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DETERMINATION OF THE MEAN RELAXATION TIME OF CONCENTRATION FLUCTUATIONS IN CRITICAL MIXTURES

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From experimental results for the absorption coefficients and propagation velocities of acoustic waves in a wide (ultrasonic and hypersonic) range, the mean lifetimes of fluctuations in concentration are determined for three critical mixtures: nitroethane-isooctane, isobutyric acid-water, and nitrobenzene-n-heptane. Evaluations are performed both in the immediate neighbourhood of, and far from the component separation temperature. A considerable increase of the mean concentration fluctuation lifetime is found in the immediate neighbourhood of the critical point.

1. *Introduction*

Acoustic investigation is a source of data on the concentration fluctuation kinetics of mixtures. Studies on the absorption of acoustic waves in a variety of critical mixtures, as well as in non-critical mixtures with positive deviations from the ideal case have revealed, for such mixtures, the existence of a region of acoustic absorption not observed in low-viscosity one-component liquids [1–4, 7, 8].

In the field of the acoustic wave, the distribution function of concentration fluctuations differs from the equilibrium function, and absorption of the wave is related with relaxation of the fluctuations in concentration. Thus, the theory assumes a spectrum of relaxation times.

The first to study relaxation time spectra in critical mixtures were Shakhparonov and Khabibullayev [1–4]. They first introduced the concept of concentration fluctuation relaxation and proposed a method to calculate spectra of the relaxation times, as well as the mean relaxation time τ_α of fluctuations in concentration of critical mixtures.

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For a continuous spectrum of relaxation times, the complex bulk elasticity modulus is of the form [5]:

$$\tilde{E} = E(\omega)+i\omega\eta(\omega) = E_0+i\omega\eta_\infty+i\omega\int_0^\infty \frac{H(\tau)d\tau}{1+\omega^2\tau^2}$$

$$= \left(E_0+\int_0^\infty \frac{\omega^2\tau H(\tau)d\tau}{1+\omega^2\tau^2}\right)+i\omega\left(\eta_\infty+\int_0^\infty \frac{H(\tau)d\tau}{1+\omega^2\tau^2}\right), \tag{1}$$

with: E_0 — the modulus at equilibrium, and η_∞ — the viscosity of the liquid at $\omega\tau \gg 1$.

The function $H(\tau)$ is referred to as the spectral density of relaxation times. The quantity $H(\tau) \cdot d\tau$ has the meaning of the over-all viscosity of all the Maxwellian mechanisms, the relaxation times of which lie within the interval from τ to $\tau+d\tau$. The function $H(\tau)$ can be said to represent the over-all modulus per unit increment of the logarithm of the relaxation time ($\ln \tau$).

Although the integration interval of (1) is infinite, integration is in practice made to extend throughout the region where $H(\tau) \neq 0$. Formula (1) leads to satisfactory results in the interpretation of experimental data in cases when the frequency-dependence range of $E(\omega)$ and $\eta(\omega)$ is very wide.

The function $H(\tau)$, which characterizes the relaxational properties of the medium, can be found by approximative methods from experimental data. In principle, strict methods exist as well; however, in order that they shall be applicable, $E(\omega)$ and $\eta(\omega)$ have to be given in the entire, infinite range of frequencies and, moreover, in analytical form. This is never the case in practice, and approximative procedures are commonly applied. We shall have recourse to a very simple method of this kind, known to yield good results. On the assumption that the function $\omega\tau/1+\omega^2\tau^2$ has the property of the δ-function, we have:

$$\omega\eta(\omega) = \omega\eta_\infty+\int_0^\infty \frac{H(\tau)}{\omega\tau}\,\frac{\omega\tau d(\omega\tau)}{1+\omega^2\tau^2} \approx \omega\eta_\infty+H\left(\frac{1}{\omega}\right),$$

$$H(\tau) = \omega[\eta(\omega)-\eta_\infty]|_{\omega=1/\tau}\,. \tag{2}$$

To elucidate the nature of the frequency-dependence of acoustic wave absorption on fluctuations in concentration one has to subtract, from the over-all absorption, the contributions due to other relaxational processes, i.e.

$$\frac{\alpha'}{f^2} = \frac{\alpha}{f^2}-B, \quad (3$$

where B accounts for the contributions to α/f^2 from all mechanisms except absorption due to fluctuations of the concentration.

