15}$$

where the expression for $R_{\rm us}$ is identical to that for the energy losses due to the ordinary shear viscosity [see Eq. (13)],

$$R_{\rm us} = 8\pi \eta_{\rm us} r_0^2 \left(\frac{\partial}{\partial r} u_2^2 \right) \Bigg|_{r=r_0}.$$

Following this way, we obtain

$$\eta_{\rm us} = \frac{C_T^{(c)}}{2 r_0 \omega^4 \rho_n} \frac{\delta p_0^2}{\delta r_0^2}. \tag{16}$$

The ultimate formula for the dissipation function R looks like

$$R = 8\pi \left(\eta_{\rm n} + \eta_{\rm m} + \eta_{\rm us} \right) \, r_0 \, \delta \dot{r}^2. \tag{17}$$

In work [10], the propagation velocity of a sound wave in the solution of 2-propanol was selected to equal $C_T^{(\rm m)2} \approx 10^5$ cm/s. As was indicated above, the characteristic size of the nucleus is $r_0 \sim (10^{-6} \div 10^{-4})$ cm. Since the water density $\rho_w = 1$ g/cm^3 and the alcohol density $\rho_a \approx 0.7$ g/cm^3, the nucleus density is of an order of $\rho_n \approx 1$ g/cm^3.

In work [10], the maximum of the ultrasound absorption was observed within the frequency interval $\omega \sim (200{\div}400)$ MHz. While evaluating the quantity δp_0^2, let us make use of the fact that the experimental power of an ultrasonic wave in work [10] did not exceed $N_{\rm exp} < 0.3$ W/cm^2 in order to avoid the cavitation phenomenon. This power limit corresponds to the pressure limit $\delta p < 0.1$ atm. With all the values indicated being taken above into account, the additional viscosity has an order of magnitude $\eta_{\rm us} \le 10^{-3}$ g/(cm s).

3. Nucleus Evolution

In the previous section, the components of the Lagrange function,

$$\begin{gathered} L(\delta r, \delta\dot r, t) = \frac{2\pi}{3} r_0^3 \left(\rho_{\rm n} + 3\rho_{\rm m}\right) \delta\dot r^2 - 6\pi r_0, \\ \left(\rho_{\rm n} {\rm m}_T^{({\rm n})2} \rho_{\rm m} {\rm m}_T^{({\rm m})2}\right) \delta r^2 + 4\pi\sigma\delta r^2 + 4\pi r_0^2 \delta P \delta r, \end{gathered} \tag{18}$$

and the Rayleigh dissipation function,

$$R(\delta r, \delta\dot r,\ t) = 8\pi \left(\eta_{\rm n} + \eta_{\rm m} + \eta_{\rm us}\right) r_0 \delta\dot r^2, \tag{19}$$

were found for the medium-nucleus system. In the general case, the Lagrange–Rayleigh equations of motion for a system with energy dissipation have the form

$$\frac{d}{dt}\frac{\partial L}{\partial \delta\dot r} - \frac{\partial L}{\partial \delta r} = -\frac{\partial R}{\partial \delta\dot r} \tag{20}$$

and lead to the following linear differential equation that describes the nucleus vibrations in the external field:

$$\delta\ddot r + 2\gamma\delta\dot r + \omega_0^2 \delta r = f e^{i\omega t}. \tag{21}$$

Here,

$$f = \frac{3\delta p_0}{r_0 \left(\rho_{\rm n} + 3\rho_{\rm m}\right)}$$

is the external force amplitude,

$$\omega_0^2 = \frac{9 r_0 \left(\rho_{\rm n} {\rm m}_T^{({\rm m})2} - \rho_m {\rm m}_T^{({\rm n})2}\right) + 6\sigma}{r_0^3 \left(\rho_{\rm n} + 3\rho_{\rm m}\right)} \tag{22}$$

is the characteristic frequency of the nucleus size oscillations, and

$$\gamma = \frac{6 \left(\eta_{\rm n} + \eta_{\rm m} + \eta_{\rm us}\right)}{r_0^2 \left(\rho_{\rm n} + 3\rho_{\rm m}\right)}$$

is the damping coefficient of nucleus vibrations.

