doi: 10.15407/ujpe61.05.0375

L.A. BULAVIN, O.I. BELOUS, O.S. SVECHNIKOVA
Taras Shevchenko National University of Kyiv, Faculty of Physics
(64/13, Volodymyrs'ka Str., Kyiv 01601, Ukraine; e-mail: bulavin221@gmail.com, o_ bilous@ua.fm, oksana.svechnikova@gmail.com)

PACS 2.60.+v; 62.80.+f

ANOMALOUS ULTRASOUND ATTENUATION NEAR THE CRITICAL POINT OF n-PENTANOL–NITROMETHANE SOLUTION STRATIFICATION

A binary n-pentanol–nitromethane solution in the homogeneous state near the critical stratification point is acoustically studied in a frequency range of 5÷2800 MHz. The experiment confirmed the existence of the anomalous ultrasound attenuation, which can be analyzed in terms of the effective ultrasound absorption. On the basis of experimental data, the regular and fluctuation components of the effective ultrasound absorption coefficient of the solution are resolved. It is shown that the fluctuation part of the effective absorption coefficient can be described in the framework of the Ferrell–Bhattacharjee theory of heat capacity relaxation. On the basis of this theory with the use of the obtained experimental data, the crossover scaling function is determined, and its parameters n and $\Omega_{1/2}$ are found.

Keywords: binary solutions, critical stratification point, ultrasound absorption coefficient, crossover function.

1. Introduction

Universal and, at the same time, unique properties of liquids and liquid systems near their critical points remain a subject of the vivid scientific discussion [1–4]. Now, considering the ample opportunities for properties of such systems to be applied in practice [5–7], the experimental and theoretical researches that allow one not only to reveal the structural features of liquids or solutions near their critical points, but also determine their governing physical mechanisms, are challenging. Experimentally, such researches are much easier to be carried out near the critical stratification point than in a vicinity of the "liquid-vapor" one. Indeed, in the former case, the pressure in the system can be atmospheric, and the temperature can be environmental, unlike the latter case where the pressure in the system is two orders of magnitude as high as the atmospheric one, and the temperature considerably exceeds room one. At the same time, the confirmed isomorphism hypothesis allows the results obtained for the critical stratification point to be extended onto the behavior of a medium near the critical "liquid-vapor" point. For this reason, the researches of properties near the critical stratification point, which can be performed using various methods – in particular, the method of acoustic spectroscopy [8, 9], – are of importance.

When an ultrasonic wave propagates through a liquid or a liquid system, the attenuation of its intensity I along the specimen thickness in the case where the specimen is thin is described by the differential equation

$$-dI = \alpha I dx, \tag{1}$$

where α is the coefficient of ultrasound attenuation. The solution of Eq. (1) is the well-known dependence of the Bouguer–Lambert–Beer type [10],

$$I = I_0 \exp\{-\alpha x\}. \tag{2}$$

The mechanism of sound attenuation in liquids that are far from their singular points in the thermodynamic space is well studied. This is the absorption of sound at the molecular level, which is associated, first of all, with the relaxation of the shear, η_s, and bulk, η_ν, viscosities in liquids and their solutions. In this case, the quantity α in Eq. (2) is the ultrasound absorption coefficient. The corresponding ultrasound wavelength exceeds the characteristic dimensions of the system – these are the sizes of molecules or intermolecular bonds – by several orders of magnitude. As a rule, in view of the quadratic dependence of the absorption coefficient on the ultrasound frequency f [10], it is the normalized quantity αf^2, rather than the absorption factor itself, that is analyzed in experiments.

The situation is essentially different in vicinities of the singular points in the thermodynamic space of liquids or solutions; these are the "liquid-vapor" critical point and the stratification one. In this case, the characteristic dimension of the system is determined by fluctuations or the correlation length R_c. For instance, when approaching the "liquid-vapor" critical point to the distance $t = \frac{T-T_\mathrm{c}}{T_\mathrm{c}} \sim 10^{-4}$, where T_c is the critical temperature, the correlation length R_c observed by the optical method increases to about 10^2 nm. The length of an ultrasonic wave with the frequency $f \sim 10^9$ Hz becomes comparable with the correlation length, which inevitably results in that the sound wave is not only absorbed, but also scattered. As a result, the exponent of the exponential function in Eq. (2) will change to $(\alpha+\Sigma)x$. At present, there is no technique to distinguish the scattering and absorption effects in the acoustic researches of this kind. Therefore, while analyzing the ultrasound attenuation in a liquid medium, the effective absorption coefficient α_EF, which makes allowance for both absorption and scattering of ultrasound, will be implied.