In a first approximation, the value of B can be determined from the expression:

$$B = \left(\frac{\alpha}{f^2}\right)_{\omega\tau \gg 1} + x_1 B_1 + x_2 B_2. \tag{4}$$

Above, B_1 is the acoustic wave absorption in the first term, and B_2 — the additional absorption in the second term. Thus Eq. (2) permits the determination of the absorption at various frequencies due to the fluctuations in concentration.

2. Experimental results and their interpretation

An acoustic investigation was carried out for the critical mixtures: nitroethane-isooctane, isobutyric acid-water, and nitrobenzene-n-heptane in a wide interval of frequency, both ultra- and hypersonic. For the physico-chemical parameters of the critical mixtures, we refer to our paper [9].

The propagation velocity and absorption coefficient was measured on three distinct experimental stands, operating at 30 to 150 MHz and 300 to 1000 MHz, applying appropriate pulse methods with resonance and non-resonance excitation of the piezoelectric transducers, as well as at hypersonic frequencies, having recourse to the shift and halfwidth of Mandelshtam–Brillouin components of the fine structure of the Rayleigh scattered line. The equipment and method are described in detail in Ref. [10].

A description of the experimental data applying Mandelshtam–Leontovich equations [11], in terms of a single relaxation time, is not possible.

By Ref. [11], the dependence of $(\alpha'/f^2)^{-1}$ on f^2 should be a linear one. In our case, it is not linear for any of the mixtures studied. As an example, Figs 1–3 show α'/f^2 vs f^2 for the critical concentrations of the three mixtures. Similar curves were obtained at all concentrations; however, we refrain from adducing them here.

To elucidate the nature of the frequency-dependence of the additional absorption α' we plotted curves of $\lg \alpha'$ vs $\lg \omega$, which turned out to be linear for all the mixtures throughout the frequency range studied (see, for example, Figs 4–6). In other words, α' can be expressed as:

$$\alpha' = a\omega^{p+1}, \tag{5}$$

where a and p are parameters, dependent on the composition and temperature of the mixture.

It should be noted that, with varying concentration and temperature, p varies in the interval $0 < p \leqslant 1$. At $x \to 1$ and $x \to 0$ the parameter p increases, tending to unity, whereas at $x \to x_{cr}$ and $t \to t_{cr}$ it decreases, and the parameter a increases (cf. Tables I–III).

Applying the equation [5]:

$$\tau_\alpha = \frac{\int\limits_0^\infty \tau H(\tau) d(\ln \tau)}{\int\limits_0^\infty H(\tau) d(\ln \tau)} = \frac{K_{1/p-1}[2\sqrt{\beta \cdot \gamma}]}{K_1[2\sqrt{\beta \cdot \gamma}]} \cdot \left(\frac{\beta}{\gamma}\right)^{1/2p} \tag{6}$$

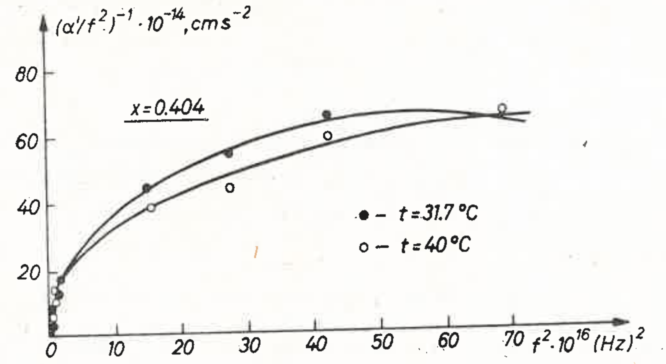

Fig. 1. $(\alpha'/f^2)^{-1}$ vs f^2 in nitroethane-isooctane mixture of critical concentration $x = 0.404$, for two temperatures (x — molar fraction of isooctane)

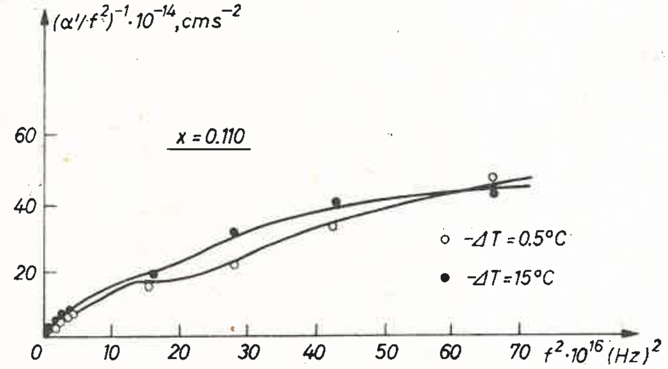

Fig. 2. $(\alpha'/f^2)^{-1}$ vs f^2 in isobutyric acid-water mixture of critical concentration $x = 0.110$, for two ΔT (x — molar fraction of isobutyric acid)