The solution of Eq. (21) is well known. It looks like [19]

$$\delta r(t) = \delta r_0(t) + \delta r_f(t), \tag{23}$$

where the component $\delta r_0(t)$ corresponds to free oscillations of the nucleus size, and the component $\delta r_f(t)$ is associated with induced nucleus vibrations. It is easy to verify that the latter component equals

$$\delta r_f\,(t) = f\,(a\,\cos\omega t\ + b\,\sin\omega t\ ), \tag{24}$$

where

$$a = \frac{\omega_0^2 - \omega^2}{\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2}.$$

The energy absorption intensity (i.e. the energy absorbed within a vibration period) is determined by the expression

$$I_{\rm abs} = \int \langle \delta\dot r_f\ f\cos\omega t\rangle\, dt.$$

It is equal to

$$I_{\rm abs} = \frac{16\pi^2 r_0^4 f^2}{2} \frac{\gamma\omega^2}{\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2}. \tag{25}$$

As one can see, the energy absorption has a resonance character. Near the resonance frequency, it has the form

$$I_{\rm abs} = 4\pi^2 r_0^4 \frac{f^2\gamma}{\varepsilon^2 + \gamma^2}, \tag{26}$$

where $\varepsilon = \omega_0 - \omega$.

4. Dependences of the Ultrasound Absorption Coefficient on the Frequency, Temperature, and Solution Concentration

Now, let us consider a possibility to consistently reproduce the experimental dependences of the ultrasound absorption coefficient regarding as a function of the sound frequency and the solution concentration at the temperatures $T = 293$ K (see Fig. 2) and $T = 343$ K (see Fig. 3). From Fig. 2, it follows that the maximum of the anomalous ultrasound absorption at the temperature $T = 293$ K is observed at the frequency $f_1 = 10$ MHz. The absorption coefficient grows nonmonotonically with the decreasing concentration (Fig. 2), so that an absorption maximum is observed at the alcohol concentration $x_s \approx 0.13$, which is slightly higher than the concentration at the singular point [1–5, 9, 10, 15, 16]. It should be noted that other literature sources give somewhat different concentration values for the singular point. For instance, the molecular light scattering [2] and the behavior of contraction curves at different temperatures [4] testify to the singular concentration value $x_s \approx 0.06$.

The magnitude of the quantity α/f^2 is very important for the correct identification of the physical nature of anomalous absorption. From experimental data, it follows that

$$\frac{\alpha}{f^2} \sim 200 \text{ if } 0.25 < x < 1.$$

At the same time, at lower concentrations, the absorption value is an order of magnitude larger:

$$700 < \frac{\alpha}{f^2} < 1300 \text{ if } 0.06 < x < 0.18.$$

The absorption behavior at the ultrasound generator frequency $f_2 = 1800$ MHz and the temperature $T = 343$ K is completely different (Fig. 3). Namely, the absorption curves are monotonically decreasing functions of the concentration. It should be marked that typical values of the absorption coefficient α/f^2 vary within the interval $25 < \alpha/f^2 < 95$ depending on the alcohol concentration. It is easy to make sure that those values correspond to the classical law of ultrasound absorption [13]:

$$\frac{\alpha}{f^2} = \frac{4\pi^2}{\rho C^3}\left[\frac{4}{3}\eta + \kappa\left(\frac{1}{C_V} - \frac{1}{C_p}\right)\right]. \tag{27}$$

For this formula to be applicable, the behavior of all parameters in it has to be imitated. In this work, the simplest approximation formulas are used:

$$\begin{aligned}
&\eta = (1-x)\,\eta_{\rm w} + x\eta_{\rm a},\\
&\kappa = (1-x)\,\kappa_{\rm w} + \kappa\eta_{\rm a},\\
&\frac{1}{C_V} - \frac{1}{C_p} = \frac{1}{(1-x)\,C_V^{(w)} + xC_V^{(a)}} - \\
&- \frac{1}{(1-x)\,C_p^{(\rm w)} + xC_p^{(\rm a)} + k_{\rm B}},
\end{aligned} \tag{28}$$

where $C_V^{(\rm w)}$ and $C_V^{(\rm a)}$ are the isochoric heat capacities of water and alcohol, respectively. The values of the sound velocity at various concentrations were taken from work [10].

