PHYSICS OF LIQUIDS AND LIQUID
SYSTEMS, BIOPHYSICS AND MEDICAL PHYSICS

https://doi.org/10.15407/ujpe63.4.308

L.A. BULAVIN,[1, 2] O.I. BILOUS,[3] A.V. BALEGA,[1] O.S. SVECHNIKOVA [1]
[1] Taras Shevchenko National University of Kyiv
(64/13, Volodymyrs'ka Str., Kyiv 01601, Ukraine; e-mail: bulavin221@gmail.com, svechnilova@gmail.com)
[2] Institute for Safety Problems of Nuclear Power Plants, Nat. Acad. of Sci. of Ukraine
(36a, Kirov Str., Chornobyl 07270, Kyiv region, Ukraine)
[3] National Aviation University
(1, Prosp. Cosmonaut Komarov, Kyiv 03058, Ukraine; e-mail: oksanabilous@univ.kiev.ua)

ANOMALIES OF THE SOUND ABSORPTION COEFFICIENT FOR BINARY SOLUTIONS WITH A CRITICAL STRATIFICATION TEMPERATURE

The results of the analysis of experimental data concerning the sound absorption in the nitromethane–n-pentanol and nitrobenzene-n-hexane solutions obtained in a wide frequency interval of 5–2800 MHz and measured along the isotherms and isoconcentrates, including their critical values, are presented. The detected anomalous dependences of the sound absorption coefficient were found to obey the laws of the dynamic scaling theory only in the fluctuation region of the problem parameters, $\omega\tau_{\text{fl}} \gg 1$. The sound frequency growth ($f \geq 110$ MHz) in the examined frequency interval, as well as moving away from the critical temperature and concentration values, is proved to transit the system from the critical region into the crossover, $\omega\tau_{\text{fl}} \sim 1$, or even hydrodynamic, $\omega\tau_{\text{fl}} \ll 1$, one.

Keywords: sound absorption coefficient, critical stratification point, binary solution, concentration fluctuations, acoustic relaxation.

1. Introduction

The influence of the temperature, concentration, pressure, and other thermodynamic parameters on the properties of substances in vicinities of their singular points has been a matter of many experimental and theoretical researches for almost two centuries [1–5]. Unlike the studies of the equilibrium properties of binary solutions in a vicinity of the critical stratification point [6], which have attracted the attention of physicists for a long time, there are much less experimental and theoretical studies of the dynamic properties of liquid systems and the kinetics of establishment of the equilibrium in them, when they are in the critical state. At the same time, the research of the kinetic properties of a substance near its critical stratification point–in particular, an abnormal behavior of the sound absorption coefficient–comprises a separate interest and results in contradictory conclusions. For instance, according to the dynamic theory of critical phenomena, the sound absorption coefficient should tend to infinity, when approaching the critical parameter values [7]. However, the available experimental data do not agree with this conclusion.

The indicated shortcomings can be eliminated by carrying out acoustic researches of the sound absorption coefficient (αf^{-2}) in a wide frequency, f, interval covering a number of variation areas for the param-

---

© L.A. BULAVIN, O.I. BILOUS, A.V. BALEGA, O.S. SVECHNIKOVA, 2018

eter $\omega\tau_{\text{fl}}$, where $\omega = 2\pi f$, and τ_{fl} is the lifetime of concentration fluctuations. In particular, this is an area located far from the critical point, $\omega\tau_{\text{fl}} \ll 1$, where the mean field theory is actual; the critical area $\omega\tau_{\text{fl}} \gg 1$ described by the fluctuation theory; and in the crossover region, for which $\omega\tau_{\text{fl}} \approx 1$. Taking the aforementioned circumstances into account, the determination of the frequency intervals corresponding to the indicated inequalities and for which the application of available theories to the analysis of the specific features in the abnormal behavior of the sound absorption coefficient would be correct is a challenging task. This work was aimed at the solution of this problem.

2. Research Objects and Experimental Technique

For experimental studies, binary solutions of nitromethane–n-pentanol and nitrobenzene–n-hexane with the upper critical stratification temperatures $T_{\text{cr}} = XXX$ and YYY K, respectively, were chosen. The fact that the indicated T_{cr} values belong to the room temperature interval allowed us to reduce the error of the experimental research.

While preparing solutions with various molar concentrations of the first component (nitromethane or nitrobenzene) in an interval of 0.1–0.8, chemically pure grade components were used. When studying the sound absorption coefficient in the solutions near their critical stratification temperature, the error of the specimen thermostating was $\pm 10^{-3}$ K.

