ACOUSTIC SPECTROSCOPY OF BINARY SOLUTIONS NEAR THE CRITICAL TEMPERATURE OF STRATIFICATION

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Experimental study of nitromethane—n-amyl alcohol and nitrobenzene—hexane binary solutions near the critical temperature of stratification have been carried out by acoustic spectroscopy in a wide frequency range (f=5÷2800 MHz). On the basis of the obtained experimental data, the frequency and temperature dependences of the sound absorption coefficient were studied in the range of low (f=5÷110 MHz) and high (f=1000÷2800 MHZ) frequencies. The obtained results confirm the conclusions of the dynamic theory of critical phenomena.

Experimental investigations of the equilibrium and kinetic properties of liquid systems in the critical state still remain one of the actual problems of condensed matter physics [1, 2]. However, a main attention is paid now to studying the equilibrium properties in the critical state. But the number of investigations of the kinetic properties of liquid systems near the phase transition, especially when acoustic methods are used, is considerably less. It is worth noting that just methods of acoustic spectroscopy, that are very sensitive to structural and fluctuation transformations in liquids [2—4], could become a reliable tool for testing the various conclusions of the modern dynamical theory of critical phenomena [5, 6]. Nowadays, however, an application of these methods is confined by the narrow range of frequencies. From our point of view, this considerably restricts the unique possibilities of this method concerning the investigation of the critical state of matter.

The aim of the work is to study the kinetic properties of liquids in the critical state by acoustic spectroscopy. In this case, we use a wide range of acoustic frequencies from 5 to 3000 MHz.

The used acoustic technique was developed at the Chair of Molecular Physics of Kyiv State University by V.S. Sperkach [7, 8] and is has been used for a long time in the investigations of various kinetic properties of liquid systems (individual liquids, binary solutions, disperse and colloid systems) in a wide range of thermodynamical parameters far from the critical state. The technique, peculiarities of carrying out the experiment, methods of processing the experimental data is described in [7—9].

In this work, the method of acoustic spectroscopy [8] has been used for the first time in studying the kinetic properties of binary solutions close to the critical temperature of stratification. As objects of the research, we have chosen nitromethane—n-amyl alcohol (the critical mole fraction X_c=0.384) and nitrobenzene-hexane (X_c=0.4) solutions. In these solutions, the measurements of the temperature dependence of the amplitude coefficient of sound absorption (α) in the single-phase region ($T > T_c$) close to the critical temperature of stratification T_c in the wide range of frequencies 5—3000 MHz were carried out.

The obtained dependences $\alpha \cdot f^{-2}$ (T) are depicted in Figs. 1 and 2. As seen, in the whole studied frequency range, the sound absorption coefficient increases with approaching the critical temperature. Moreover, one can see that the sound absorption at low frequencies (ω ≈5÷10 MHz) is much stronger than that at high frequencies (ω ≥100 MHz). The obtained data (Figs. 1 and 2) were used to analyze the temperature dependence $\alpha \cdot f^{-2}(t)$ in the form

$$\frac{\alpha}{f^2} = A_0 t^{-n(\omega)} A_0 \left(\frac{T - T_c}{T_c}\right)^{-n(\omega)} . \qquad (1)$$

Here, A_0 is a coefficient which depends on frequency, and $n(\omega)$ is an effective exponent.

The coefficients $A_0(\omega)$ and effective exponents $n(\omega)$ were calculated for each used frequency ω. For example, dependence (1) on log-log scale for the frequency ω ≈10 MHz is shown in Fig. 3.

On the basis of these data, we derived for nitromethane–n-amyl alcohol solution: n=1.1±0.1, A_0=4.6·10^{-16} m^{-1}s^2; for nitrobenzene–hexane solution n=1.25±0.02, A_0=1.04·10^{-16} m^{-1}s^2. Values of the effective exponent n were found to be close to similar ones calculated on the basis of the data on $\alpha \cdot f^{-2}(t)$ [4, 10] in the same frequency range ω ≈10 MHz.

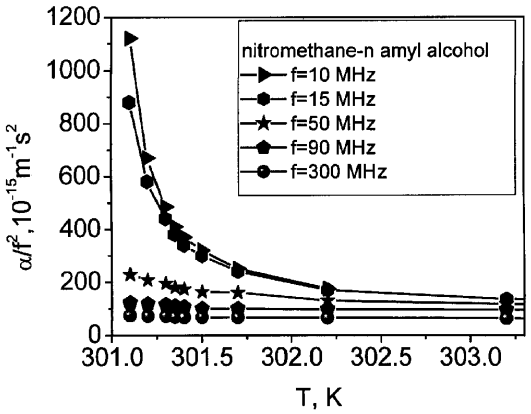

Fig. 1. The dependences of α/f^2 magnitude on temperature in nitromethane–n-amyl alcohol solution with critical mole fraction 0.384 of amyl alcohol for various frequencies

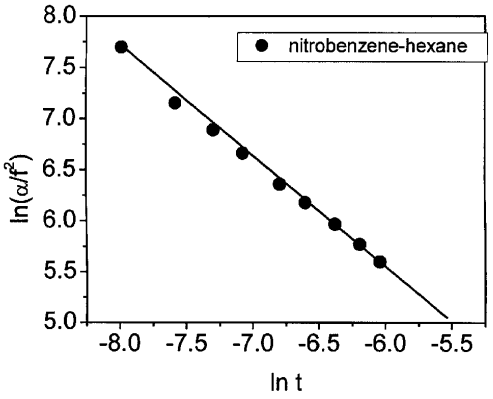

Fig 3. The dependence of α/f^2 magnitude on temperature t in log-log scale at frequency f=10 MHz for nitrobenzene–hexane solution with mole fraction of nitrobenzene 0.4