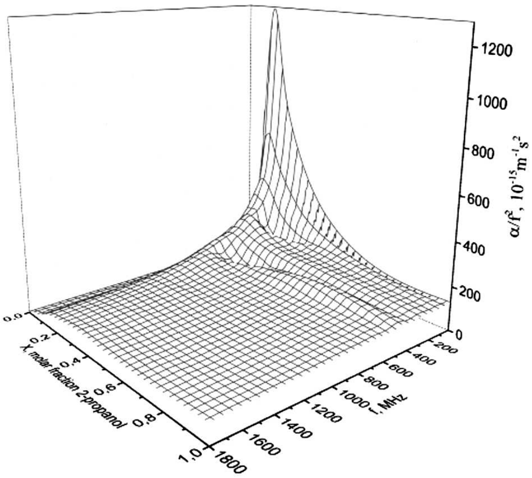

Fig. 2. Dependence the ultrasound absorption coefficient on the ultrasound frequency and the solution concentration of the aqueous alcoholic solution of 2-propanol at the temperature $T = 293$ K (according to the results of work [10])

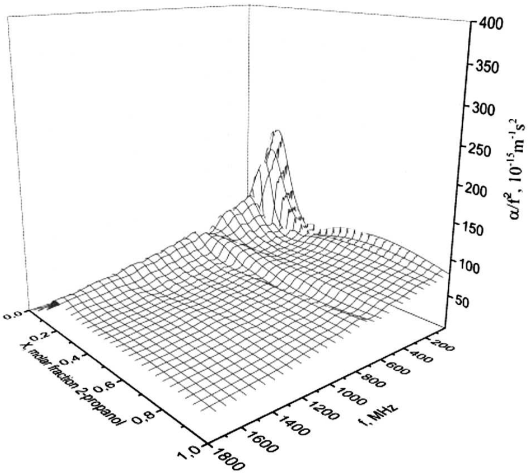

Fig. 3. The same as in Fig. 2, but for the temperature $T = 343$ K

The contribution of the classical term at high sound frequencies and the solution concentration $x \approx 0.13$ is illustrated in Fig. 4. As one can see, a quite satisfactory agreement takes place between the experimental temperature dependence and formula (27). The same agreement is also observed for all other solution concentrations.

Let us also evaluate the classical contribution at low frequencies. The result of the comparison for a solution with the same concentration is shown in Fig. 5. Now, the classical absorption gives only a

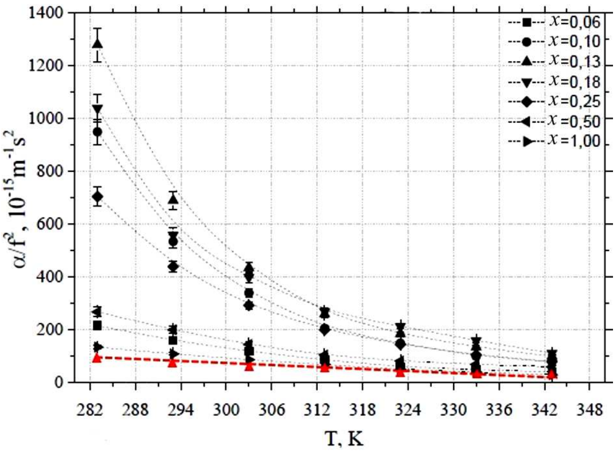

Fig. 4. Temperature dependences of the ultrasound absorption coefficient in aqueous solutions of 2-propanol at the frequency $f = 10$ MHz for various alcohol concentrations x. The solid curve corresponds to the results of calculations using formula (27) for $x \approx 0.13$ and the parameter dependences (28). Dashed curves and symbols correspond to the experimental data of work [10]. Numerical values of constant parameters were taken from work [20]