The sound absorption coefficient was researched experimentally using the pulsed method, which was described in work [8] in detail. In particular, in a frequency interval of 5–150 MHz, the pulsed method with a variable distance was applied together with the resonance excitation of a quartz piezocrystal, whereas, in a frequency interval of 300–2800 MHz, the method of non-resonance excitation of a lithium niobate single crystal was used. Depending on the experimental conditions, the relative measurement errors for the sound absorption coefficient fell within an interval of 2–5%.

3. Peculiarities in the Behavior of the Sound Absorption Coefficient Along Isoconcentrates

Let us first analyze the experimental temperature dependences of the sound absorption coefficient obtained for the examined binary solutions with various concentrations, but at a fixed frequency. For illustration, we selected the nitrobenzene–n-hexane solution with the critical molar concentration of nitrobenzene $x_{\text{cr}} = 0.401$ and the nitromethane–n-pentanol solution with the critical molar concentration of nitromethane $x_{\text{cr}} = 0.385$.

As an example, in Fig. 1, the temperature dependences of αf^{-2} for the nitromethane–n-pentanol solution are shown. The curves depict the approximations of the corresponding temperature dependences by the formula [9]

$$\alpha f^{-2} \approx \eta_\nu \approx R_c^{Z_\mu} \approx A_0 t^{-\alpha_t \pm Z_\mu \nu}, \tag{1}$$

which was derived by the authors of the dynamic scaling theory. Here, A_0 is a frequency-dependent coefficient, $t = (T - T_{\text{cr}})/T_{\text{cr}}$ is the reduced temperature, $Z_\mu = 3.05$ is the dynamic critical index [10], $\alpha_t = 0.091$ is the critical index for the temperature dependence of the isochoric heat capacity, and $\nu = 0.633$ is the critical index for the temperature dependence of the correlation radius [10]. Earlier [11], it was shown that the sign in the power exponent in formula (1) can vary depending on the examined frequency interval.

Let us analyze the presented experimental data. In the low-frequency interval $\omega\tau_{\text{ri}} \ll 1$, where τ_{ri} is the acoustic relaxation time in the i-th dispersion interval (see Fig. 1, panels *1* and *2* for 10 and 30 MHz, respectively), the experimental values of the sound absorption coefficient (they are depicted by symbols) change monotonically, as the temperature grows. Such a universal dependence is typical of binary solutions with a critical stratification temperature. In particular, the sound absorption coefficient decreases with the temperature growth, as was predicted by the authors of the dynamic scaling theory [6–10]. This universal behavior was also clearly observed for the solution of nitrobenzene-n-hexane with the critical concentration in the indicated frequency interval.

If the frequency increases further, $f \geq 110$ MHz, the experimental data shown in Fig. 1 demonstrate anomalous, not universal critical dependences of the sound absorption coefficient. At even higher frequencies, these anomalies do not disappear, but radically change their temperature dependence. The absorption peak, which was observed at low frequencies in the fluctuation area ($\omega\tau_{\text{fl}} \gg 1$), decreases signifi-

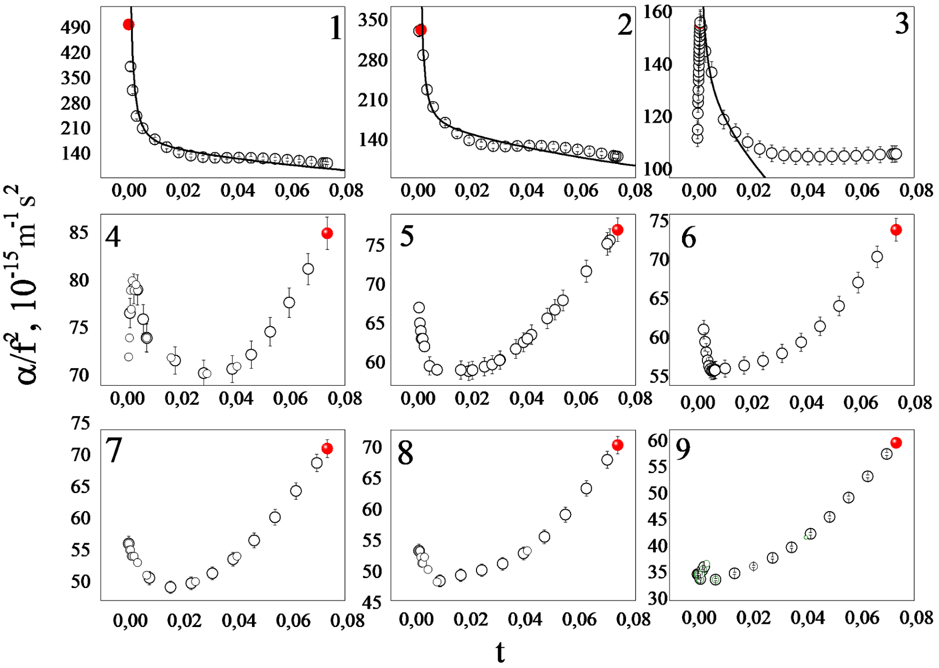


Fig. 1. Experimental temperature dependences of the sound absorption coefficient in the nitromethane–n-pentanol solution with the nitromethane molar concentration $x_{\rm cr} = 0.385$ at various frequencies $f = 10$ (*1*), 15 (*2*), 25 (*3*), 30 (*4*), 110 (*5*), 300 (*6*), 900 (*7*), 1500 (*8*), and 2500 MHz (*9*)

