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COMPLEX INVESTIGATIONS OF THE CRITICAL N-AMYLIC ALCOHOL-NITROMETHANE MIXTURE WITH ACOUSTO-OPTIC METHODS

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Acoustic properties of the critical n-amylic alcohol-nitromethane mixture have been analysed in the ultra- and hypersonic range for two concentrations and at two temperatures. On the basis of obtained values of propagation velocities and acoustic wave absorption coefficients, fundamental physical, chemical and acoustic parameters have been determined, as well as the ratio of the total intensity of the central component to two MANDELSZTAM-BRILLOUIN components for individual concentrations of the investigated mixture.

Experimental results of investigations of absorption coefficients in a wide range of acoustic wave frequencies have been compared to the theories of FIXMAN and CZABAN. Also average life-times of concentration fluctuations in the n-amylic alcohol-nitromethane mixture have been estimated with the application of experimental results. This was done not only in the direct nearness of the temperature of component separation, but at temperatures distant from it also, according to the method given by M. J. SZACHPARONOW and P. K. CHABIBUŁŁAJEW.

The method of determining the mean correlation radius of concentration fluctuations and the mean radius of intermolecular interactions on the basis of the intensity of dispersed light in terms of the angle is described and measurement results of these quantities in the investigated mixture in the direct nearness of the critical point are given.

The kinetics of concentration fluctuations in the n-amylic alcohol-nitromethane mixture are analysed. With the application of the achieved mean concentration relaxation time, τ_a, correlation radius of concentration fluctuations, ξ, and the diffusion coefficient, D, the average length of concentration waves, Λ_a, in the mixture under investigation has been determined.

Introduction

The structure of liquid mixtures and their molecular miscibility hitherto has not been sufficiently explained. Among others optic and acoustic methods are applied in these problems. The method of molecular dispersion of light has proved itself to be very effective in explaining the state of short-range order in liquids and the molecular miscibility of liquids in terms of various factors. Molecular dispersion of light is caused by non-homogeneities in the dispersive medium. Density fluctuations, concentration fluctuations and orientation fluctuations of anisotropic molecules can be such non-homogeneities in liquids.

Research on acoustic wave absorption in various critical mixtures have shown that these mixtures exhibit an additional range of acoustic dispersion, which is not observed in individual liquids with low viscosity [1]–[3]. It has been proved [4]–[6] that quantity α/f^2 depends on frequency, temperature and concentration. The curve illustrating α/f^2 in terms of concentration has a maximum which corresponds to the critical concentration of the mixture. A strong increase of the value of the critical concentration is observed with the decrease of the acoustic wave frequency. At all concentrations the existing dispersion of the quantity α/f^2 is not accompanied by any significant change of the propagation velocity of an acoustic wave in terms of frequency.

The strong increase of absorption of acoustic waves in mixtures in the direct nearness of the critical point, intensity increase of the central component in the fine structure of Rayleigh dispersion of light and the significant decrease of the diffusion coefficient are all caused by the increase of concentration fluctuations and the increase of their radius of correlation when approaching this point.

This paper presents results of complex acousto-optic investigations of the critical n-amylic alcohol-nitromethane mixture. Molecular processes have been analysed and significant physical and chemical properties of this mixture have been determined.

1. Ultra- and hypersonic properties of the critical n-amylic alcohol-nitromethane mixture

The n-amylic alcohol-nitromethane mixture has a top critical point. Its critical parameters are respectively: $T_k = 27.8°\mathrm{C}$ and $x_k = 0.385$ (x — mole fraction of n-amylic alcohol). The critical temperature has been determined visually after the phase boundary had disapeared and after the maximum of the intensity of the central component of light dispersion. The temperature of component separation is given in Table 1.

The index of refraction in terms of concentration in the n-amylic alcohol-nitromethane mixture at a temperature of 29.2°C has been determined with the use of a refractometer in a thin layer of mixture. Measurement results are presented in Fig. 1. Measurements showed that n versus composition is a nearly linear function and the critical point does not influence it. At 29.2°C refractivities of pure components of this mixture differ from each other insignificantly, hence critical opalescence does not occur and the fine structure of Rayleigh light dispersion can be also observed in the direct nearness of the temperature of separation of components.

Table 1

n-$C_5H_{11}OH$ w CH_3NO_2	0.0	0.1	0.3	0.385	0.5	0.9	1.0
T_m (°C)	—	15.5	27.6	27.8	26.9	8.2	—
n	1.3776	1.3792	1.3886	1.3891	1.3933	1.4023	1.4104
$\Delta\nu$ (cm^{-1})	0.141	0.132	0.130	0.128	0.133	0.132	0.130
f_h (GHz)	4.23	3.96	3.90	3.84	3.99	3.96	3.90
c_0 (m/s)	1340	1270	1248	1232	1240	1243	—
c_h (m/s)	1374	1285	1257	1257	1281	1264	1237
$I_c/2I_{MB}$	0.6	0.7	6.4	17.8	7.2	0.5	0.3
$\alpha/f^2\cdot10^{15}$ (s^2/m)	19.15	28.04	73.89	82.62	64.66	47.50	20.02
$\Delta\nu_{MB}\cdot10^3$ (cm^{-1})	5	6	15	16	14	10	4
ϱ (kg/m^3)	1124.1	1079.0	972.4	958.2	927.6	839.6	814.8

Chemically pure media were used in the experiment. They were additionally chemically purified and destilled several times. The degree of purity was checked by measurement of the index of refraction, density and boiling point.

Acoustic properties of the n-amylic alcohol-nitromethane mixture were investigated at the following concentrations: $x = 0.1;\ 0.3;\ 0.385;\ 0.5;\ 0.9$ — mole fraction of n-amylic alcohol.

The propagation velocity of an acoustic wave was determined for two frequencies: 28 MHz and ~3900 MHz. While the amplitude absorption coefficient for acoustic waves was determined in the ultrasonic range, in the interval from 29.6 MHz to 128.6 MHz with the application of the pulse method and the utilization of resonance excitation of piezoelectric transducers; and in the hypersonic range with the utilization of the fine structure of Rayleigh light dispersion.

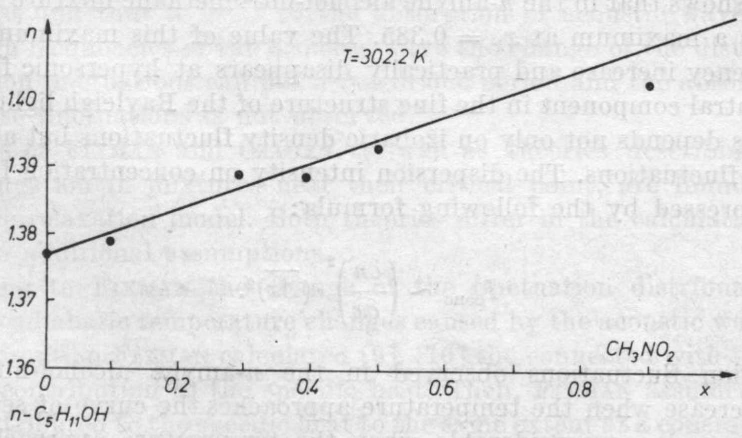

Fig. 1. Refractive index in terms of concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 29.2$°C

The measuring apparatus for ultrasonic testing and photoelectric recording of the fine structure of the Rayleigh light dispersion in liquid media, as well as the method of calibration and evaluation of the accuracy of the propagation velocity and the absorption coefficient of a hypersonic wave have been described in paper [4].

Table 1 includes fundamental physical, chemical and acoustic parameters of the mixture, determined at the temperature of 29.2°C and for the angle of dispersion equal to 90°.

Research has proved that in pure nitromethane [7], oscillation relaxation occurs, while in pure *n*-amylic alcohol [8] structural relaxation takes place. Therefore, for frequencies not exceeding we can admit that acoustic dispersion $\sim 10^9$ Hz in the *n*-amylic alcohol-nitromethane mixture will be caused by the relaxation of concentration fluctuations.

Table 2

f (MHz)	$\alpha/f^2\cdot 10^{15}$ ($\mathrm{m^{-1}\cdot s^2}$)								
	$x = 0.1$		$x = 0.3$		$x = 0.385$		$x = 0.5$		$x = 0.9$
	29.2°C	40°C	29.2°C	40°C	29.2°C	40°C	29.2°C	40°C	29.2°C
29.6	65	58	300	138	354	143	219	97	80
48.4	65	57	226	108	246	116	172	81	77
68.6	62	56	174	92	197	108	138	77	76
88.8	64	56	142	85	156	94	113	70	75
128.6	64	55	125	77	132	88	99	69	74
$\sim$ 3900	52	32	51	62	64	58	57	60	45

Table 2 states determined values of α/f^2 for various concentrations and two temperatures in the investigated frequency range. The analysis of data given in Table 2 shows that in the *n*-amylic alcohol-nitromethane mixture the quantity α/f^2 has a maximum at $x_k = 0.385$. The value of this maximum decreases with frequency increase and practically disappears at hypersonic frequencies.