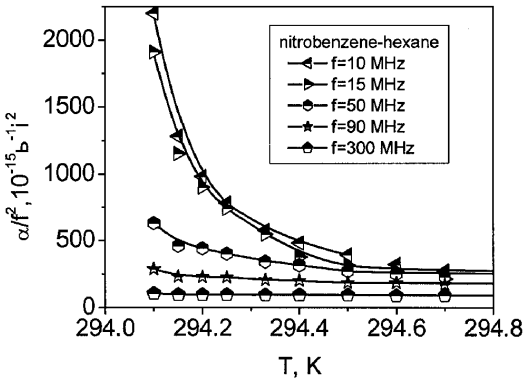

Fig. 2. The same as in Fig. 1 for nitrobenzene–hexane solution with critical mole fraction of nitrobenzene

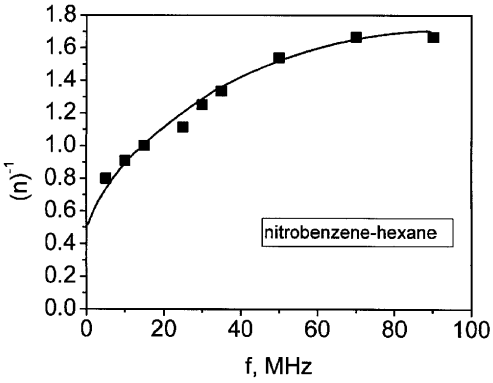

Fig. 4. The dependence of reciprocal magnitude of the exponent n_1 on frequency for given binary solution with critical concentration

Similarly, the dependences $\alpha \cdot f^{-2}(t)$ (1) were analyzed for the rest studied frequencies ω. In this case, the values of the effective coefficients $A_0(\omega)$ and exponents $n(\omega)$ were found. It was revealed that the exponent $n(\omega)$ increases with decrease in the ultrasound frequency ω.

The dependence $n^{-1}(\omega)$ for nitrobenzene–hexane solution is shown in Fig. 4. As seen, it tends to a finite value $n^{-1} \approx 0.5$ as $\omega \to 0$. So, the exponent in relation (1) that describes the temperature dependence of the sound absorption coefficient at $\omega \to 0$ equals $(n\omega \to 0) \approx 2$.

Let's compare this result with the conclusions of the dynamical theory of critical phenomena [5, 6] concerning relation (1). According to [5, 6], in the hydrodynamic region which is characterized by the inequalities $qR_c << 1$ and $\omega\tau_c << 1$, the temperature dependence of the volume viscosity coefficient satisfies the relation $\eta_v \sim R_c^z \sim t^{z\nu}$ (here, $R_c = r_0 t^{-\nu}$ and $\tau_c \sim R_c^3$ are the correlation length and the relaxation time of fluctuations, respectively). According to [11, 12], z=3.065.

At high frequencies ($\omega\tau_c >> 1$), in accordance with the dynamical theory of critical phenomena [5], the volume viscosity and the absorption coefficient in the system are determined by the relation $\alpha \cdot f^{-2} \sim \eta_v \sim R_c \sim t^{-\nu}$ [9, 10] on the critical isochore.

According to [2], the critical exponent of the correlation length is $\nu \approx 2/3$. We have obtained the same value, $\nu \approx 0.62$, in [13, 14] from the on data the temperature behaviour of the shear viscosity coefficient in the same solutions, nitromethane–n-amyl alcohol and nitrobenzene–hexane.

Thus, the obtained temperature dependences $\alpha \sim t^{-3\nu} \sim t^{-2}$ in the case of $\omega\tau_c << 1$, and $\alpha \sim t^{-\nu} \sim t^{-2/3}$ for the case of $\omega\tau_c >> 1$ for the high frequencies confirm the theoretical conclusions of scaling theory [2, 5, 6].

So, the use of the method of acoustic spectroscopy just in the wide range of frequencies for investigating

the temperature dependence of the sound absorption coefficient along the direction of critical isoconcentrate ($T > T_c$, $X = X_c$) of binary solutions allowed us to confirm the conclusions of the dynamical theory of critical phenomena in the extreme cases $\omega\tau_c << 1$, $\omega\tau_c >> 1$.

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АКУСТИЧНА СПЕКТРОСКОПІЯ БІНАРНИХ РОЗЧИНІВ ПОБЛИЗУ КРИТИЧНОЇ ТЕМПЕРАТУРИ РОЗШАРУВАННЯ

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Р е з ю м е

Методами акустичної спектроскопії в широкому діапазоні частот ($f = 5 \div 2800$ МГц) проведено експериментальні дослідження бінарних розчинів нітрометан—н-аміловий спирт та нітробензол—гексан поблизу критичної температури розшарування. На основі отриманих експериментальних даних побудовано частотну та температурну залежності коефіцієнта поглинання звуку в указаних об'єктах в області низьких ($f = 5 \div 110$ МГц) і високих ($f = 1000 \div 2800$ МГц) частот. Отримані результати підтверджують висновки динамічної теорії критичних явищ.