This work was aimed at studying the effective ultrasound absorption coefficient near the upper critical point of stratification in homogeneous n-pentanol($C_5H_{11}OH$)–nitromethane(CH_3NO) solutions with various concentrations along their isoconcentration curves in the temperature interval $0.1\ \mathrm{K} \leq \leq T - T_\mathrm{c} \leq 15$ K. The researches were carried out in an ultrasound frequency range of 5–2800 MHz.

2. Experimental Specimens and Method

For experimental researches, we chose the binary solution n-pentanol–nitromethane. It was done, first of all, because the critical stratification temperature of this liquid system is close to the so-called room temperatures, which simplifies the experimental procedure.

The experimental researches of the normalized effective absorption coefficient $\alpha_\mathrm{EF} f^{-2}$ were carried out, by using the pulse ultrasound method, which was described in work [11] in detail. The pulse method with variable distance and the resonance excitation of quartz piezocrystals were used in a frequency range of 5÷150 MHz, and the method of non-resonance excitation of a lithium-niobate single crystal in a frequency range of 300÷2800 MHz. The total measurement error for the effective ultrasound absorption was equal to 2–5%, depending on experimental conditions.

The characteristics of studied objects are shown in Table. In the table, the concentrations X of the researched solutions are indicated in mole fractions of the first component (n-pentanol). N-pentanol and nitromethane that were used in the measurements were of the chemically pure grade.

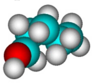
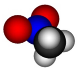
3. Ultrasound Absorption Coefficient

A large body of experimental data obtained for a number of n-pentanol concentrations in the examined binary solution allowed us to determine the dependence of the normalized ultrasound absorption coefficient $\alpha_\mathrm{EF} f^{-2}$ on the ultrasound frequency and the solution temperature. Note that our results correlate with rare data reported by other authors, which performed similar acoustic researches in a different frequency interval [12, 13].

In Figs. 1 and 2, the experimental values of effective ultrasound absorption coefficient in the n-pentanol–nitromethane solutions with the n-pentanol concentrations $X = 0.384$ and 0.3 (solutions 4 and 3, respectively, in Table) are exhibited. The data obtained evidently testify to the anomalous ultrasound attenuation when approaching the critical stratification temperature from the homogeneous-state side.

Figures 1 and 2 show that the experimental data form surfaces in the three-dimensional space "effective absorption coefficient – temperature – frequency". At certain frequencies and temperatures, the behavior of those surfaces has a characteristic feature, namely, a

Parameters of studied n-pentanol–nitromethane solutions

Solution type	Structural models of solution components	Molar fraction of n-pentanol	Critical stratification temperature T_c, K	Critical stratification concentration X_c
n-pentanol($C_5H_{11}OH$)–nitromethane(CH_3NO)	n-pentanol 	1. $X = 0$; 2. $X = 0.2$; 3. $X = 0.3$; 4. $X = 0.384$; 5. $X = 0.4$;	300.9 ± 0.2	0.385 ± 0.005
	nitromethane 	6. $X = 0.5$; 7. $X = 0.6$; 8. $X = 0.7$; 9. $X = 0.8$; 10. $X = 1$	300.8–301.0 [8, 12]	0.378–0.390 [8, 12]