The central component in the fine structure of the Rayleigh light dispersion in mixtures depends not only on izobaric density fluctuations but also on concentration fluctuations. The dispersion intensity on concentration fluctuations can be expressed by the following formula:

$$I_{\mathrm{conc}} \sim \left(\frac{\partial n}{\partial x}\right)^2 \cdot \overline{(\Delta x)^2}.$$

Concentration fluctuations observed in the *n*-amylic alcohol-nitromethane mixture increase when the temperature approaches the curve of separation of components and are considerable when the temperature approaches critical parameters of the mixture.

Therefore, the $I_C/2I_{MB}$ ratio for this mixture achieves the maximal value near the critical parameters. This is shown in Table 1, where the values of $I_C/2I_{MB}$ are given for investigated concentrations at a temperature of $T = 29.2°\mathrm{C}$.

A significant increase of the $I_C/2I_{MB}$ ratio when critical parameters are approached means that a strong light dispersion takes place on concentration fluctuations and izobaric density fluctuations, while at the same time the influence of adiabatic density fluctuations decreases.

A considerate depolarization spectrum is observed in the n-amylic alcohol-nitromethane mixture. It achieves its maximum in the direct nearness of the critical point. Hence, the dispersion on orientation fluctuations is also visible and registered.

2. Experimental investigations of acoustic wave absorption in the critical n-amylic alcohol-nitromethane mixture. A comparison with theories of Fixman and Czaban

From among many trials of explaining the characteristic behaviour of mixw tures in the surroundings of the critical point those were most successful which took into consideration the coupling between concentration fluctuations and the acoustic wave. Concentration fluctuations in various volume elements of the mixture can be considered as independent at a considerable distance from the critical point. When approaching the critical point the magnitude of the fluctuations and their correlation radius quickly increases.

An acoustic wave in the medium influences the mean fluctuation amplitude and its distribution function. The fluctuation distribution attains the equilibrium value with a certain delay, which depends on the diffusion coefficient D. Part of the energy of the acoustic wave causes a change in the distribution of concentration fluctuations and then is changed into heat. This is an irreversible process and thus it leads to the absorption of acoustic waves. At adequately high frequencies of the acoustic wave the change of the distribution of concentration fluctuations can not occur in one period and the absorption caused by these fluctuations is not observed.

Theories of FIXMAN and CZABAN, as well as theories describing acoustic wave propagation in mixtures near their critical point, are founded on the given above relaxation model. Both theories differ in the calculation method and certain additional assumptions.

According to FIXMAN the change of the fluctuation distribution occurs only due to adiabatic temperature changes caused by the acoustic wave. Basing on this assumption FIXMAN calculated [9], [10] the connected with this process additional contribution to the specific heat. Then, FIXMAN assumed that this process contributed to the specific heat to the same extent at a constant pressure and constant volume (present research has proved this assumption to be false [11]) and on the basis of this assumption calculated the acoustic wave velocity and its absorption coefficient. Applying Debye's formula [12]

$$\varkappa^2 = (6/l^2 \cdot T_k)|T-T_k|, \tag{1}$$

where $\varkappa^{-1} = \xi$ is the correlation radius of concentration fluctuations; l is the radius of intermolecular interactions; T_K is the critical temperature, the final result of Fixman's theory can be presented analytically as follows:

$$a/f^2 = Af^{-5/4}\,\mathrm{Im}[f(d)]+B, \tag{2}$$

$$d = Cf^{-1/2}|T-T_k|, \tag{2a}$$

$$c = c_\infty\{1-Ac_\infty f^{-1/4}\,\mathrm{Re}[f(d)]\} \tag{3}$$

where c_∞ – acoustic wave velocity at $\omega\tau \gg 1$.

Function $f(d)$ was defined numerically by Kendig and others [13]. Its analytic form, which was applied by the authors, was given by Fixman [10]. Constants A and C are slightly dependent on temperature and independent from frequency.

Basing on latest works of Kawasaki [14], Kadanoff and Swift [15], Czaban modified Fixman's assumptions concerning the change of the fluctuation distribution due to an acoustic wave. Czaban accepted that the change of the fluctuation distribution influenced by an acoustic wave occurs not only due to adiabatic temperature changes, but also due to abrupt changes of the critical temperature caused by the acoustic wave pressure. On the basic of the above assumptions Czaban determined the complex adiabatic compressibility of a medium with strong concentration fluctuations [16]. Changes of the distribution of fluctuations due an acoustic wave were calculated with the application of the fluctuation dissipative theorem. Czaban derived the propagation velocity and the acoustic wave absorption coefficient from the real and imaginary part of the adiabatic compressibility, respectively [17]. Final results of his considerations are as follows:

$$c = c_0\left\{1-\frac{Mc_0}{2\pi\tau_1}[|T-T_k|+d|x-\overline{x}_k|]^{-0.2}\left[F_2(\omega\tau)-\frac{b-\arctan b}{12}\right]\right\}, \tag{4}$$

$$a/f^2 = M[|T-T_k|+|x-\overline{x}_k|^3]^{-2}F_1(\omega\tau)+L. \tag{5}$$

Functions $F_1(\omega\tau)$ and $F_2(\omega\tau)$ have been given in paper [17]:

$$\tau = \frac{\tau_1}{2\pi}[|T-T_k|+d|x-\overline{x}_k|^3]^{-1.8} \tag{6}$$

c_0 – acoustic wave velocity at $\omega\tau \ll 1$,
x_k – critical concentration of the mixture,

M and L – constants weakly dependent on temperature and concentration and independent of frequency. It results from the scaling theory that $b \cong 5$ [18].

Expressions (4) and (5) are true when $\omega\tau \lesssim 340$ [18].

Constants A, C and M and τ, are represented by parameters of the mixture both in FIXMAN'S and CZABAN'S theories. However it is difficult to determine some of them, i.e. the correlation radius or the diffusion constant. Thus, most frequently these constants are determined on the basis of the condition of greatest consistency of theory with experiment. Also in this paper this method has been applied.

The least square method has been used in determining parameters of the curve of *greatest consistency*.

The value of function $\mathrm{Im}[f(d)]$ was calculated from its analytic form presented in paper [7]. Derivatives of functions $\mathrm{Im}[f(d)]$ and $F_1(\omega\tau)$ were approximated by the differential quotient

$$F' \cong \frac{f(x_0+\delta x)-f(x_0)}{\delta x}. \tag{7}$$

Successive approximations have to be applied in the process of matching because non-linear dependencies occur in both CZABAN'S and FIXMAN'S theories.

2.1. *Results and discussion*

The calculation procedure presented in the preceeding paragraph was used to determine parameters of *best fitting curves* in the n-amylic alcohol-nitromethane mixture for FIXMAN'S and CZABAN'S theories.

Presented in Table 3 values of parameters of *best fitting curves* were obtained on the basis of FIXMAN'S theory for the n-amylic alcohol-nitromethane mixture.

Table 3

Molar fraction of n-amylic alcohol	$A \cdot 10^3$ ($\mathrm{s}^{+3/4} \cdot \mathrm{m}^{-1}$)	C ($\mathrm{s}^{-1/2} \cdot \mathrm{deg}^{-1}$)	$B \cdot 10^{15}$ ($\mathrm{m}^{-1} \cdot \mathrm{s}^2$)
0.385	2.07	574	66.6
0.300	1.72	567	65
0.500	1.35	942	61.2

Experimental points describing a/f^2 in terms of frequency for three concentrations and two temperatures, respectively, have been marked in Figs. 2–4. Full lines in these figures were calculated from formulae (2) and (2a), which result from FIXMAN'S theory.