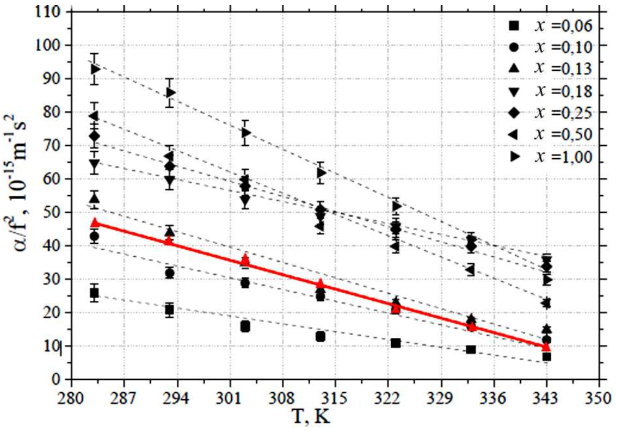

Fig. 5. The same as in Fig. 4, but for the ultrasound frequency $f = 1800$ MHz

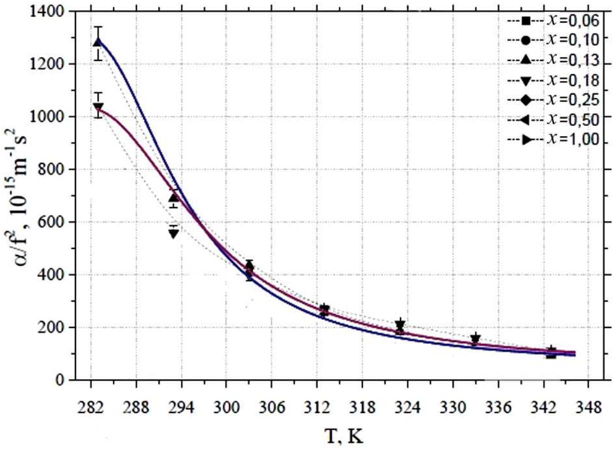

Fig. 6. Temperature dependence of the ultrasound absorption coefficient in aqueous solutions of 2-propanol at the frequency $f = 10$ MHz. The solid curve corresponds to the results of calculations using formula (31). Dashed curves and symbols correspond to the experimental data of work [10]. Numerical values of constant parameters were taken from work [20]

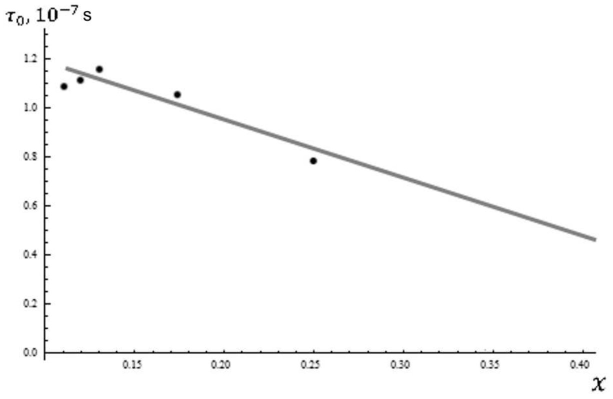

Fig. 7. Concentration dependence of the relaxation time minimum value

small fraction, (5÷15)%, of the total ultrasound absorption. Hence, almost all absorption has an anomalous character.

In order to reproduce the behavior of the anomalous ultrasound absorption, formulas (25) and (26) were applied, and the characteristic frequency $\omega_0(x,t)$ of the system was put equal to

$$\omega_0 \approx 0.63 \times 10^8 \text{ s}^{-1} \tag{29}$$

in the adopted approximation. The dependences of ω_0 on the solution concentration and temperature are weak, so that they can be neglected. The intensity of the anomalous ultrasound absorption can be written in the form

$$I(\omega) = H_0 \frac{1/\tau}{(\omega-\omega_0)^2 + 1/\tau^2}. \tag{30}$$

Here, the quantity τ has a sense of the nucleus lifetime. To determine this parameter as a function of the temperature at a fixed concentration of the solution, let us take advantage of the experimental data from work [10]. We also assumed that the radiation frequency equals ω_0, so that, according to work [10], ω_0 is equal to the generator frequency in this case, and

$$I(\omega_0) = H_0\tau. \tag{31}$$

It is easy to make sure that the temperature dependence of the relaxation time τ is described by the formula

$$\tau = \frac{\tau_0}{t^2 + t_0^2}, \tag{32}$$

where $t = (T - T_0)/T_0$ and $T_0 = 282$ K, which corresponds to the leftmost points in the plots in Fig. 5.

The agreement between the temperature dependences of the ultrasound absorption coefficient taken from work [10] and calculated using formula (31) is quite satisfactory (see Fig. 6). This dependence is justified by the fact that the absorption intensity maximum is described by formula (31), and the absorption intensity must be expanded in an even-power series of the temperature. The values of the main parameters were determined by fitting the calculated dependences to the experimental data. As a result, the following values were obtained:

$$\tau_0 \sim 10^{-7}\ \text{s},\ \ t_0 \approx 0.039,\ \ H_0 \approx 0.7 \times 10^{-4}\ \text{cm}^{-1}\text{s}^{-3}. \tag{33}$$

The relaxation time near the singular point ($x \approx 0.13$ and $T = 282$ K) equals $\tau \approx 5 \times 10^{-7}$ s (unfortunately, the exact position of the singular point, as well as the behavior of the ultrasound absorption intensity in its vicinity, are unknown).