peak of the effective ultrasound absorption coefficient is observed. The experimental researches of a number of binary n-pentanol–nitromethane solutions with various concentrations showed that the peak magnitude is maximum for the solution with the n-pentanol concentration $X = 0.384$. A comparison of Fig. 1 with Fig. 2 corresponding to the solution with $X = 0.300$ demonstrates that, at other solution concentrations, the peak magnitude decreases, and the peak itself becomes wider. Really, the maximum values found for the normalized ultrasound absorption factor $\alpha_{\mathrm{EF}} f^{-2}$ at a temperature of 300.9 K and a frequency of 10 MHz amounted to 500×10^{-15} s^2/m for the solution with the concentration $X_1 = 0.384$ (see Fig. 1) and to 460×10^{-15} s^2/m for the solution with the concentration $X_1 = 0.300$ (see Fig. 2). Note that the further increase of the ultrasound frequency resulted in a drastic peak reduction for the effective ultrasound absorption coefficient. The analysis of the obtained dependences allowed us to determine the critical concentration for the n-pentanol–nitromethane solution, $X_c = 0.384 \pm 0.005$, and its critical stratification temperature, $T_c = 300.90 \pm 0.25$ K. These results agree with the data of other authors [8, 9] (see Table).

4. Discussion of the Results Obtained

Owing to a complicated geometry of the surfaces exhibited in Figs. 1 and 2, let us express the effective ultrasound absorption coefficient as a sum of its regular, $(\alpha f^{-2})_{\mathrm{REG}}$, and fluctuation, $(\alpha f^{-2})_{\mathrm{FL}}$, components,

$$\alpha f^{-2} = (\alpha f^{-2})_{\mathrm{REG}} + (\alpha f^{-2})_{\mathrm{FL}}. \tag{3}$$

The both components are functions of the temperature and the concentration of the examined solution. The regular part of the effective absorption coefficient corresponds to the actual ultrasound ab-

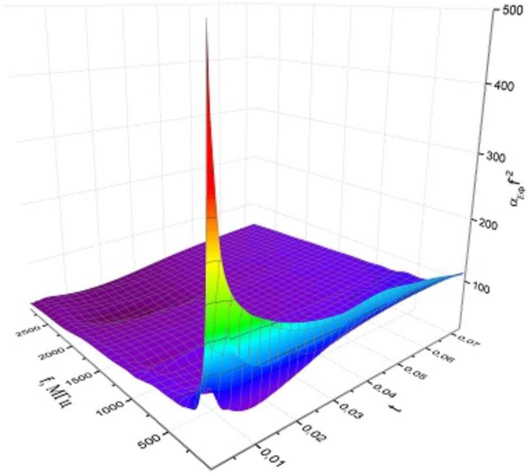


Fig. 1. Dependence of the normalized effective ultrasound absorption factor $\alpha_{\mathrm{EF}} f^{-2}$ in the n-pentanol–nitromethane solution with the molar fraction of n-pentanol $X = 0.384$ on the ultrasound frequency and the solution temperature

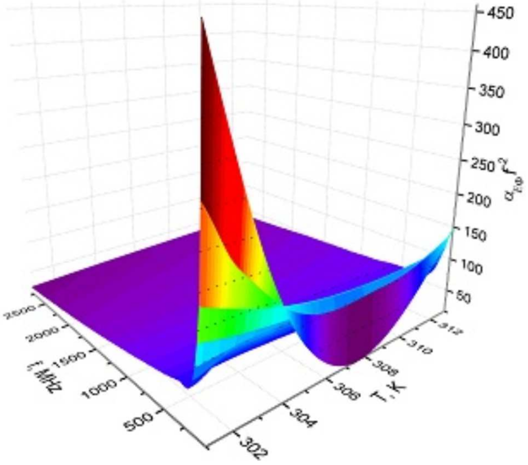


Fig. 2. The same as in Fig. 1, but for the n-pentanol–nitromethane solution with the molar fraction of n-pentanol $X = 0.300$