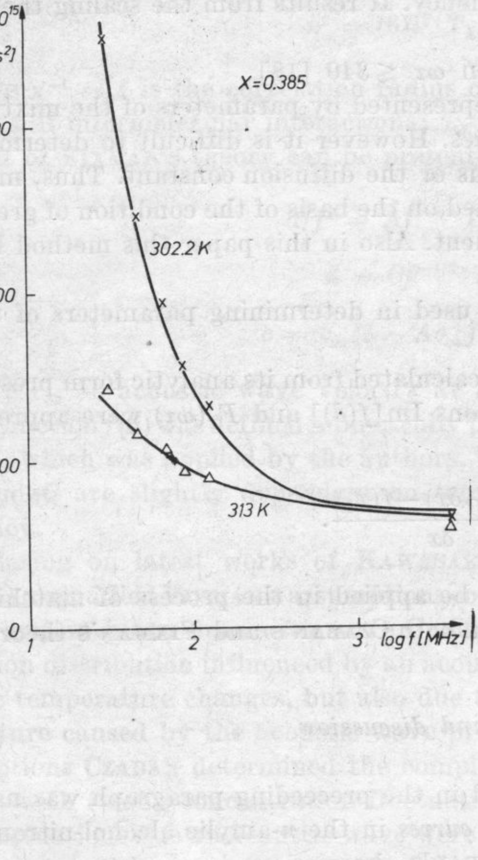

Fig. 2. α/f^2 versus log$f$ in the n-amylic alcohol-nitromethane mixture with critical concentration $x = 0.385$ (x — molar fraction of n-amylic alcohol) at two temperatures. Full lines obtained from formulae (2) and (2a); ×, △ — experimental points

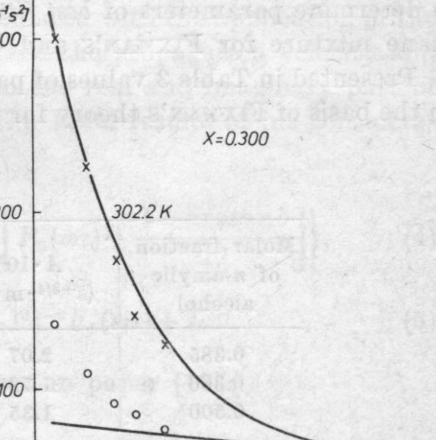

Fig. 3. α/f^2 versus log$f$ in the n-amylic alcohol-nitromethane mixture with concentration $x = 0.300$ (x — molar fraction of n-amylic alcohol) at two temperatures. Full lines obtained from formulae (2) and (2a); ×, △ — experimental points

The following values of parameters of *best fitting curves* have been obtained on the basis of CZABAN'S theory for the n-amylic alcohol-nitromethane mixture:

$M = 2.751 \ 10^{-11} \, [\mathrm{s^2 deg^2 m^{-1}}]$

$\tau_1 = 2.166 \ 10^{-7} \, [\mathrm{s}]$

$L = 60.1 \ 10^{-15} \, [\mathrm{s^2 m^{-1}}]$

Quantity d in equation (6) was determined from the separation temperature-concentration dependence for the mixture. It equals: $d = 400$ deg/mole fraction.

Full lines in Figs. 5–7 were plotted on the basis of formulae (5) and (6), which result from CZABAN'S theory.

The value of velocity dispersion of an acoustic wave at the critical concentration and temperature of 29.2°C was evaluated for the n-amylic alcohol-nitromethane mixture from formulae (3) and (4). According to FIXMAN'S theory this value equals $\sim 3.5\,\%$, and according to CZABAN $\sim 0.6\,\%$. Whereas, experimentally determined dispersion equals $\sim 0.4\,\%$.

α/f^2 in terms of concentration and temperature for the n-amylic alcohol-nitromethane mixture is shown in Figs. 8 and 9. In the n-amylic alcohol-nitromethane mixture α/f^2 has its maximum at $x_k = 0.385$. The magnitude of this

Fig. 4. α/f^2 versus $\log f$ in the n-amylic alcohol-nitromethane mixture with concentration $x = 0.500$ (x – molar fraction of n-amylic alcohol) at two temperatures. Full lines obtained from formulae (2) and (2a); ×, △ – experimental points

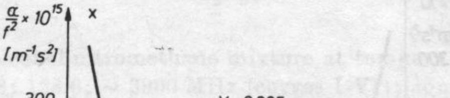

Fig. 5. α/f^2 versus $\log f$ in the n-amylic alcohol-nitromethane mixture with concentration $x = 0.385$ (x – molar fraction of n-amylic alcohol) at two temperatures. Full lines obtained from formulae (5) and (6); ×, ○ – experimental points

maximum decreases when frequency is increased and it nearly disappears at hypersonic frequencies.

This effect can not be explained by the increase of laver viscosity, because it slightly increases only in the direct nearness of the critical point [19], or by relaxation processes taking place in pure components of the mixture. Measurements conducted in pure components of the mixture have shown that α/f^2 is only slightly dependent on frequency and it is several orders of magnitude lower than in the *n*-amylic alcohol-nitromethane mixture.

The mean square of concentration fluctuations increases strongly in critical mixtures when $x \to x_k$ and $T \to T_k$ [20]. Therefore, the existance of a relation between the increase of $\overline{(\Delta x)^2}$ and the increase of acoustic wave absorption can be suggested.

According to the found consistency between experiment and theories of FIXMAN and CZABAN — based on the same relaxation model — this effect can be attributed to strong concentration fluctuations in the neighbourhood of the critical point of the mixture. However, it should be mentioned that the closer the values of parameters of a mixture are to critical, the better the consistency This is especially important for CZABAN'S theory, because its values of parame

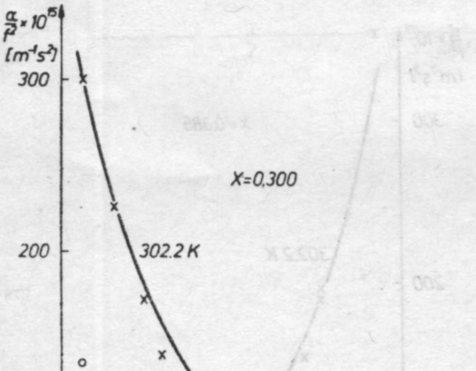

Fig. 6. α/f^2 versus log$f$ in the *n*-amylic alcohol-nitromethane mixture with concentration $x = 0.300$ (x — molar fraction of *n*-amylic alcohol) at two temperatures. Full lines obtained from formulae (5) and (6); ×, ○ — experimental points

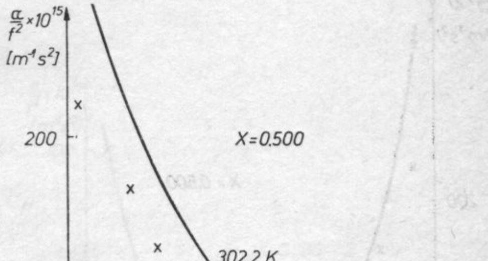

Fig 7. α/f^2 versus log$f$ in the *n*-amylic alcohol-nitromethane mixture with concentration $x = 0.500$ (x — molar fraction of *n*-amylic alcohol) at two temperatures. Full lines obtained from formulae (5) and (6); ×, ○ — experimental points

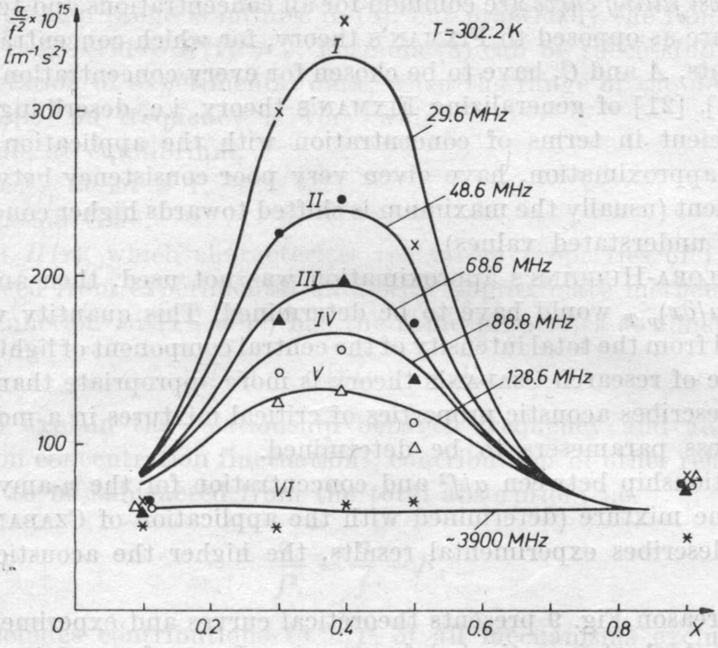

Fig. 8. α/f^2 versus concentration in the *n*-amylic alcohol-nitromethane mixture at temperature of 29.2°C for frequencies 29.6; 48.6; 68.6; 88.8; 128.6; ~ 3900 MHz (curves I-VI); concentration of components expressed in molecular fractions of *n*-amylic alcohol. Full lines obtained from formulae (5) and (6); ×, ●, ▲, ○ △ — experimental points

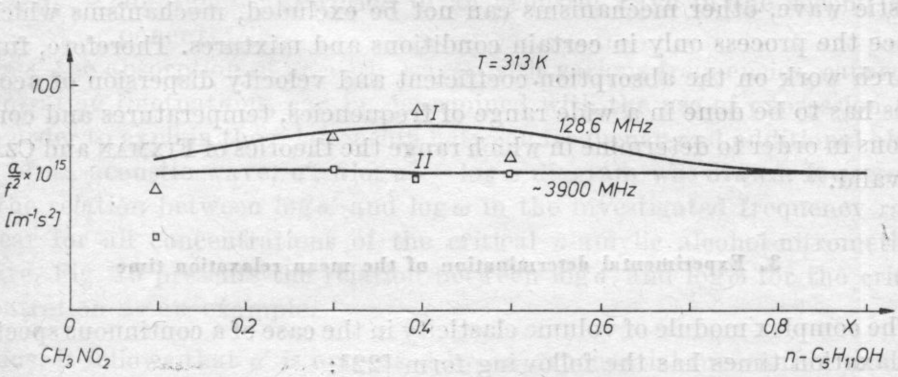

Fig. 9. α/f^2 versus concentration in the *n*-amylic alcohol-nitromethane mixture at temperature of 40°C for frequencies 128.6; ~ 3900 MHz (curves I, II); concentration of components expressed in molecular fractions of *n*-amylic alcohol. Full lines obtained from formulae (5) and (6); △, □ — experimental points

ters of the *best fitting curve* are common for all concentrations and temperatures of the mixture as opposed to Fixman's theory, for which concentration-dependent constants, A and C, have to be chosen for every concentration separately.