The concentration dependence of τ_0 is depicted in Fig. 7. One can see that this dependence is weak.

Let us use estimate (29) obtained for the characteristic vibration frequency of the nucleus in order to evaluate its characteristic size r_0. On the basis of expression (22) and neglecting the surface tension effect, we find that

$$r_0 = 3\sqrt{\frac{\left(\rho_\text{n} C_T^{(\text{m})2} - \rho_\text{m} C_T^{(\text{n})2}\right)}{\left(\rho_\text{n} + 3\rho_\text{m}\right)\omega_0^2}} \approx$$
$$\approx 0.7 \times 10^{-4}\ \text{cm}. \tag{34}$$

Let us compare this result with the nucleus size r_0 determined from the estimation of the relaxation time,

$$r_0 = \sqrt{\frac{6\tau\left(\eta_\text{n} + \eta_\text{m} + \eta_\text{us}\right)}{\left(\rho_\text{n} + 3\rho_\text{m}\right)}}. \tag{35}$$

Using the values for τ_0 and $\tau = \tau_0/t_0^2$ [see Eq. (33)], we obtain the estimate

$$r_0 \approx 4 \times 10^{-4}\ \text{cm}, \tag{36}$$

which is in a rather satisfactory agreement with estimate (34).

Finally, the dependence of the ultrasound absorption intensity on the solution concentration and the sound frequency has the form

$$I = \frac{I_0}{1 + \left(\omega - \omega_0\right)^2\tau^2 + \zeta^2\left(x - x_0\right)^2}. \tag{37}$$

5. Conclusions

In this work, the anomalous absorption of ultrasound in an aqueous solution of propyl alcohol near its singular point has been analyzed. The basic idea of the proposed approach consists in that the effect of anomalous ultrasound absorption appears due to the interaction of ultrasound with elastic radial vibrations of nuclei that arise in the system. As a result, the relaxation in the system becomes considerably slower. Instead of the relaxation time $\tau \sim$ $\sim (10^{-12} \div 10^{-10})$ s, which is typical of molecular processes, the relaxation time $\tau \sim (10^{-7} \div 10^{-6})$ s is dealt with. The corresponding dimensions of nuclei, as was shown above, lie within the interval $r_0 \sim$ $\sim (0.7 \div 4) \times 10^{-4}$ cm, which agrees with the wavelength of light, $\lambda \sim 10^{-4}$ cm, that was used in works [2, 4].

The temperature dependences of the ultrasound absorption coefficient at fixed ultrasound frequencies and various solution concentrations are plotted. It is shown that, at relatively low frequencies ($f \sim$ ~ 10 MHz) and at concentrations close to the concentration at the singular point of the system ($x \approx 0.13$), a quite satisfactory reproduction of experimental dependences is obtained. This fact testifies that the assumption about the formation of nuclei of a new phase in the system is sufficiently substantiated. It is clear that, for the description of all experimental dependences to be more accurate, it is necessary to apply more adequate dependences for the parameters of the medium inside a nucleus in comparison with dependences (28) used in this work and corresponding to the ideal solution model. More profound studies should be carried out also in the field of experimental researches, since it is of importance, in particular, to elucidate why the ultrasound absorption maximum is observed at a concentration that is somewhat different from the concentration of the system at its singular point. The indicated and other relevant issues will be the subject of subsequent works.