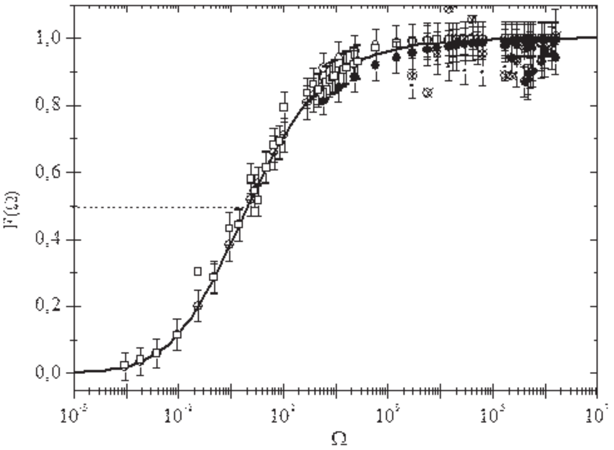


Fig. 3. Dependence of the crossover dynamic ultrasound absorption function $F(\Omega)$ on the reduced frequency Ω for the n-pentanol–nitromethane solution with a critical concentration of 0.384. Symbols correspond to different proximities ΔT of experimental values to T_c: $\Delta T = 0.1$ K (□), 0.2 K (△), 0.3 K (●), and 0.4 K (⊗). The curves correspond to the result of theoretical calculations of $F(\Omega)$ by formula (10) [20]

sorption coefficient of the solution making no allowance for fluctuations. This component is governed by structural features of the studied solutions. The fluctuation part is associated with processes that occur in the solution, when its temperature approaches the critical stratification one. This component is determined by growing fluctuations of the concentration of a solution.

To describe the regular part of the ultrasound absorption coefficient, the Hill model can be applied [14]. This model takes into account the presence of two relaxation regions in the system,

$$(\alpha f^{-2})_{\mathrm{REG}} =$$

$$= \left[\frac{A_1}{(1+(\omega\tau_1)^{2s})^{\frac{m+n}{2s}}} + \frac{A_2}{(1+(\omega\tau_2)^{2s})^{\frac{m+n}{2s}}}\right] + B, \quad (4)$$

where $\omega = 2\pi f$ is the cyclic frequency of ultrasound; τ_1 and τ_2 are the relaxation times in the low- and high-frequency relaxation regions, respectively; $f_1 = (2\pi\tau_1)^{-1}$ and $f_2 = (2\pi\tau_2)^{-1}$ are the corresponding relaxation frequencies; A_1 and A_2 are the amplitudes of ultrasound absorption in the corresponding relaxation regions; and $B = \lim_{f\to\infty}(\alpha_{\mathrm{EF}} f^{-2})$ is the high-frequency limit of the quantity $\alpha_{\mathrm{EF}} f^{-2}$. The indices m, n, and s were introduced by Hill in order to account for the collective processes that occur between the molecules of a solution at the molecular level; they are equal to 0 or 1 [14]. As was shown in work [15], $m = n = s = 1$ for the analyzed solutions.

The obtained experimental results were analyzed as follows. The parameters of model (4) were calculated with the help of the software package Matcad [16] for those experimental data, which, according to Figs. 1 and 2, were not associated with the anomalous or critical behavior of the absorption coefficient. According to our estimations, this region was determined by the criterion $t > 1.3 \times 10^{-2}$. Then, the experimental data were used to determine analytical expressions for the temperature dependences of the coefficients A_1, A_2, B, τ_1, and τ_2. Later, those dependences were extrapolated onto the whole examined temperature interval of acoustic researches in the n-pentanol–nitromethane solution. This procedure, owing to the extrapolation operation, allowed us to find the regular component of the effective absorption coefficient factor in the fluctuation region. The fluctuation component was determined on the basis of formula (3). This component was analyzed in the framework of the Ferrell–Bhattacharjee theory of heat capacity relaxation [17–19], by using the formula

$$(\alpha f^{-2})_{\mathrm{FL}} = (\alpha f^{-2})_{\mathrm{c}} F(\Omega), \quad (5)$$

where $(\alpha f^{-2})_{\mathrm{c}}$ is the effective ultrasound absorption coefficient at the critical point, $F(\Omega)$ a scaling crossover function introduced by the authors of work [20], $\Omega = \frac{\omega}{\omega_D}$ is the scaling parameter of the crossover function, and ω_D is the characteristic frequency of the concentration fluctuation relaxation.