Trials [6], [21] of generalizing Fixman's theory, i.e. describing the absorption coefficient in terms of concentration with the application of Flora-Huggins's approximation, have given very poor consistency between theory and experiment (usually the maximum is shifted towards higher concentrations, which have understated values).

If the Flora-Huggins's approximation was not used, then an additional quantity $(\partial\mu/\partial x)_{p,T}$ would have to be determined. This quantity would have to be derived from the total intensity of the central component of light dispersion. At this stage of research Czaban's theory is more appropriate than Fixman's, because it describes acoustic properties of critical mixtures in a more complex way with less parameters to be determined.

The relationship between α/f^2 and concentration for the n-amylic alcohol-nitromethane mixture (determined with the application of Czaban's theory), the better describes experimental results, the higher the acoustic wave frequency.

For this reason Fig. 9 presents theoretical curves and experimental results only for two highest investigated frequencies. Lower frequencies exhibit far worse conformity.

Because Czaban [17] observed a similar correctness in other critical mixtures, maybe this conclusion can be generalized.

Theories of Fixman and Czaban are based on a fundamental assumption that anomal behaviour of an acoustic wave in mixtures near their critical point is caused by strong concentration fluctuations. Although according to present research concentration fluctuations are responsible for such a behaviour of an acoustic wave, other mechanisms can not be excluded, mechanisms which influence the process only in certain conditions and mixtures. Therefore, further research work on the absorption coefficient and velocity dispersion of acoustic waves has to be done in a wide range of frequencies, temperatures and concentrations in order to determine in which range the theories of Fixman and Czaban are valid.

3. Experimental determination of the mean relaxation time

The complex module of volume elasticity in the case of a continuous spectrum of relaxation times has the following form [22]:

$$\tilde{E} = E_0 + \int\limits_0^\infty \frac{\omega^2\tau \mathrm{H}(\tau)\,d\tau}{1+\omega^2\tau^2} + i\omega\left(\eta_\infty + \int\limits_0^\infty \frac{H(\tau)\,d\tau}{1+\omega^2\tau^2}\right). \tag{8}$$

Function $H(\tau)$ is the density of the spectrum of relaxation times.

The integration range is infinite in (8), but practically the function is integrated in a range where $H(\tau) \neq 0$. Formula (8) can be successfully applied in the interpretation of experimental data, when the range of the dependence of $E(\omega)$ and $\eta(\omega)$ on frequency is very wide

E_0 — module at equilibrium,
η_∞ — viscosity at $\omega\tau \gg 1$,
τ — relaxation time.

Function $H(\tau)$, which characterizes relaxation properties of the medium, can be derived from experimental data with approximate methods. If we assume that function $\omega\tau/(1+\omega^2\tau^2)$ has the same properties as function δ, then

$$H(\tau) = \omega[\eta(\omega) - \eta_\infty]_{\omega=1/\tau}. \tag{9}$$

In order to explain the relationship between frequency and acoustic wave absorption on concentration fluctuations, contributions of other relaxation processes have to be subtracted from the total absorption, i.e.

$$\frac{a'}{f^2} = \frac{a}{f} - B, \tag{10}$$

where B includes contributions to a/f^2 of all mechanisms excluding absorption due to concentration fluctuations.

The value of B in the first approximation can be determined from expression

$$B = \left(\frac{a}{f^2}\right)_{\omega\tau\geqslant 1} \approx x_1 B_1 + x_2 B_2, \tag{11}$$

where: B_1 — absorption of an acoustic wave in the first component,
B_2 — additional absorption of an acoustic wave in the second component.

Thus, the absorption of acoustic waves with various frequencies, caused by concentration fluctuations, can be determined with the use of expression (11).

In order to explain the relationship between frequency and additional absorption of an acoustic wave, a', a $\log a'$ — $\log \omega$ diagram was drawn. It occuvred that the relation between $\log a'$ and $\log \omega$ in the investigated frequency range is linear for all concentrations of the critical n-amylic alcohol-nitromethane mixture. Fig. 10 presents the relation between $\log a'$ and $\log \omega$ for the critical concentration as an example.

Thus, it follows that a' is expressed by an exponential function in terms of frequency:

$$a' = a^* \omega^{p+1}, \tag{12}$$

where a^* and p — parameters dependent on the composition and temperature of the mixture.

Hence, the density of the spectrum of relaxation times, $H(\tau)$, for concentration fluctuations in an n-amylic alcohol-nitromethane mixture equals

$$H(\tau) = K_1 \tau^{-p}. \tag{13}$$

This shows that $H(\tau)$ in the frequency range under investigation is expressed by a hyperbolic function. The relaxation time spectrum discontinue in the range of small $\tau < (10^{-11} - 10^{-12})_s$ because relaxation is not observed at high frequencies ($\sim 10^9$ Hz). The relaxation time spectrum should disappear also in the range of large τ if the mixture is in a thermodynamic steady state.

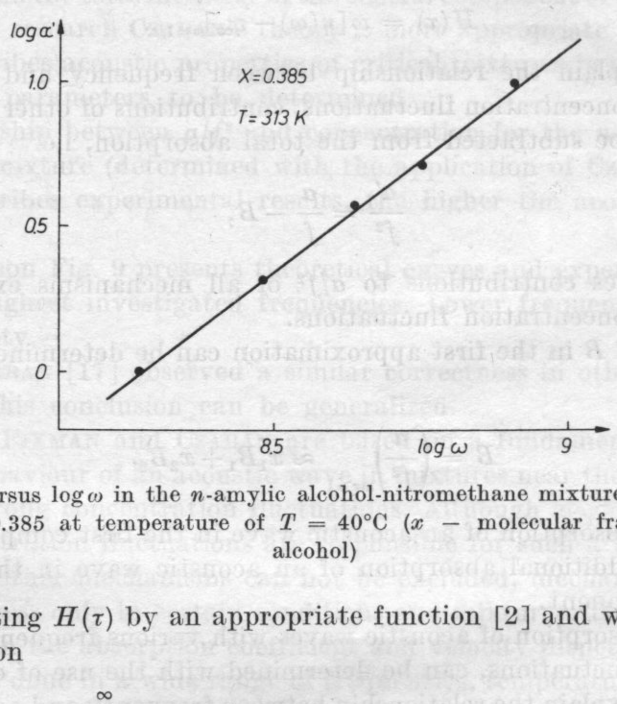

Fig. 10. $\log\alpha'$ versus $\log\omega$ in the n-amylic alcohol-nitromethane mixture with critical concentration $x = 0.385$ at temperature of $T = 40°\mathrm{C}$ (x – molecular fraction of n-amylic alcohol)

Approximating $H(\tau)$ by an appropriate function [2] and with the application of equation

$$\tau_a = \frac{\int\limits_0^\infty \tau H(\tau)\, d(\ln\tau)}{\int\limits_0^\infty H(\tau)\, d(\ln\tau)} = \frac{K_{1/p-1}(2\sqrt{\beta\cdot\gamma})}{K_1(2\sqrt{\beta\cdot\gamma})}\left(\frac{\beta}{\gamma}\right)^{1/2p} \tag{14}$$

the average relaxation time, τ_a, which characterizes the time of occurance of the Fourier component of concentration fluctuations, can be calculated. Here, $K(z)$ denotes the MacDonald function. Because $(\beta\gamma)^{1/2} \ll 1$, $K(z)$ can be expanded into a series according to the order of the argument $z = \sqrt{\beta\gamma}$. If only the first term, $0 < z < 1$, is taken into consideration, then we obtain:

$$\tau_a = 10^{-2+1/p}\left(\frac{1}{p} - 2\right)!\; m^{2-1/p}\cdot\tau_A\left(\frac{\tau_A}{\tau_B}\right)^{p-1}, \tag{15}$$

Table 4

Molar fraction of n-$C_5H_{11}OH$	T (°C)	$B \cdot 10^{15}$ ($cm^{-1} \cdot s^2$)	a^*	p	τ_a (s)
0.1	29.2	35	$1.38 \cdot 10^{-17}$	0.97	$4.05 \cdot 10^{-10}$
	40	38	$3.95 \cdot 10^{-17}$	0.89	$5.03 \cdot 10^{-10}$
0.3	29.2	31	$1.07 \cdot 10^{-10}$	0.25	$4.04 \cdot 10^{-8}$
	40	27	$9.44 \cdot 10^{-13}$	0.45	$3.60 \cdot 10^{-9}$
0.385	29.2	32	$4.21 \cdot 10^{-10}$	0.19	$2.23 \cdot 10^{-7}$
	40	28	$1.46 \cdot 10^{-13}$	0.55	$1.91 \cdot 10^{-9}$
0.5	29.2	35	$7.36 \cdot 10^{-11}$	0.25	$3.99 \cdot 10^{-8}$
	40	30	$2.16 \cdot 10^{-14}$	0.62	$1.34 \cdot 10^{-9}$