cantly by the absolute value and shifts toward the parameter values corresponding to the non-fluctuation area (see panels *4* to *9* in Fig. 1). The increase of the frequency (see panel *3* in Fig. 1) evidently results in the narrowing of the temperature interval, where formula (1) is applicable, to $T - T_{\rm cr} = 1$ K. The observed critical anomalies in the binary nitrobenzene–n-hexane solution with the critical parameters $T_{\rm cr}$ and $x_{\rm cr}$ are less pronounced than in the nitromethane–n-pentanol solution, despite that the absolute values of the sound absorption coefficient in the binary nitrobenzene–n-hexane solution are larger. Hence, the experimental data shown in Fig. 1 and similar temperature dependences obtained for the other binary solution with the corresponding critical stratification temperature and critical concentration testify that the abnormal temperature dependences of the sound absorption coefficient were revealed at frequencies $f \gg 110$ MHz. Those anomalies cannot be described by the known dependence (1). If the sound frequency grows further, the temperature dependence of the sound absorption coefficient totally transforms (see panels *5* to *9* in Fig. 1). Even the maximum value of the sound absorption coefficient (it is marked by the solid symbol) becomes abnormally shifted into the hydrodynamic temperature region.

However, a thorough analysis of the existing temperature dependences for the sound absorption coefficient demonstrated the absence of critical anomalies like those exhibited in Fig. 1, both for solutions with noncritical concentrations $x \lessgtr x_{\rm cr}$ and for pure solution components. As an example, the experimental temperature dependences of the sound absorption coefficients in the researched binary solutions with concentrations close to the critical stratification one, which are shown in Fig. 2, do not reveal characteristic anomalies. At the same time, the frequency dependences for all binary solutions are described by equations with two sections of acoustic relaxation. Expectedly, the temperature dependences of the sound absorption coefficient at $f =$ const are different for different binary solutions along their isoconcentrates $x \neq x_{\rm cr}$, because they are governed by individual molecular mechanisms rather than universal fluctuation ones.

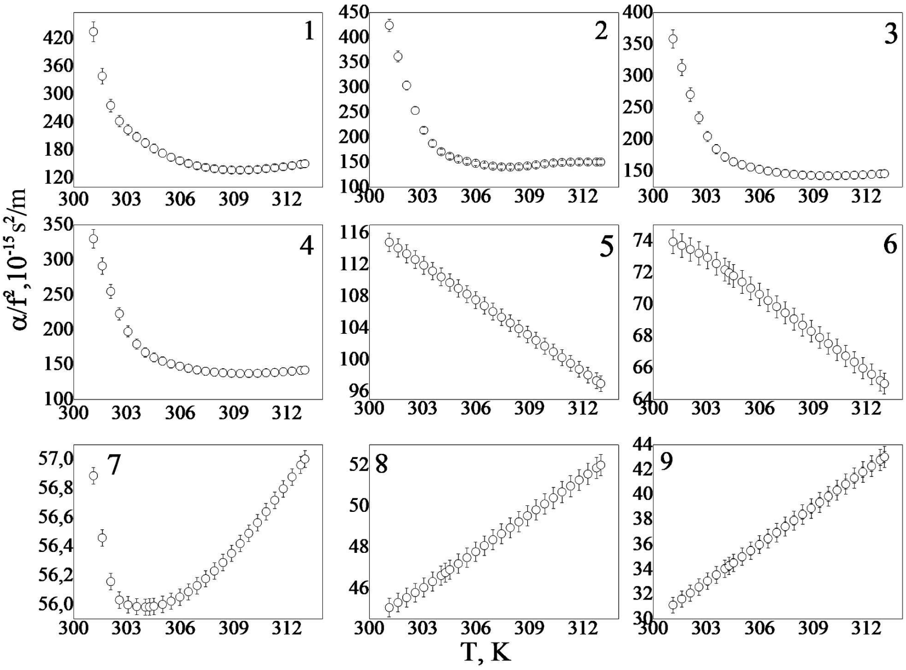


Fig. 2. The same as in Fig. 1, but for the nitromethane molar concentration $x = 0.3$