For solutions with the critical concentration, the characteristic relaxation frequency is determined by the formula [21]

$$\omega_D = \omega_0 t^{-Z\nu}, \quad (6)$$

where ω_0 is the amplitude of the characteristic frequency of concentration fluctuations, Z the dynamic critical index, and ν the critical index in the temperature dependence of the correlation length. According to Eq. (6), in vicinities of the critical points, where $t \to 0$, the characteristic relaxation frequency of concentration fluctuations tends to zero. The amplitude of the characteristic frequency of concentration fluctuations can be calculated, by using the formula

$$\omega_0 = \frac{kT_{\mathrm{c}}}{3\pi\eta_0 R_0^3}, \quad (7)$$

where k is the Boltzmann constant, η_0 the amplitude of the dynamic viscosity (its value $\eta_0 = (0.98 \pm \pm 0.05)$ MPa was obtained by us from a rheological experiment), and R_0 the amplitude in the temperature dependence of the correlation length (according to literature data [12], its value equals $R_0 = = 0.14 \pm 0.5$ nm). The value calculated in this way for the amplitude of the ultrasound absorption coefficient in the n-pentanol–nitromethane solution amounts to $\omega_0 = (1.79 \pm 0.3) \times 10^{11}$ s^{-1} and agrees with the data of work [12].

Substituting the dynamical critical index $Z = = 3.065$ [21] and the critical index in the temperature dependence of the correlation length $\nu = 0.63$ [22] into formula (6), and taking the value obtained for ω_0 into account, the temperature dependence of the relative frequency Ω looks like

$$\Omega = 3.5 \times 10^{-11}\, f\, t^{-1.93}. \tag{8}$$

Since f is the frequency, Ω also has the dimension of frequency.

For the determination of the effective absorption coefficient at the critical point, let us use the formula [17]

$$(\alpha f^{-2})_{\rm c} = S\, f^{-[1+\frac{\alpha_1}{Z\nu}]}, \tag{9}$$

where $\alpha_1 = 0.091$ is the critical index for the isochoric heat capacity [17], and the ν- and Z-values were determined above. By analyzing the critical absorption of ultrasound at various frequencies and using formula (9), we can find the value of S, which equals $S = (2.0 \pm 0.5) \times 10^{-5}$ s$^{0.94}$/m for the n-pentanol–nitromethane solution [13].

Hence, formula (9) can be used to calculate the critical ultrasound absorption at the critical stratification point of the n-pentanol–nitromethane solution. Moreover, using formulas (5) and (8), we can construct the scaling crossover function for the ultrasound absorption, $F = F(\Omega)$. In Fig. 3, this function obtained for the absorption of ultrasound in the n-pentanol–nitromethane solution is plotted.

According to work [20], the shape of the scaling crossover function is described by the formula

$$F(\Omega) = \frac{1}{\left[1 + 0.414\left(\frac{\Omega_{1/2}}{\Omega}\right)^{n}\right]^{2}}. \tag{10}$$

The corresponding processing of the experimentally obtained scaling crossover function in the framework of the Ferrell–Bhattacharjee theory of heat capacity relaxation allowed us to determine the following values for the parameters in formula (10): $n = 0.53 \pm 0.03$ and $\Omega_{1/2} = 2.50 \pm 0.05$. The obtained values should be compared with the results of other works; for instance: $n = 0.5$ and $\Omega_{1/2} = 2.1$ [23]; $n = 0.63$ and $\Omega_{1/2} = 3.1$ [24]; and $n = 0.5$ and $\Omega_{1/2} = 6.2$ [25]. One can see that our results obtained by analyzing the experimental data for the normalized ultrasound absorption factor have the best agreement with the results of calculations performed by Ferrell and Bhattacharjee in work [23].

5. Conclusions

Binary n-pentanol–nitromethane solutions with various component ratios are acoustically studied in the homogeneous state in a vicinity of their critical stratification point in an ultrasound frequency interval of 5–2800 MHz. The analysis confirmed the existence of the anomalous ultrasound attenuation, which can be interpreted in terms of the effective ultrasound absorption. In the experimental data obtained for the solutions concerned, the regular and fluctuation components of the effective ultrasound absorption coefficient are resolved. It is shown that the fluctuation part can be described in terms of the Ferrell–Bhattacharjee theory of heat capacity relaxation, and the corresponding scaling crossover function is determined. Its analysis in the framework of the approach of work [17] allowed us to find the following values of parameters: $n = 0.53 \pm 0.03$ and $\Omega_{1/2} = 2.50 \pm 0.05$.