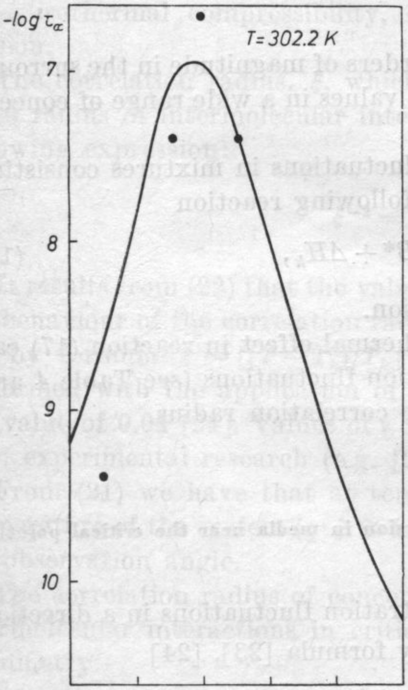

Fig. 11. $\log \tau_a$ versus concentration in the n-amylic alcohol-nitromethane mixture at temperature of $T = 29.2$°C. Full line obtained from formula (16); ● – experimental points

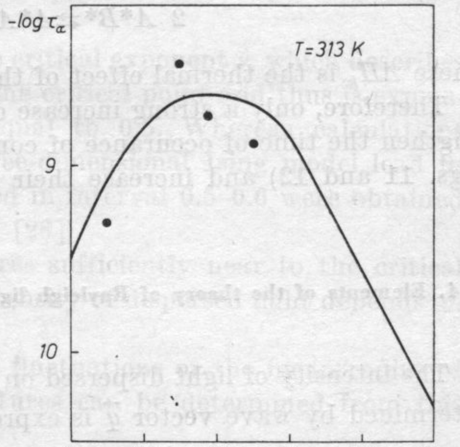

Fig. 12. $\log \tau_a$ versus concentration in the n-amylic alcohol-nitromethane mixture at temperature of $T = 40$°C. Full line obtained from formula (16); ● – experimental points

where p — parameter determined from experimental data, from the relation between the angle of inclination of line α' in terms of $\log\omega$, τ_A and τ_B — times corresponding to respectively the maximal and minimal frequency at which measurements were conducted ($\tau_A \simeq 10^{-11}$ s, $\tau_B \simeq 10^{-8}$ s).

Values of τ_a for investigated concentrations of the critical n-amylic alcohol--nitromethane mixture were calculated from formula (15) for two temperatures. Results of calculations are given in Tab. 4, and τ_a in terms of concentration for two different temperatures is presented in Figs. 11 and 12.

Values τ_a in Figs. 11 and 12, determined from experimental data, are denoted by points, while solid curves were drawn on the basis of the formula which results from Czaban's theory. This formula is as follows [17]:

$$\tau_a = \tau_1(|T-T_k|+d'|x-x_k|^3)^{-1.8}. \tag{16}$$

In the course of calculations it was accepted that [7]:

$\tau_1 = 2.166\cdot 10^{-7}$ s
$d' = 400$ deg
$\bar{x}_k = 0.385$ mole fraction
$T_k = 27.8°$C.

As it can be seen, τ_a increases by several orders of magnitude in the surroundings of the critical point and maintains high values in a wide range of concentrations and temperatures.

The relaxation process of concentration fluctuations in mixtures consisting of components A^* and B^* is based on the following reaction

$$2\ A^*B^* \rightleftarrows A^*A^* + B^*B^* + \Delta H_k, \tag{17}$$

where ΔH_k is the thermal effect of the reaction.

Therefore, only a strong increase of the thermal effect in reaction (17) can lengthen the time of occurance of concentration fluctuations (see Table 4 and Figs. 11 and 12) and increase their average correlation radius.

4. Elements of the theory of Rayleigh light dispersion in media near the critical point

The intensity of light dispersed on concentration fluctuations in a direction determined by wave vector $\vec{q}$ is expressed by formula [23], [24]

$$I(\vec{q}) = I_0\frac{\pi V}{\lambda^4 R^2}\left(\frac{\partial\varepsilon}{\partial x}\right)_{T,\varrho} S(\vec{q}), \tag{18}$$

where R is the distance between the dispersive centre with volume V and the observation point; λ is the wave length of inciding light; and $S(\vec{q})$ is the structural factor. This last quantity is defined as the mean of the square of the q-Fourier component fluctuation of concentration fluctuations. Hence,

$$S(\vec{q}) = \langle |\Delta x(\vec{q})|^2 \rangle \tag{19}$$

In accordance with previous research it can be assumed that a correlation exists between fluctuation in neighbouring volume elements in the surroundings of the critical point. If this correlation can be expressed by Ornstein's and Zernik's function [20]

$$G(r) = \frac{a}{r} e^{-r/\xi}, \tag{20}$$

where ξ is the correlation radius, then the structural factor can be expressed by [24]

$$S(\vec{q}) = \frac{k_B T x^2 \beta_T}{1 + q^2 \cdot \xi^2} = \frac{k_B T x^2 \beta_T}{1 + \frac{16\pi^2}{\lambda^2} n^2 \xi^2 \sin^2 \frac{\vartheta}{2}}; \tag{21}$$

β_T – isothermal compressibility, n – refractive index, ϑ – angle of dispersion.

The correlation radius, ξ, which occurs in formula (20), is related to the mean radius of intermolecular interactions introduced by Debye [12] by the following expression:

$$\xi^{-2} = \frac{6}{l^2 T_k} |T - T_k|. \tag{22}$$

It results from (22) that the value of the critical exponent ν, which describes the behaviour of the correlation radius in the critical point and thus is expressed by formula $\xi \sim [(T - T_k)/T_k]^{-\nu}$, is equal to 0.5. Whereas calculations performed with the application of the three-dimensional Ising model lead to the value of 0.64 [24]. Values of ν contained in interval 0.5–0.6 were obtained from experimental research (e.g. [25] and [26]).

From (21) we have that at temperatures sufficiently near to the critical temperature of the system ($q \cdot \xi \gtrsim 1$) the intensity of dispersed light depends on the observation angle.

The correlation radius of concentration fluctuations or the mean radius of intermolecular interactions in critical mixtures can be determined from this asymmetry.

4.1. Results of measurements of dispersed light intensity in terms of the angle in the n-amylic alcohol-nitromethane mixture

Both liquids, which constitute the mixture, i.e. *n*-amylic alcohol and nitromethane, have very similar refractive indexes. For this reason, and because the exciting laser beam had a small diameter and the path of the dispersive beam in the medium was relatively short (approximately 2 cm) [27], the influence of repeated dispersion on the registered dispersed light intensity was not considered.

The dispersion was investigated under two angles: $\vartheta_1 = 43°$ and $\vartheta_2 = 140°$, which were determined with the accuracy of $\Delta\vartheta_1 = \Delta\vartheta_2 = \pm 0.5°$ with the application of the apparatus described in paper [31].

The minimal dispersion asymmetry which could be measured equaled $(I_{\vartheta 1} - I_{\vartheta 2})/I_{\vartheta 1} \sim 4\%$ due to light intensity fluctuations caused by technical instabilities and unstable laser or interrupter system functioning.

Measurements were done for a mixture with the critical concentration of $x_k = 0.385$ molecular fraction of *n*-amylic alcohol.

The dispersion asymmetry, i.e. the value of ratio $k = I_{43°}/I_{140°}$ differing from one, was observed in the temperature range: $0.05°\mathrm{C} \leqslant |T - T_k| \leqslant 0.2°\mathrm{C}$. Results of measurements are presented in Fig. 13.