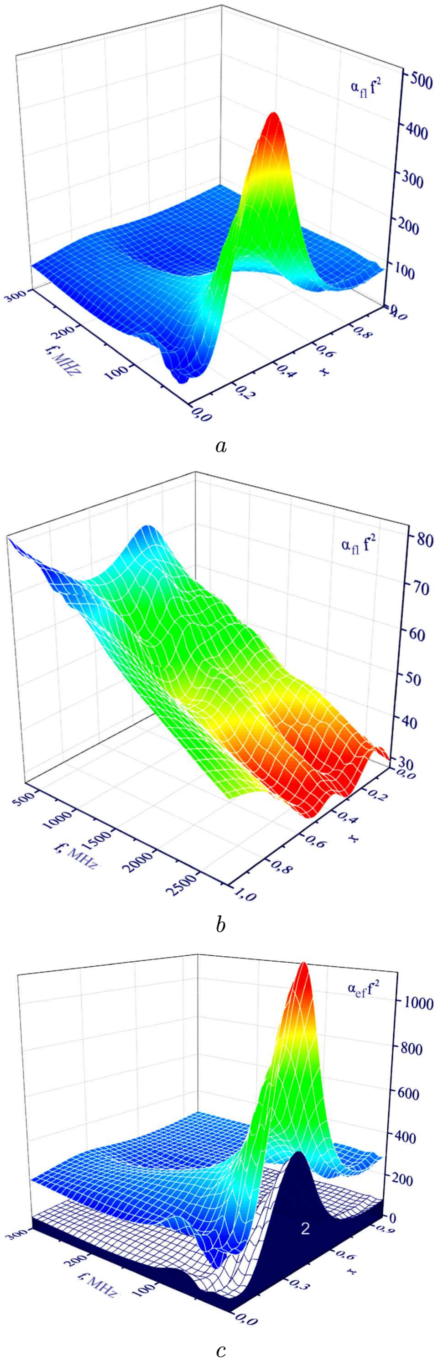
There are no such anomalies in the temperature dependences of the sound absorption coefficient for the pure components of the examined solutions. Nevertheless, the quantity $\alpha f^{-2}(f,T)$ increases with the temperature in the whole frequency interval in pure nitrobenzene and nitromethane, but decreases in pure n-pentanol and hexane. This dependence decreases linearly in the case of n-amyl alcohol and by the power law in the case of hexane. The analysis of the frequency dependences for the pure components of the examined binary solutions revealed only one region of acoustic relaxation, with the absolute value of the sound absorption coefficient being insignificant in comparison with the corresponding values for binary solutions. In hexane, nitromethane, and nitrobenzene, the relaxation processes can be described in the framework of a model, where a liquid is considered as a mixture of broken and unbroken bonds. The structural relaxation in n-pentanol is assumed to be associated with the break of hydrogen bonds in associatives. Unlike molecular mechanisms, which are completely responsible for the relaxation processes in pure liquids, the fluctuation mechanisms are responsible for the anomalous behavior of the dependence $\alpha f^{-2}(f,T)$ for binary solutions in vicinities of their critical stratification temperature.

Hence, the analysis of the experimental and literature data obtained for the sound absorption coefficient in binary or ternary solutions [12, 13] showed that the considered abnormal non-universal temperature dependences are observed, if the temperature dependences of the sound absorption coefficient are different – decreasing or increasing – for the pure components of the examined solutions. This conclusion is definitely confirmed by the experimental data obtained for the temperature dependences of the sound absorption coefficient in the frequency interval $f \gg 110$ MHz.

As a result, one more conclusion can be drawn that the anomalies in the temperature dependences of the sound absorption coefficient stem from both concentration fluctuations and structural peculiarities in the binary solutions under consideration.

4. Three-Dimensional Representations for the Sound Absorption Coefficient at Various Frequencies

Let us denote the component of the sound absorption coefficient associated with the molecular mechanisms as a regular part, $\alpha_{\text{reg}} f^{-2}$, and the component associated with concentration fluctuations as a fluctuation



a

b

c

Fig. 3. Three-dimensional representations of the dependence $\alpha f^{-2}(f,x)$ for the binary nitromethane–n-pentanol solution along the isotherm $\Delta T = 0.1$ K: the fluctuation part $\alpha_{\rm fl} f^{-2}(f,x)$ of the absorption coefficient [see Eq. (2)] in the low-frequency interval (10–300 MHz) (*a*), the fluctuation part $\alpha_{\rm fl} f^{-2}(f,x)$ in the high frequency interval (400–2800 MHz) (*b*), the total sound absorption coefficient and its regular part (*c*)