1. M.P. Kozlovskii, Condens. Matter. Phys. **8**, 473 (2005).
2. K.A. Chalyy, L.A. Bulavin, and A.V. Chalyi, J. Phys. Stud. **9**, 66 (2005).
3. O.V. Chalyi and O.V. Zaitseva, Ukr. J. Phys. **54**, 366 (2009).
4. M.P. Kozlovskii and R.V. Romanik, J. Molec. Liq. **167**, 14 (2012).
5. D. Nikitin and V. Mazur, Int. J. Therm. Sci. **62**, 44 (2012).
6. S. Artemenko, T. Lozovsky, and V. Mazur, J. Phys.: Condens. Matter **20**, 244119 (2008).
7. L.A. Bulavin, O.Yu. Aktan, and Yu.F. Zabashta, Phys. Sol. State **50**, 2270 (2008).
8. I. Iwanowski, S.Z. Mirzaev, K. Orzechowski *et al.,* J. Molec. Liq. **145**, 103 (2009).
9. S.Z. Mirzaev and U. Kaatze, Chem. Phys. **393**,129 (2012).
10. V.A. Shutilov, *Fundamental Physics of Ultrasound* (Gordon and Breach, New York, 1988).

11. V.S. Sperkach, A.D. Alekhin, and O.I. Bilous, Ukr. J. Phys. **49**, 655 (2004).
12. T. Hornowski and M. Lobowski, Acta Phys. Pol. A **5**, 671 (1991).
13. I. Iwanowski, R. Behrends, and U. Kaatze, J. Chem. Phys. **120**, 9192 (2004).
14. R.M. Hill, Phys. Status Solidi B **103**, 319 (1981).
15. V.S. Sperkach, A.D. Alekhin, and O.I. Bilous, Ukr. J. Phys. **49**, 975 (2004).
16. Mathcad Prime 3.0/Mathcad Prime 2.0; http://mathcad.com.ua/down-math.php.
17. J.K. Bhattacharjee and R.A. Ferrell, Phys. Rev. A **24**, 1643 (1981).
18. J.K. Bhattacharjee, I. Iwanowski, and U. Kaatze, J. Chem. Phys. **131**, 174502 (2009).
19. J.K. Bhattacharjee and S.Z. Mirzaev, Int. J. Thermophys. **33**, 469 (2012).
20. H.C. Burstyn, J. V. Sengers, J.K. Bhattacharjee *et al.*, Phys. Rev. A **28**, 1577 (1983).
21. M.A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, Philadelphia, 1991).
22. A.D. Alekhin and O.I. Bilous, Teplofiz. Vys. Temp. **53**, 204 (2015).
23. R.A. Ferrell and J.K. Bhattacharjee, Phys. Rev. A **31**, 1788 (1985).
24. R. Folk and G. Moser, Phys. Rev. E **57**, 705 (1998).
25. A. Onuki, J. Phys. Soc. Jpn. **66**, 511 (1997).

Received 31.01.16
Translated from Ukrainian by O.I. Voitenko

Л.А. Булавін, О.І. Білоус, О.С. Свечнікова

АНОМАЛЬНЕ ПОСЛАБЛЕННЯ УЛЬТРАЗВУКУ ПОБЛИЗУ КРИТИЧНОЇ ТОЧКИ РОЗШАРУВАННЯ РОЗЧИНУ Н-ПЕНТАНОЛ–НІТРОМЕТАН

Резюме

Проведене акустичне дослідження бінарного розчину н-пентанол–нітрометан при підході до його критичної точки розшарування з боку гомогенного стану в інтервалі частот 5–2800 МГц підтвердило існування аномального послаблення ультразвуку, яке може бути проаналізовано в термінах ефективного поглинання ультразвуку. На основі експериментальних даних в роботі виділені регулярна та флуктуаційна частини ефективного коефіцієнта поглинання звуку в дослідженому розчині. Показано, що флуктуаційна частина ефективного коефіцієнта поглинання може бути описана в термінах теорії релаксуючої теплоємності Феррела–Бхатачаржи, в рамках якої на основі отриманих експериментальних даних визначена масштабна кросоверна функція. Аналіз побудованої масштабної кросоверної функції дозволив знайти її параметри n та $\Omega_{1/2}$.