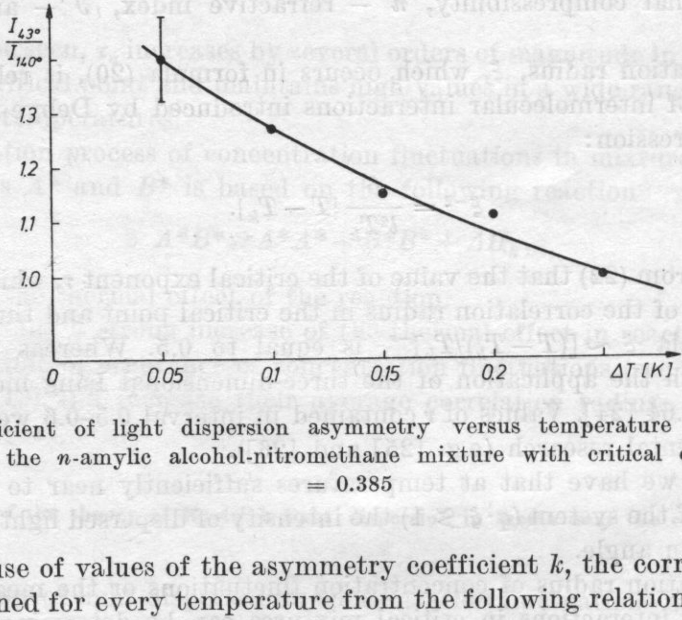

Fig. 13. Coefficient of light dispersion asymmetry versus temperature difference ($\Delta T = T - T_k$) in the *n*-amylic alcohol-nitromethane mixture with critical concentration $x = 0.385$

Making use of values of the asymmetry coefficient k, the correlation radius was determined for every temperature from the following relationship resulting from expression (21)

$$\xi^{-2} = \frac{16\pi^2 n}{\lambda^2} \cdot \frac{\sin^2\vartheta_2/2 - k\sin^2\vartheta_1/2}{k-1}, \tag{23}$$

where λ is the wave length of He-Ne laser light. Results of measurements are presented in Fig. 14. Approximating experimental points with a straight line a correlation coefficient equal to 0.98 was obtained. While approximating them with a power curve, $\xi^{-2} \sim (\Delta T)^{\gamma}$, an exponent equal to $\gamma = 0.96$ and a slightly worse correlation coefficient was achieved. Therefore, we can risk a statement that there is a linear dependence between ξ^{-2} and ΔT in the investigated temperature range. Thus, the mean radius of intermolecular interactions may be determined from the value of the slope of the straight line and formula (22). The following value was achieved:

$$l = 7 \pm 1 \ [\text{Å}].$$

This value is very close to the value of l determined for similar two-component mixtures with light dispersion methods and X-ray methods [27].

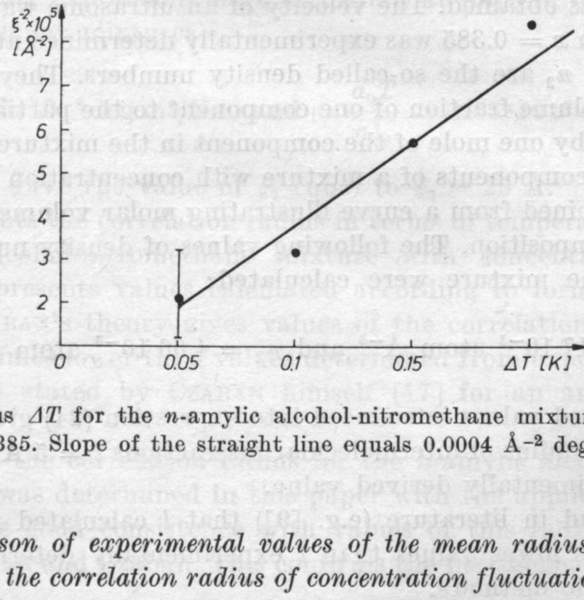

Fig. 14. ξ^{-2} versus ΔT for the n-amylic alcohol-nitromethane mixture with critical concentration $x = 0.385$. Slope of the straight line equals 0.0004 Å^{-2} deg^{-1}

4.2. A comparison of experimental values of the mean radius of intermolecular interactions and the correlation radius of concentration fluctuations in the n-amylic alcohol-nitromethane mixture with values resulting from theories of FIXMAN *and* CZABAN

FIXMAN's theory establishes a relationship between the propagation process of an acoustic wave and the diffusion process, and it is based on a definite relaxation method. Basing on correlation distribution functions M. FIXMAN [10] derived formula (2) describing acoustic wave absorption induced by concentration fluctuations. With the application of constants A and C the mean radius of intermolecular interactions can be determined from expression

$$l^6 = \frac{27 T_k \cdot C \cdot (\gamma_0 - 1) R_g^2}{A \cdot 2\,\pi^2 (n_1 + n_2)^2 c_0^2 (C_p^{mix})^2} \tag{24}$$

Values of constants A and C for the n-amylic alcohol-nitromethane mixture were established on the basis of experimental results of acoustic wave absorption (condition of the greatest consistence of theory with experiment). The following values were obtained for concentration $x = 0.385$: $A = 2.07\ 10^{-3}\ \mathrm{s}^{3/4}\ \mathrm{m}^{-1}$ and $C = 574\ \mathrm{s}^{-1/2}\ \mathrm{deg}^{-1}$. Values of the quantities in formula (24) were estimated from own measurements and data from literature.

The value of specific heat was calculated from values for pure components with the application of formula (for ideal mixtures)

$$C_p^{mix} = C_p^1 x + C_p^2 (1-x). \tag{25}$$

Value $C_p^{mix} = 146\ \mathrm{J\ mol^{-1}\ deg^{-1}}$ was obtained. The specific heat ratio, $\gamma_0 = c_p/c_v$, was estimated from relation $c_p - c_v = 5R$, where R is the gas constant. Value $\gamma_0 = 1.4$ was obtained. The velocity of an ultrasonic wave in a mixture with concentration $x = 0.385$ was experimentally determined at $c_0 = 1232$ m/s. Quantities n_1 and n_2 are the so-called density numbers. They are defined as the ratio of the volume fraction of one component to the partial molar volume (volume occupied by one mole of the component in the mixture). Partial molar volumes for both components of a mixture with concentration $x = 0.385$ were graphically determined from a curve illustrating molar volume of the mixture in terms of its composition. The following values of density numbers for both components of the mixture were calculated:

$$n_1 = 3.17\, 10^{-3}\ \text{atom Å}^{-3} \text{ and } n_2 = 4.66\, 10^{-3}\ \text{atom Å}^{-3}.$$

All above mentioned values introduced into expression (24) give the following value of the mean radius of intermolecular interactions $l = 5$ Å. It is relatively close to the experimentally derived value.

It can be found in literature (e.g. [9]) that l calculated from FIXMAN'S theory usually has lower values than l experimentally determined with the application of optic methods.

On the other hand, CZABAN accepted [16], [17] that the anomal behaviour of an acoustic wave in critical mixtures is caused by the interdependence between the volume and concentration of the mixture. It appears that the volume is influenced by concentration fluctuations. Considering the diffusive delay of the distribution change of concentration fluctuations, related to it change of volume will also be delayed in respect to the acoustic wave pressure and this leads to anomal absorption and dispersion of the acoustic wave.

The expression for the absorption coefficient of an acoustic wave is given by formula (5), in which

$$M = \frac{1.44 \cdot k_B \varrho c_0 \tau_1}{4 \cdot \pi^2 \xi_1^2} \left(-\frac{\partial T_k}{\partial p} + \frac{T a_0}{\varrho c_p} \right)^2$$

is a quantity weakly dependent on temperature and concentration of the mixture.

The dependence of the correlation radius on temperature and concentration of the mixture is described by expression

$$\xi = \xi_1(|T-T_k|+d'|x-\overline{x}_k|^3)^{-0.6}. \tag{26}$$

Values of constants M, τ_1 and d' have been determined from experimental data in paper [7]. The maximal consistence of theory with experiment was the principle of their selection. The following values were achieved:

$$M = 2.75\,10^{-11}\,\mathrm{s^2deg^2m^{-1}};\quad \tau_1 = 2.17\,10^{-17}\,\mathrm{s}\ \text{and}\ d' = 400\,\text{deg/mol. fraction.}$$

Having M, τ_1 and d', ξ_1 can be calculated from formula (5). To this end the values of following expressions were estimated at (on the basis of data from literature for similar mixtures)

$$\frac{\partial T_k}{\partial p} = 5\cdot 10^{-8}\,\mathrm{deg\,m^2/N}\quad \text{and}\quad \frac{a_0 T}{\varrho c_p} = 1.55\cdot 10^{-7}\,\mathrm{deg\,m^2/N}.$$

This estimation gave the value of ξ_1 equal to $\xi_1 = 25$ Å.

Fig. 15 presents the correlation radius in terms of temperature for the critical n-amylic alcohol-nitromethane mixture with concentration $x = 0.385$. The full line represents values calculated according to formula (26). Fig. 15 proves that CZABAN'S theory gives values of the correlation radius, ξ, about one and a half times lower than values determined from experiment. A similar relationship was stated by CZABAN himself [17] for an aniline-cyclohexane mixture.