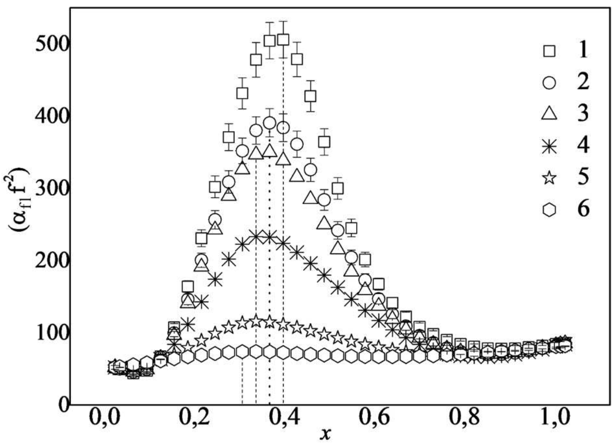


Fig. 4. Concentration dependences of the sound absorption coefficient αf^{-2} for the binary nitromethane–n-pentanol solution in the low-frequency interval at the frequencies $f = 10$ (*1*), 25 (*2*), 30 (*3*), 50 (*4*), 110 (*5*), and 300 MHz (*6*). $\Delta T = 0.1$ K

one, $\alpha_{\rm fl} f^{-2}$, so that the total sound absorption coefficient equals to their sum [14]:

$$\alpha f^{-2} = \alpha_{\rm fl} f^{-2} + \alpha_{\rm reg} f^{-2}. \tag{2}$$

Our experimental studies of the peculiarities in the behavior of the sound absorption coefficient for various binary solutions in wide frequency, concentration, and temperature intervals allowed us not only to reveal and analyze the features of temperature anomalies, and to study their molecular and fluctuation mechanisms, but also to plot three-dimensional representations of the dependences $\alpha f^{-2}(f,T)$. Figure 3 demonstrates those dependences for the binary nitromethane–n-pentanol solutions.

Let us analyze these dependences. As one can see, in a frequency interval of 10–300 MHz, the fluctuation part of the sound absorption coefficient in the binary solution gradually increases when the concentration approaches the critical value. A further frequency growth to 400–2800 MHz results in the appearance of nontypical anomalous dependences for the fluctuation part of the sound absorption coefficient; i.e. the anomalies have a non-universal character, which may probably be associated with both molecular mechanisms and the sound scattering by concentration fluctuations [15] (see panels *5* to *9* in Fig. 1). As a result, this behavior can no longer be described by the power-law dependence (1) even in a narrow temperature interval. The dependences shown

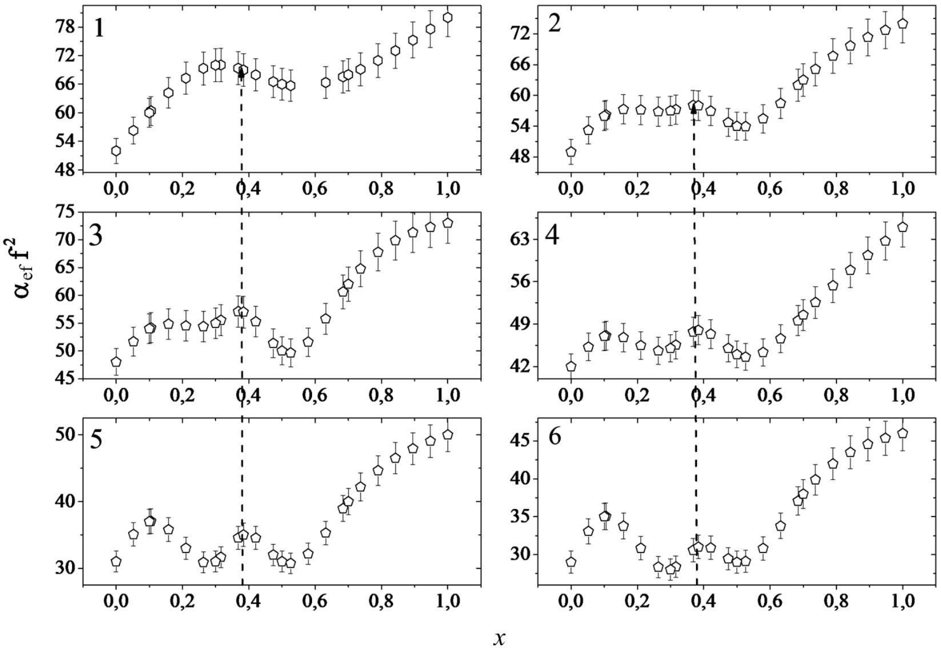


Fig. 5. The same as in Fig. 4, but in the high-frequency interval: f = 10 (*1*), 25 (*2*), 30 (*3*), 50 (*4*), 110 (*5*), and 300 MHz (*6*)

in Fig. 3, *c*, as well as similar plots for other examined binary solutions [12, 13], testify that the fluctuation part of the sound absorption coefficient is smaller than the regular part even along the critical isotherm and isoconcentrate. Therefore, our research cancels the inequality

$$\frac{(\alpha f^{-2})_{\rm fl}(f,x)}{(\alpha f^{-2})_{\rm reg}(f,x)} > 1,$$

which was obtained in the framework of the dynamic theory of critical phenomena [10, 12].