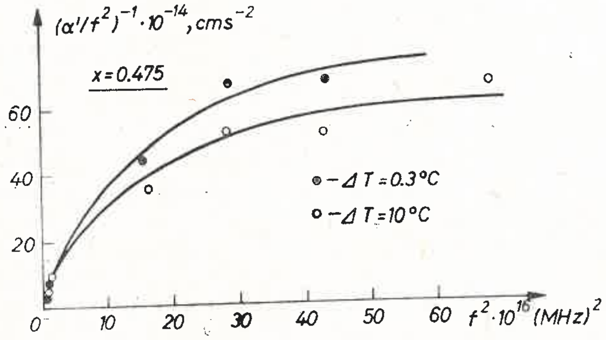

Fig. 3. $(\alpha'/f^2)^{-1}$ vs f^2 in nitrobenzene-n-heptane mixture of critical concentration $x = 0.475$, for two ΔT (x — molar fraction of nitrobenzene)

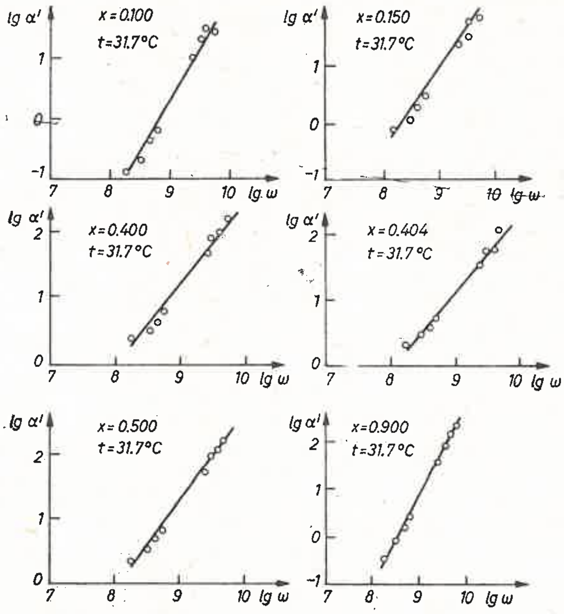

Fig. 4. lg α' vs lg ω in nitroethane-isooctane mixture for various concentrations, at $t = 31.7$°C (x — molar fraction of isooctane)

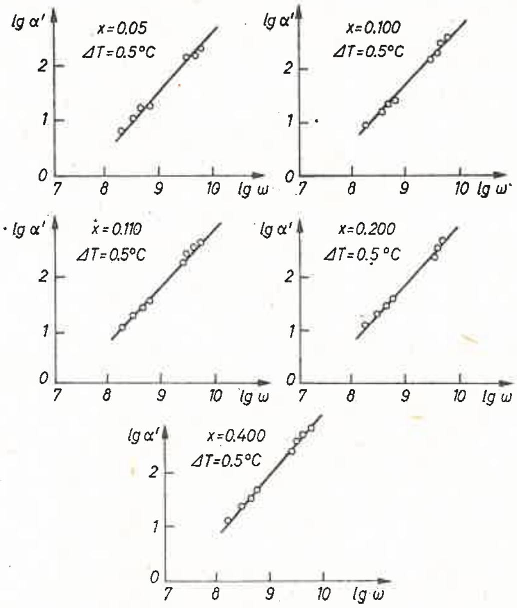

Fig. 5. lg α' vs lg ω in isobutyric acid-water mixture for various concentrations at $\Delta T = 0.5$°C (x — molar fraction of isobutyric acid)