The value of the correlation radius for the n-amylic alcohol-nitromethane mixture, which was determined in this paper with the application of an optic method, exhibits good consistence with values of this radius obtained from theories of Fixman and Czaban. This confirms the pertinence of the theoretical

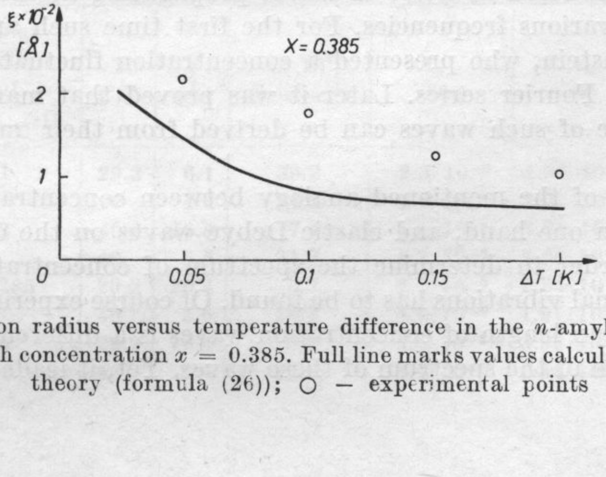

Fig. 15. Correlation radius versus temperature difference in the n-amylic alcohol-nitromethane mixture with concentration $x = 0.385$. Full line marks values calculated from CZABAN'S theory (formula (26)); ○ – experimental points

model, on which both theories are founded. However, obtained results do not univocally point to one of these theories. At this stage of research it can be stated that CZABAN'S theory is more convenient, because it allows a more complex description of parameters of critical mixtures (at a smaller number of parameters to be determined).

Trials of determining the correlation radius for the *n*-amylic alcohol-nitromethane mixture for other from critical concentrations have been carried out. However, they did not deliver satisfactory results due to a too small value of the coefficient of dispersion asymmetry, k, even very near to the critical point ($\Delta T = 0.05°\mathrm{C}$). In fact, when we estimate from formula (26) the value of the correlation coefficient for concentration $x = 0.5$ we achieve a value of $k = 0.3\,\%$. This is a value too small to measure with the presented system. Therefore, there is a need of certain improvements in the system (e.g. a concurrent measurement of the dispersion intensity of light under two angles), which would allow a very accurate measurement of the value of the correlation radius of concentration fluctuations in a possibly wide temperature range.

5. The determination of the average length of a concentration wave and of the diffusion coefficient in the critical n-amylic alcohol-nitromethane mixture

The determination of the spectrum of concentration waves in a series of critical mixtures would contribute significantly to the solution of the problem of kinematics of concentration fluctuations and to the explanation of such processes as light dispersion or propagation of acoustic waves in such media. Yet, this is a very complicated problem — even in the case of a solid body, not to mention liquids with their disordered particle motion. The problem of the spectrum of concentration waves in liquid media is mostly expressed in the form of qualitative predictions rather then accurate empirical or theoretical conclusions.

An opinion was presented in accordance with which concentration fluctuations can be considered as a set of waves propagating in the medium in all directions with various frequencies. For the first time such an approach was proposed by Einstein, who presented a concentration fluctuation in the form of the sum of a Fourier series. Later it was proved that many informations about the nature of such waves can be derived from their analogy to elastic Debye waves.

On the basis of the mentioned analogy between concentration waves and density waves on one hand, and elastic Debye waves on the other, it can be found that in order to determine the spectrum of concentration waves, the spectrum of normal vibrations has to be found. Of course experimental determination of the mean length of concentration waves is a different problem from the determination of the spectrum of these waves. Yet, it leads to several conclusions concerning the behaviour of such a spectrum in terms of temperature and concentration of the mixture.

The distribution function of concentration fluctuations in the field of an acoustic wave differs from the distribution function at equilibrium. Hence, mean amplitudes of concentration waves, $\bar{c}_q$, assume new values, c_q^t. When an acoustic wave has passed through the mixture, the system will tend to the initial state and $c_q^t \to \bar{c}_q$. If we assume that the change of mean amplitudes of concentration waves occurs in accordance with Fick's diffusion equation [30], then the length of a q-concentration wave, τ_q, which fades in relaxation time, Λ_q, can be expressed by formula

$$\frac{1}{\tau_q} = 4\pi^2 D/\Lambda_q^2. \tag{27}$$

An analogical relation can be written also for such a concentration wave, for which the mean amplitude fades in relaxation time τ_k. This is the mean relaxation time of concentration fluctuations, defined by expressions (14).

Concentration waves, which initially were considered only as an effect of a formal expansion of concentration fluctuations into a Fourier series, are equivalent to density waves, in mixtures; and these, as MANDELSZTAM proved [23], are elastic Debye waves. Using this analogy and basing on Debye's argumentation, the smallest possible length of a concentration wave in the expression presented in paper [23] can be estimated. The maximal frequency of elastic Debye waves and their minimal wave-length, estimated with the application of this method, equal $\omega_{max} = 10^{14}$ Hz and $\Lambda_{min} = 1.5$ A, respectively.

In order to determine the mean length of concentration waves after formula (27), we have to know the mean relaxation time of concentration fluctuations and the diffussion coefficient of the mixture. Relaxation times, τ_a, in the critical n-amylic alcohol-nitromethane mixture were found with the application of the method described in paragraph 3 for various concentrations and two

Table 5

Molar fraction of n-$C_5H_{11}OH$	T (°C)	ξ (Å)	$D \cdot 10^7$ ($cm^2 \cdot s^{-1}$)	Λ_a (cm)	τ_a (s)
0.1	29.2	6.1	39.2	$2.5 \cdot 10^{-6}$	$4.05 \cdot 10^{-10}$
	40	4.0	74.3	$3.8 \cdot 10^{-6}$	$5.03 \cdot 10^{-10}$
0.3	29.2	18.5	7.4	$1.1 \cdot 10^{-5}$	$4.04 \cdot 10^{-8}$
	40	5.5	31.2	$6.7 \cdot 10^{-6}$	$3.60 \cdot 10^{-9}$
0.385	29.2	20.4	5.7	$2.2 \cdot 10^{-5}$	$2.23 \cdot 10^{-7}$
	40	5.6	26.3	$4.4 \cdot 10^{-6}$	$1.91 \cdot 10^{-9}$
0.5	29.2	16.4	5.9	$9.6 \cdot 10^{-6}$	$3.99 \cdot 10^{-8}$
	40	5.4	22.9	$3.4 \cdot 10^{-6}$	$1.34 \cdot 10^{-9}$

temperatures. Values of the diffusion coefficient for the same temperatures and concentrations have been calculated from formula [24]

$$D = k_B T / 6\,\pi \eta_s \xi . \tag{28}$$

The correlation radius for this mixture has been determined with the application of the Rayleigh light dispersion effect (see paragraph 4).

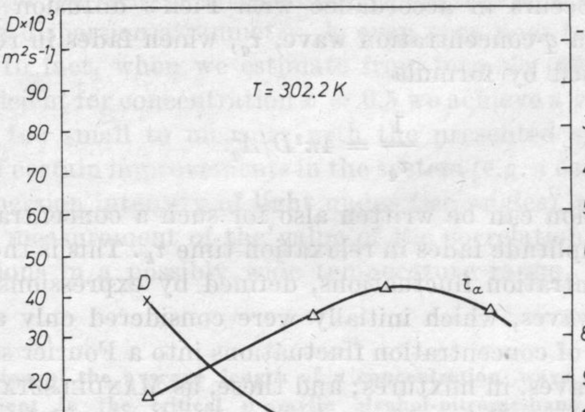

Fig. 16. D and τ_α versus concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 29.2°C$

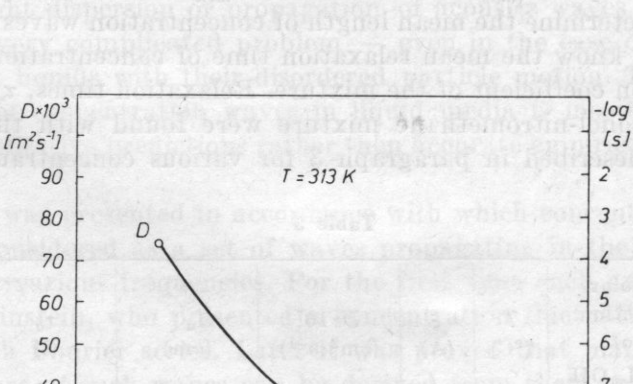

Fig. 17. D and τ_α versus concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 40°C$

Values of the correlation radius for definite concentrations and temperatures were calculated from expression (26) (see paragraph 4b) [31], [32].

Final results of calculations are presented in Table 5. Figs. 16 and 17 illustrate D and τ_a in terms of concentration in the critical *n*-amylic alcohol-nitromethane mixture at two temperatures: 29.2° and 40°C, respectively. In complience with the predictions of the theory the mean relaxation time of concentration fluctuations increases when the critical point is approached, while the diffusion coefficient decreases. Figs. 18 and 19 present the mean length of concentration waves in terms of the concentration of the mixture at the same two temperatures. As it can be seen the mean length of concentration waves increases by an order of magnitude when the conditions of the mixture approach critical conditions. This means that the spectrum of concentration waves moves towards lower frequencies.