5. Peculiarities in the Behavior of the Sound Absorption Coefficient Along Isotherms

Figures 4 and 5 demonstrate the x-cross-sections of the dependences $\alpha f^{-2}(f,x)$. The corresponding detailed analysis shows that if the sound frequency in the low-frequency interval ($\omega\tau_{\rm ri} \ll 1$, Fig. 4) increases, the concentration corresponding to the maximum of the absorption coefficient decreases.

The analysis of the dependences obtained in the high-frequency interval (Fig. 5) testifies that the concentration dependences of the sound absorption coefficient along the isotherm $\Delta T = = 0.1$ K are non-universal. In particular, according to the analysis of the data depicted in Fig. 4, the concentration corresponding to the maximum of the fluctuation part of the sound absorption coefficient (2) becomes shifted into the concentration region below the critical value, $x < x_{\rm cr}$. Provided this condition, the plotted dependence $x_{\rm cr}(f)$, which is analogous to the Widom line, demonstrates that the frequency growth results in a decrease of the concentration corresponding to the maximum of the sound absorption coefficient. A further increase of the frequency shifts the concentration corresponding to the maximum of the sound absorption coefficient toward the values of the pure components of the researched solutions.

The analysis of the dependences obtained in the high-frequency interval (Fig. 5) shows that the concentration dependences of the effective sound absorption coefficient along the critical isotherm $\Delta T = 0.1$ K have a non-universal behavior. In particular, in a frequency interval of 400–2800 MHz (Fig. 5), the maximum of the sound absorption coefficient corresponds to pure nitromethane.

The dependences of the anomalous sound absorption coefficient $\alpha f^{-2}(f,x)$ plotted for the other an-

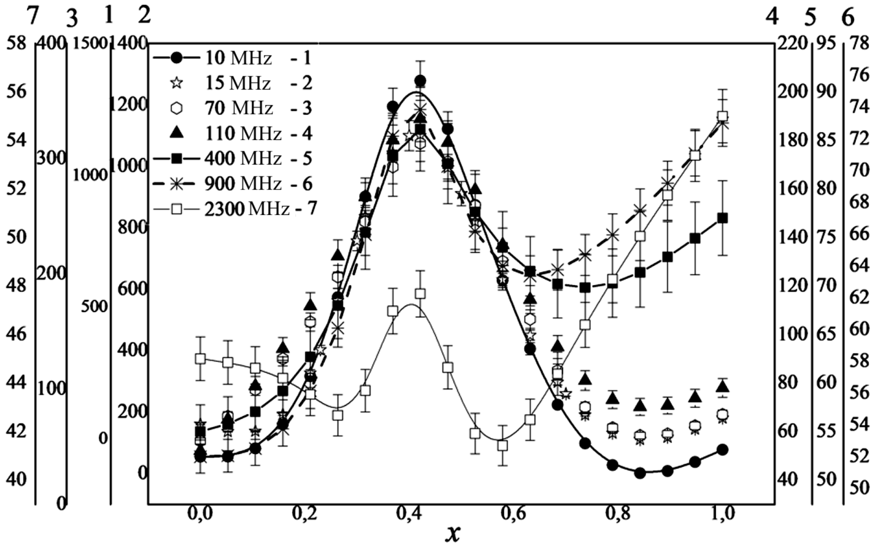
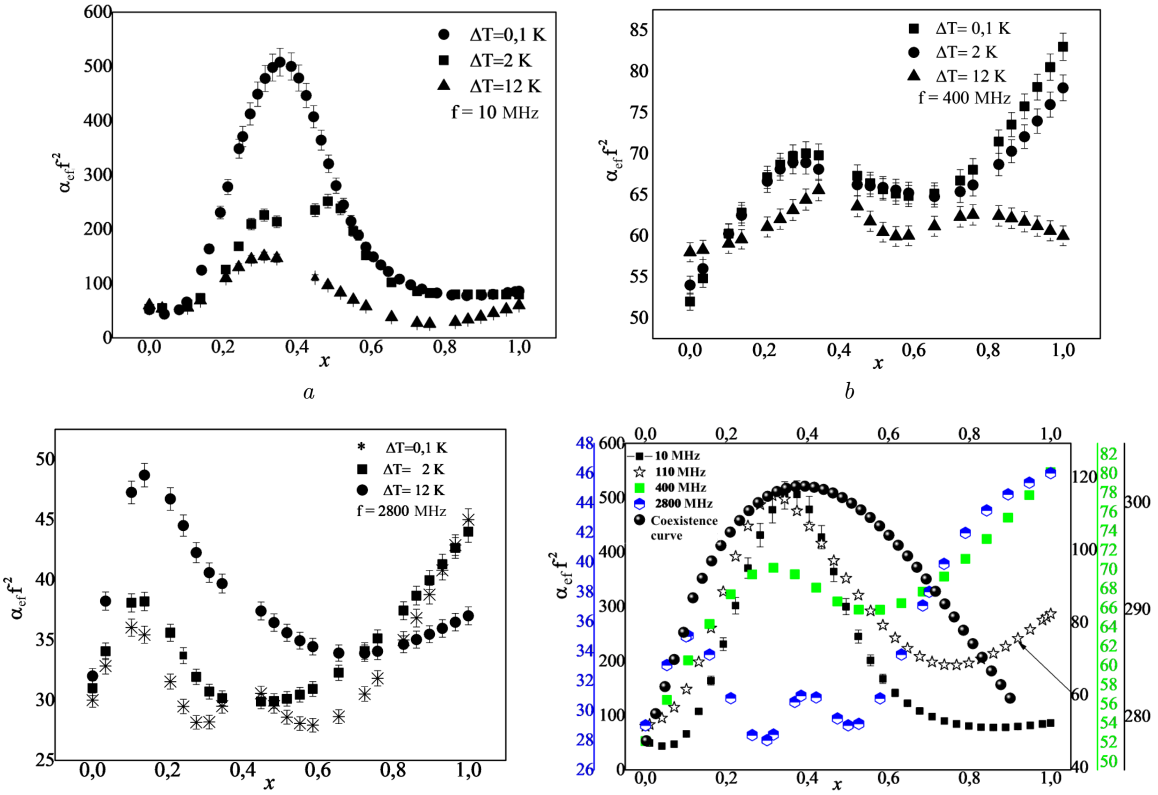