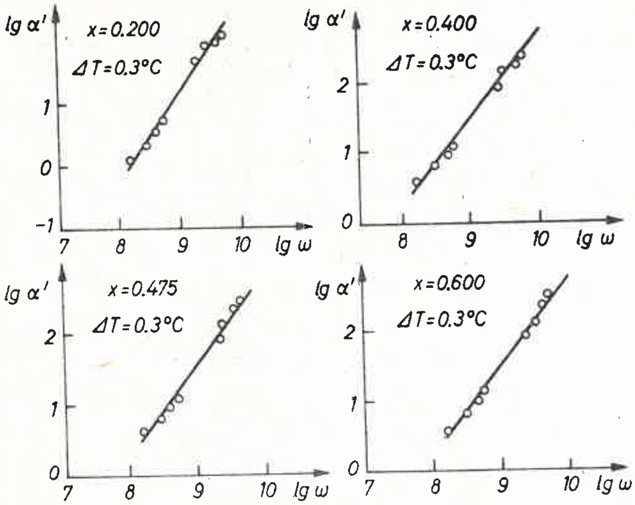

Fig. 6. $\lg \alpha'$ vs $\lg \omega$ in nitrobenzene-n-heptane mixture for various concentrations at $\Delta T = 0.3°C$

TABLE I

Nitroethane-isooctane

x, molar fraction of nitroethane	T [°C]	a	p	τ_α, s
0.100	31.7	1.4×10^{-16}	0.67	1.41×10^{-10}
0.150		6.1×10^{-15}	0.39	6.03×10^{-9}
0.400		7.5×10^{-10}	0.23	5.89×10^{-7}
0.404		4.1×10^{-10}	0.18	1.58×10^{-5}
0.500		6.3×10^{-11}	0.33	2.34×10^{-8}
0.900		2.6×10^{-17}	0.88	0.24×10^{-10}
0.100	35	1.6×10^{-16}	0.64	1.90×10^{-10}
0.150		6.5×10^{-11}	0.28	1.02×10^{-7}
0.400		2.0×10^{-10}	0.24	4.90×10^{-7}
0.404		1.4×10^{-11}	0.20	3.98×10^{-6}
0.500		3.3×10^{-11}	0.28	1.02×10^{-7}
0.900		1.3×10^{-17}	0.87	0.26×10^{-10}
0.100	40	3.2×10^{-16}	0.78	0.55×10^{-10}
0.150		2.0×10^{-11}	0.37	9.12×10^{-9}
0.400		1.9×10^{-10}	0.30	5.36×10^{-8}
0.404		1.2×10^{-10}	0.25	3.16×10^{-7}
0.500		4.1×10^{-11}	0.30	5.36×10^{-8}
0.900		3.1×10^{-17}	0.89	0.22×10^{-10}

TABLE II

Isobutyric acid-water

x, molar fraction of isobutyric acid	ΔT [°C]	a	p	τ_α, s
0.05	0.5	3.4×10^{-9}	0.15	2.29×10^{-4}
0.100		1.0×10^{-9}	0.11	7.42×10^{-2}
0.110		2.1×10^{-8}	0.02	—
0.200		9.3×10^{-8}	0.072	—
0.400		2.2×10^{-9}	0.154	1.55×10^{-4}
0.05	8	1.0×10^{-10}	0.17	3.46×10^{-5}
0.100		1.1×10^{-9}	0.11	7.41×10^{-2}
0.110		4.0×10^{-8}	0.03	—
0.200		2.2×10^{-8}	0.123	6.03×10^{-3}
0.400		4.7×10^{-9}	0.136	1.2×10^{-4}
0.05	15	4.7×10^{-9}	0.154	6.32×10^{-4}
0.100		1.4×10^{-9}	0.135	2.72×10^{-3}
0.110		3.8×10^{-8}	0.05	—
0.200		2.7×10^{-9}	0.13	2.69×10^{-3}
0.400		4.0×10^{-9}	0.15	2.29×10^{-4}

TABLE III

Nitrobenzene-n-heptane

x, molar fraction of nitrobenzene	ΔT [°C]	a	p	τ_α, s
0.200	0.3	1.1×10^{-12}	0.455	1.95×10^{-9}
0.400		1.1×10^{-11}	0.288	7.94×10^{-8}
0.475		2.1×10^{-10}	0.206	2.75×10^{-6}
0.600		5.0×10^{-10}	0.242	4.37×10^{-7}
0.200	10	2.1×10^{-13}	0.579	3.67×10^{-10}
0.400		2.0×10^{-12}	0.411	4.07×10^{-9}
0.475		2.4×10^{-11}	0.311	3.89×10^{-8}
0.600		8.1×10^{-11}	0.359	5.13×10^{-8}

we now proceed to calculate the mean relaxation time τ_α, characterizing the lifetime of the Fourier component of the fluctuation. Above, $K(z)$ is a MacDonald function.