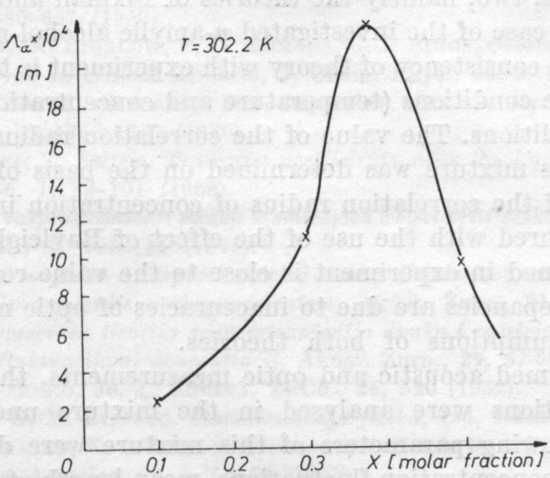

Fig. 18. Mean length of concentration waves in terms of concentration in the critical *n*-amylic alcohol-nitromethane mixture at temperature of $T = 29.2°C$

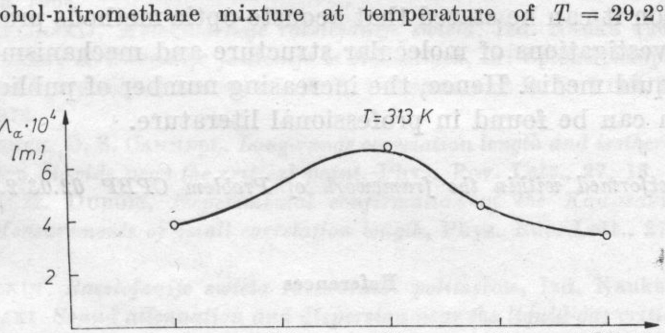

Fig. 19. Mean length of concentration waves in terms of concentration in the critical *n*-amylic alcohol-nitromethane mixture at temperature of $T = 40°C$

6. Conclusions

Results obtained in the complex investigations of the critical *n*-amylic alcohol-nitromethane mixture lead to the following conclusions:

1. It was stated that the acoustic behaviour of this mixture does not differ from the behaviour of other critical mixtures. And so: quantity α/f^2 depends on frequency, temperature and concentration. The α/f^2 curve has a maximum corresponding to the critical composition of the mixture. The value of this maximum strongly increases with the decrease of the acoustic wave frequency. At all concentrations the existing dispersion of quantity α/f^2 is not accompanied by significant changes of the propagation velocity of the acoustic wave in terms of frequency.

2. It was found that out of existing theories of acoustic wave propagation in critical mixtures, two, namely the theories of Fixman and Czaban, describe this process in the case of the investigated *n*-amylic alcohol-nitromethane mixture correctly. The consistency of theory with experiment is the better, the closer thermodynamic conditions (temperature and concentration) of the mixture are to critical conditions. The value of the correlation radius of concentration fluctuations in this mixture was determined on the basis of this consistence.

3. The value of the correlation radius of concentration in the investigated mixture was measured with the use of the effect of Rayleigh light dispersion. The value determined in experiment is close to the value resulting from both theories. The discrepancies are due to inaccuracies of optic measurements and to simplifying assumptions of both theories.

4. Using performed acoustic and optic measurements, the kinetics of concentration fluctuations were analysed in the mixture under investigation. Values of the following parameters of this mixture were determined: mean relaxation time of concentration fluctuations, mean length of the concentration wave and the diffusion coefficient.

In conclusion it can be stated that acousto-optic methods prove to be very effective in investigations of molecular structure and mechanism of molecular processes in liquid media. Hence, the increasing number of publications in this domain, which can be found in professional literature.

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References

[1] *Fiziczeskaja Akustika*, ed. Mason, Vol. 1, 2, Izd. Mir 1968.
[2] M. I. Szachparonow, J. G. Szoroszow, S. S. Alijew, M. G. Chaliulin, P. K. Chabibułłajew, ŻFCh, **43**, 10, 2543 (1963).
[3] W. Schaaffs, *Molekularakustik*, Springer Verlag, Berlin 1963.

[4] M. Łabowski, *Ultra- and hypersonic properties of chosen liquids and critical mixtures*, UAM Poznań 1980 (in Polish).

[5] S. S. Alijew, P. K. Chabibułłajew, *Wiestnik MGU*, Chimija, **6**, 115 (1969).

[6] G. D'Arrigo, D. Sette, *Ultrasonic Absorption and velocity near the critical region of nitrobenzene- n-hexane mixtures*, J. Chem. Phys., **48**, 2, 691–698 (1968).

[7] M. Łabowski, T. Hornowski, A. Skumiel, *Ultra- and hypersonic properties of the critical n-amylic alcohol-nitromethane mixture. A comparison with the theories of Fixman and Czaban*, Acustica, **57**, 175–184 (1985).

[8] P. K. Chabibułłajew, K. Parpijew, S. S. Alijew, L. E. Kwasowa, L. W. Łanszyna, *Wiestnik MGU*, Chimija (1971).

[9] M. Fixman, *Heat capacity of critical mixtures*, Journ. Chem. Phys., **36**, 8, 1957–1960 (1962).

[10] M. Fixman, *Absorption and dispersion of sound in critical mixtures*, Journ. Chem. Phys., **36**, 8, 1961–1964 (1962).

[11] L. Mistura, P. Tartaglia, *Sound propagation in critical mixtures*, Phys. Lett., **36A**, 4, 345–348 (1971).

[12] P. Debye, *Angular dissymmetry of the critical opalescence in liquid mixtures*, J. Chem. Phys. **31**, 3, 680–687 (1959).

[13] A. P. Kendig, R. N. Bigelow, P. D. Edmons, C. J. Pings, *Comment on absorption and dispersion of sound in critical mixtures*, J. Chem. Phys., **40**, 5, 1452 (1964).

[14] K. Kawasaki, *Sound attenuation and dispersion near the liquid-gas critical point*, Phys. Rew., 1A, 6, 1750–1757 (1970).

[15] L. K. Kadanoff, I. Swift, *Transport coefficients near the liquid-gas critical point*, Phys. Rev., **166**, 1, 89–101 (1968).

[16] I. A. Czaban, *O rasprostranienii zwuka w smiesjach wblizi kriticzeskoj toczki rassłaiwanija*, Akust. Żurn., **21**, 1, 104–111 (1975).

[17] I. A. Czaban, *K woprosu o rasprostraniejni zwuka w smiesjach wblizi kriticzeskoj toczki rassłaiwanija. Sprawnienije s ekspierimentom*, Akust. Żurn., **21**, 2, 286–293 (1975).

[18] I. A. Czaban, *Obszczaja tieorija rasprostranienija zwuka i rassiejanija swieta w rastworach s silnymi fluktuacijami koncentracii*, Akust. Żurn., **29**, 5, 685–692 (1983).

[19] W. K. Senienczenko, Je. Ł. Zorina, ŻFCh., **26**, 520 (1952).

[20] L. D. Landau, E. M. Lifszyc, *Statisticzeskaja fizika*, Izd. Nauka 1976.

[21] K. Ravindra Prasad, K. C. Ready, *Ultrasonic studies in the critical system benzyl-alcohol + iso-octane*, Acustica, **53**, 1, 55–58 (1983).

[22] I. G. Michajłow, W. A. Sołowjew, J. P. Syrnikow, *Osnowy molekularnoj akustiki*, Izd. Nauka 1964.

[23] I. L. Fabielinskij, *Molekularnoje rassiejanije swieta*, Izd. Nauka 1965.

[24] H. L. Swinney, *Kriticzeskije jawlenije w żidkostiach*, in: Spiektroskopije opticzeskog smieszenija i korrelacija fotonow, ed. H. Z. Cummins and E. R. Pike, Izdatelstwo Mir Moscow 1978.

[25] J. H. Lunacek, D. S. Cannell, *Long-range correlation length and isothermal compressibility of carbon dioxide near the critical point*, Phys. Rev. Lett., **27**, 13, 841–844 (1971).

[26] P. Berge, M. Dubois, *Experimental confirmation of the Kawasaki-Einstein-Stokes formula; Measurements of small correlation length*, Phys. Rev. Lett., **27**, 17, 1125–1127 (1971).

[27] W. Je. Eskin *Rassiejanije swieta rastworami polimerow*, Izd. Nauka, Moscow 1973.

[28] K. Kawasaki *Sound attenuation and dispersion near the liquid-gas critical point*, Phys. Rev., **1A**, 1750 (1970).

[29] L. P. Kadanoff, J. Swift, *Transport coefficients near the liquid-gas critical point*, Phys. Rev., **166**, 89 (1968).

[30] L. Landau, E. Lifszyc, *Mechanics of continuous media* (in Polish), PWN, Warsaw 1958.

[31] T. Hornowski, M. Łabowski, *Experimental acoustooptical determination of some physical parameters of the critical n-amylic alcohol-nitromethane mixture*, Acta Physica Polonica, **A69**/4 (in print).

[32] T. Hornowski, M. Łabowski, *Experimental determination of the correlation radius of concentration fluctuations in the critical n-amylic alcohol-nitromethane mixture* (in Polish), Proc. XXXII OSA, 179–182, Cracow 1985.