Fig. 6. Concentration dependences of the sound absorption coefficient $\alpha f^{-2}(f,x)$ along the isotherm at various f = const for the binary nitrobenzene–n-hexane solution



a *b*

c *d*

Fig. 7. Concentration dependences of the fluctuation part of the sound absorption coefficient along the isotherm at various f = const for the binary nitromethane–n-pentanol solution

alyzed binary solution, nitrobenzene-n-hexane, are shown in Fig. 6. The main conclusion, which can be drawn on the basis on the data depicted in Figs. 4 to 6, consists in that the existing anomalies of the sound absorption coefficient should be analyzed in three frequency areas – $\omega\tau_{\text{fl}} \gg 1$, $\omega\tau_{\text{fl}} \sim 1$, and $\omega\tau_{\text{fl}} \ll 1$ – in which their behaviors are different. Therefore, let us analyze the dependences $\alpha f^{-2}(f, x)$ (Fig. 6) and $\alpha f_{\text{fl}}^{-2}(f, x)$ (Fig. 7), which were obtained for two studied binary solutions, along the isotherms and at constant frequencies (f = const), but in different frequency regions.

The concentration dependences of the ultrasound absorption coefficient along the isotherms (see Fig. 7, *a*) have a universal character (i.e. typical anomalies) in the fluctuation region ($\omega\tau_{\text{fl}} \gg 1$), a transient character in the crossover region ($\omega\tau_{\text{fl}} \sim 1$), and a character typical of solutions with noncritical parameters in the hydrodynamic region ($\omega\tau_{\text{fl}} \ll 1$). At higher frequencies (Fig. 7, *b*), the maximum of the sound absorption coefficient is observed at the mole fraction of nitromethane $x = 1$ for all studied frequency regions ($\omega\tau_{\text{fl}} \gg 1$, $\omega\tau_{\text{fl}} \sim 1$, and $\omega\tau_{\text{fl}} \ll 1$), This behavior is inherent to solutions with noncritical parameters. If the sound frequency grows further toward the hypersonic range (Fig. 7, *c*), besides the observed non-universal anomalies of the sound absorption coefficient (Fig. 7, *b*), the temperature corresponding to the maximum of the sound absorption coefficient becomes shifted from $\Delta T = 0.1$ K to $\Delta T = 12$ K. Figure 7, *d* exhibits the “coexistence” curve for the nitromethane–n-pentanol solution (black balls) obtained taking into account different absorption coefficient values at different frequencies. The corresponding fluctuation region of temperatures $\Delta T = 0.1$ K.