Since $(\beta\gamma)^{1/2} \ll 1$, we can expand $K(z)$ in a power series in the argument $z = \sqrt{\beta\cdot\gamma}$; breaking off at the first term at $0 < z < 1$, we obtain:

$$\tau_\alpha = \tau_0(\beta\cdot\gamma)^{1-1/p} = 10^{-2+1/p}\left(\frac{1}{p}-2\right)!\; m^{2-1/p}\tau_A\left(\frac{\tau_A}{\tau_B}\right)^{p-1}, \tag{7}$$

where p is to be determined experimentally from the slope of lg α' vs lg ω, and $\tau_A = 1/2\pi f_{\max}$, $\tau_B = 1/2\pi f_{\min}$ are times corresponding to the maximal and minimal frequencies used in the measurements ($\tau_A \simeq 10^{-11}$ s), ($\tau_B \simeq 10^{-8}$ s); moreover, $m \leqslant 3$ and $10^{-4} < \gamma\beta < 10^{-2}$.

Using Eq. (7), we calculated τ_α for the three mixtures at all frequencies and temperatures applied. The results are given in Tables I–III whereas Fig. 7 shows, as an example, τ_α as a function of concentration for the mixture nitroethane-isooctane at three distinct temperatures.

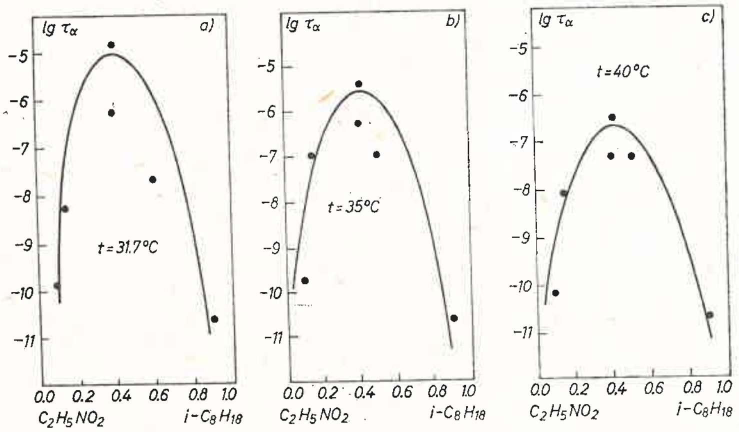

Fig. 7. τ_α vs concentration in nitroethane-isooctane mixture at the temperatures a) $t = 31.7$°C, b) $t = 35$°C, c) t = 40°C. The concentration is in molar fractions of isooctane

It is seen from Tables I–III that τ_α increases by several orders of magnitude in the neighbourhood of the critical point, and maintains very large values throughout a wide range of concentrations and temperatures.

The basis for the process of relaxation of concentration fluctuations in mixtures consisting of components A and B is given by the following reaction:

$$2AB \rightleftarrows AA + BB + \Delta H_k, \tag{8}$$

with ΔH_k — the heat effect of the reaction. The relaxating specific heat $\delta c_k \sim (\Delta H_k)^2$.

The processes of separation of fluctuations in concentration in the mixture isobutyric acid-water can be thought to involve much greater losses in energy than in the other mixtures, since in the former no hydrogen bonds exist between the molecules of the components. Hence, the relaxating part of the specific heat and the over-all relaxational force involved have to be relatively large i.e. the dispersion of the acoustic wave velocity has also to be large. In fact, our experimental results point to the largest dispersion of all in the case of isobutyric acid-water mixture [9].

Hence, from what has been said, the sharp increase in heat effect of the reaction [8], providing the basis for the process of relaxation of the concentration fluctuations, leads to a considerable increase in lifetime of the latter (see, Tables I–III) and an increase in their mean correlation radius.

3. Conclusions

a) It has been shown that the excess acoustic wave absorption in the critical mixtures studied is due to relaxation of fluctuations in concentration.

b) The mean concentration fluctuation lifetimes τ_α were determined for all three critical mixtures in the close neighbourhood as well as far from the critical temperature.

c) In the neighbourhood of the critical point, τ_α increases by several orders of magnitude and maintains high values in a wide range of concentrations and temperatures.

d) The study of α and v in critical mixtures in a wide range of frequencies can provide an effective means of disclosing the growth and decay kinetics of the concentrational fluctuations.

e) It is worth stressing that the τ_α-values obtained are approximate. In order to enhance the accuracy of τ_α determination, data have to be available concerning acoustic wave absorption in a still wider frequency range, including the audible range.

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