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1. L.A. Bulavin, V.Ya. Gotsulskii, N.P. Malomuzh, V.E. Chechko. Relaxational and equilibrium properties of dilute aqueous alcohol solutions. *Izv. Ross. Akad. Nauk Ser. Khim.* **4**, 851 (2016) (in Russian)
2. L.A. Bulavin, V.Ya. Gotsulskiy, V.E. Chechko. Light scattering by aqueous solutions of alcohols near their singular points. *Ukr. J. Phys.* **59**, 882 (2014).
3. L.A. Bulavin, T.V. Lokotosh, N.P. Malomuzh. Role of the collective self-diffusion in water and other liquids. *J. Mol. Liq.* **137**, 1 (2007).
4. V.Ya. Gotsulskiy, V.E. Chechko, Yu.A. Melnik. The origin of light scattering by aqueous solutions of alcohols in vicinities of their singular points. *Ukr. J. Phys.* **60**, 782 (2015).
5. M.A. Anisimov, V.S. Esipov, V.M. Zaprudskii. Anomaly of heat capacity and structural phase transition of the ordering type in the aqueous solution of tertiary alcohol. *Zh. Strukt. Khim.* **18**, 835 (1977) (in Russian).
6. D. Subramanian, M. Anisimov. Resolving the mystery of aqueous solutions of tertiary butyl alcohol. *J. Phys. Chem.* **155**, 9179 (2011).
7. D. Subramanian, C. Boughter, J. Klauda, M. Anisimov. Mesoscale inhomogeneities in aqueous solutions of small amphiphilic molecules, *Faraday Discuss.* **167**, 217 (2013).
8. J. Leys, D. Subramanian, E. Rodezno, A. Anisimov. Mesoscale phenomena in solutions of 3-methylpyridine, heavy water, and an antagonistic salt. *Soft Matter* **9**, 9326 (2013).
9. L.V. Lanshina, A.L. Sobirov. Ultrasonic velocity and adiabatic compressibility of dilute aqueous solutions of ethylenediamine. *Vestn. Moscow Gos. Univ. Ser. 2* **30**, 210 (1989) (in Russian).
10. L.A. Bulavin, A.V. Chalyi, O.I. Bilous. Anomalous propagation and scattering of ultrasound in 2-propanol water solution near its singular point. *J. Mol. Liq.* **235**, 24 (2017).
11. L.A. Bulavin, O.I. Bilous, V.E. Chechko, V.Ya. Gotsulskii. Physical properties of aqueous solutions of alcohols near its peculiar point. In *The 19th Small Triangle Meeting on Theoretical Physics* (Medzilaboece, 2017).
12. L.D. Landau, E.M. Lifshitz. *Fluid Mechanics* (Pergamon Press, 1993).
13. I.G. Mikhailov, V.A. Solovyev, Yu.P. Syrnikov. *Fundamentals of Molecular Acoustics* (Nauka, 1964) (in Russian).
14. L.D. Landau, E.M. Lifshitz. *Mechanics* (Butterworth Heinemann, 2001).
15. V.E. Chechko, T.V. Lokotosh, N.P. Malomuzh, V.G. Zaremba, V.Ya. Gotsul'skii. Clusterization and anomalies of fluctuations in water-alcohol solutions of low concentrations, *J. Phys. Stud.* **7**, 175 (2003).
16. Yu.M. Stula. Physical nature of relaxation time in aqueous alcoholic solutions. *Ukr. J. Phys.* **63**, 138 (2018).
17. A. Messiah. *Quantum Mechanics. Vol. 1* (North-Holland, 1967).
18. A.G. Sveshnikov, A.N. Bogolyubov, V.V. Kravtsov. *Lectures on Mathematical Physics* (Moscow State Univ. Publ. House, 1993) (in Russian).
19. L.D. Landau, E.M. Lifshitz. *Statistical Physics, Part 1* (Pergamon Press, 1980).
20. *Tables of Physical Quantities.* Edited by I.K. Kikoin (Atomizdat, 1976) (in Russian).

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ТЕОРЕТИЧНИЙ АНАЛІЗ ПОГЛИНАННЯ УЛЬТРАЗВУКУ ВОДНИМИ РОЗЧИНАМИ СПИРТІВ

Резюме

Робота присвячена теоретичному дослідженню поглинання ультразвуку в водно-спиртових розчинах в околі їх особливих точок. Приймається, що аномальне поглинання ультразвуку відбувається внаслідок утворення нестабільних зародків нової фази. Запропоновано модель, яка описує еволюцію цих зародків з часом, а також дозволяє пояснити виникнення резонансного поглинання ультразвуку в околі особливої точки водного розчину 2-пропанол. Досліджено характер залежності інтенсивності поглинання від параметрів зародка, температури та частоти ультразвуку. Оцінено внесок звукового випромінювання зародків у ефективну зсувну в'язкість розчинів. Виконано порівняння теоретичних результатів з наявними експериментальними даними.