6. Conclusions

In this work, the dependences of the sound absorption coefficient along the isotherms and isoconcentrates have been studied at various frequencies for two binary solutions: nitromethane–n-pentanol and nitrobenzene–n- hexane. A conclusion can be drawn that the theory of dynamic scaling describes the anomalies of the sound absorption coefficient only in the fluctuation frequency region $\omega\tau_{\text{fl}} \ll 1$. In the examined frequency interval of 5–2800 MHz, the growth of the frequency above $f = 110$ MHz, as well as the deviations of the temperature or the solution concentration from their critical values, brings the system into the crossover ($\omega\tau_{\text{fl}} \sim 1$) or even hydrodynamic ($\omega\tau_{\text{fl}} \gg 1$) area.

1. M.J. Amani, M.R. Gray, J.M. Shaw. Phase behavior of Athabasca bitumen+water mixtures at high temperature and pressure. *J. Supercrit. Fluid.* **77**, 142 (2013).
2. M.A. Anisimov. Universality versus nonuniversality in asymmetric fluid criticality. *Condens. Matter. Phys.* **16**, 23603 (2013).
3. D.A. Beysens, Y. Garrabos. The phase transition of gases and liquids. *Physica A* **281**, 361 (2000).
4. J. Bonart. Phase transitions and diffusion in dissipative classical and quantum systems. *Paris* **6** (2013).
5. M. Gross, F. Varnik. Critical dynamics of an isothermal compressible nonideal fluid. *Phys. Rev. E* **86**, 61119 (2012).
6. L.A. Bulavin, Yu.O. Plevachuk, V.M. Sklyarchuk, *Critical Stratification Phenomena in Liquids on the Earth and in Space* (Naukova Dumka, 2001) (in Ukrainian).
7. R.A. Ferrell. Decoupled-mode dynamical scaling theory of the binary-liquid phase transition. *Phys. Rev. Lett.* **24**, 1169 (1970).
8. V.S. Sperkach, M.I. Shakhparonov. Theory of viscosity in liquids. Mechanism of water viscosity. *Zh. Fiz. Khim.* **55**, 1732 (1981) (in Russian).
9. R.A. Ferrell, J.K. Bhattacharjee. Dynamic universality and the critical sound velocity in a binary liquid. *Phys. Rev. B* **24**, 4095 (1981).
10. M.A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, 1991).
11. V.S. Sperkach, A.D. Alekhin, O.I. Bilous. Acoustic properties of liquid systems near the critical temperature. *Ukr. Fiz. Zh.* **49**, 976 (2004) (in Ukrainian).
12. S.Z. Mirzaev, U. Kaatze. Adiabatic coupling constant of mitrobenzene–n. *Int. J. Thermophys.* **37**, 1 (2016).
13. K. Jagannathan, A. Yethiraj. Dynamics of fluids near the consolute critical point: A molecular-dynamics study of the Widom–Rowlinson mixture. *J. Chem. Phys.* **122** (24), 244506 (2005).
14. J.K. Bhattacharjee, U. Kaatze. Fluctuations near the critical micelle concentration. I. Premicellar aggregation, relaxation rate, and isentropic compressibility. *J. Phys. Chem. B* **117**, 3790 (2013).
15. L.A. Bulavin, O.I. Bilous, O.S. Svechnikova. Relaxation time of concentration fluctuations in a vicinity of the critical stratification point of the binary mixture n-pentanol–nitromethane. *Ukr. Fiz. Zh.* **61**, 885 (2016) (in Ukrainian).

Received 02.10.17.
Translated from Ukrainian by O.I. Voitenko

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

АНОМАЛІЇ КОЕФІЦІЄНТА ПОГЛИНАННЯ ЗВУКУ БІНАРНИХ РОЗЧИНІВ З КРИТИЧНОЮ ТЕМПЕРАТУРОЮ РОЗШАРУВАННЯ

Резюме

У роботі наведено результати аналізу експериментально отриманих даних коефіцієнта поглинання звуку у широкому діапазоні частот 5–2800 МГц вздовж ізотерм та ізоконцентрат, включно з їхніми критичними значеннями для н-пентанолу-нітрометану та нітробензолу-н-гексану. Встановлено, що зафіксовані аномальні залежності коефіцієнта поглинання звуку підпорядковуються законам, отриманим у теорії динамічного скейлінгу, тільки у флуктуаційній області їхніх параметрів $\omega\tau_{\text{фл}} \gg 1$. Доведено, що збільшення частоти звуку ($f \geq 110$ МГц), для досліджуваного діапазону частот, як і відхід від критичних значень температури чи концентрації, виводить систему з критичної у кросоверну $\omega\tau_{\text{фл}} \sim 1$, або навіть гідродинамічну область $\omega\tau_{\text{фл}} \ll 1$.