

Ultra- and hypersonic properties of the critical mixture *n* - amyl alcohol - nitromethane

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This paper gives the results of experimental investigations of the propagation velocity and the absorption coefficient of acoustic waves, both in the ultra- and hypersonic ranges, in the critical mixture *n* - amyl alcohol - nitromethane for two temperatures. The values of α/f^2 obtained experimentally were compared with those resulting from FIXMAN's and CHABAN's theory. It was found that both theories can, with some restrictions, describe experimental results.

1. Introduction

The investigations of the absorption of acoustic waves in a large number of critical mixtures showed that in those mixtures there is an additional range of acoustic dispersion which is not observed in low - viscosity single - component liquids [1-3]. It was shown [4-6] that the quantity α/f^2 depends on frequency, temperature and concentration. On the curve of the dependence of α/f^2 on concentration there is a maximum corresponding to the critical composition of the mixture, whose value increases rapidly as the frequency of acoustic waves decreases. For all concentrations the existing dispersion of the quantity α/f^2 is not accompanied by changes in the acoustic wave propagation velocity on the frequency scale which are measurable by the methods used.

The rapid increase in the absorption of acoustic waves in mixtures in the direct neighbourhood of the critical point, an increase in the intensity of the central component in the fine structure of Rayleigh light scattering and a large decrease in the diffusion coefficient are caused by an increase in the fluctuation of concentration and an increase in its correlation length with decreasing distance from this point.

It is very essential to investigate phase transitions in liquids and their mixtures of various physical nature, since comparison of the results obtained

with the behaviour of pure media provides the possibility of explaining the character of mutual interactions among the different molecules of the liquid. Therefore, of necessity, the gathering of experimental data on the properties of mixtures over a wide range of temperatures, pressures, concentrations and frequencies is now an important cognitive problem.

The present paper gives the results of investigations of acoustic properties over a wide frequency range in a pure component and in the critical mixture *n* - amyl alcohol - nitromethane for different concentrations and two temperatures. The results obtained were compared with those based on formulae resulting from FIXMAN's and CHABAN's respective theories.

The choice of this mixture for the investigations was suggested by lack of information on its acoustic properties over a wide frequency range, and in addition by the purpose of carrying out hypersonic investigations in the neighbourhood of the critical point. This was possible because the refractive indices in individual components are hardly different from each other and due to this, critical opalescence does not occur in the neighbourhood of the critical point.

2. Method of the experiment

The propagation velocity and the absorption coefficient of acoustic waves were measured at two independent measuring stands operating at frequencies of 20 MHz to 150 MHz, by using appropriately the pulse method with resonance excitation of piezoelectric transducers, and at hypersonic frequencies, by taking advantage of the shift and half - width of the Mandelsztam - Brillouin components in the fine structure of the Rayleigh light scattering lines [1, 7]. A detailed description of the measurement equipment, the investigation method and the accuracy of determining the propagation velocity and the absorption coefficient of acoustic waves, both in the ultra - and hypersonic ranges (with photoelectrical registration of the Mandelsztam - Brillouin components) were given in paper [4].

3. Theory

Among the large number of attempts to explain the characteristic behaviour of mixtures close to the critical point, it appeared that the most useful were those which consider the coupling between the concentration fluctuation and the acoustic wave. Far from the critical point, the concentration fluctuation in different volume elements can be regarded as independent. With decreasing distance from the critical point there is a rapid increase in the magnitude of the fluctuations and in their correlation length.

The presence of the acoustic wave in the medium causes a change in the mean amplitude of the concentration fluctuation and in its distribution fun-

ction. The fluctuation distribution reaches a value in equilibrium with some delay, depending on the diffusion coefficient D . The energy of the acoustic wave is used for the change in the fluctuation distribution and then dissipated in the form of heat. This process is irreversible, i.e. it leads to the absorption of acoustic waves. At appropriately high frequencies of the acoustic wave over one period, there is not enough time for a change to occur in the distribution of the concentration fluctuations and no absorption caused by these fluctuations can be observed.

This relaxation model is the basis for both FIXMAN's and CHABAN's theories, which describe the propagation of acoustic waves in mixtures close to their critical point. The two theories differ in the method of calculations and by some additional assumptions.

According to FIXMAN, a change in the fluctuation distribution occurs only under the effect of adiabatic temperature changes caused by the acoustic wave. On this assumption, FIXMAN calculated [8, 9] the additional contribution to the specific heat, related to this process. He also assumed that this process makes the same contribution to the specific heat at constant pressure and at constant volume (in the light of the current investigations, this assumption is not true [10]), and on this assumption he calculated the velocity and the absorption coefficient of the acoustic wave.

From DEBYE's formula [11],

$$\kappa^2 = (6/l^2 T_c) |T - T_c|, \tag{1}$$

where $\kappa^{-1} = \xi$ is the correlation length of the concentration fluctuation, l is the radius of intermolecular interactions and T_c is the critical temperature; the final result of FIXMAN's theory can be given in the following from:

$$\frac{\alpha}{f^2} = A f^{-5/4} \text{Im}[f(d)] + B, \tag{2}$$

$$v = v_\infty \{1 - A v_\infty f^{-1/4} \text{Re}[f(d)]\}, \tag{3}$$

where

$$f(d) = \frac{1}{\sqrt{d}} \int_0^\infty \frac{z^4}{(z^2 + 1) [z^2(z^2 + 1) - id^{-2}]} dz, \quad z = k\xi, \tag{4}$$

$$d = C f^{-1/2} |T - T_c|, \tag{5}$$

with v_∞ being the acoustic wave velocity at $\omega\tau \gg 1$. The constants A and C weakly dependent on temperature and independent of frequency.

The function $f(d)$ was defined numerically by KENDIG and others [12].

The analytical form of this function,

$$f(d) = \frac{1}{2} \pi i d^{3/2} \{1 - i(1 + 4id^{-2})^{-1/2} (x_1^{5/2} + x_2^{5/2})\}, \quad (6)$$

$$x_1 = -\frac{1}{2} + \frac{1}{2} (1 + 4id^{-2})^{1/2}, \quad x_2 = -(x_1 + 1),$$

which will be used in the further part of this paper, was given by FIXMAN.

CHABAN, on the basis of the more recent papers by KAWASAKI [13], KADANOFF and SWIFT [14], modified to some extent FIXMAN's assumptions about the change in the fluctuation distribution under the effect of acoustic waves. This permitted some intrinsic inconsistencies of FIXMAN's theory to be avoided [15].

CHABAN assumed that the change in the fluctuation distribution under the effect of acoustic waves occurs not only as a result of adiabatic temperature changes, but it is also caused by rapid changes in the critical temperature effected by the pressure of the acoustic wave.

On the basis of these assumptions, CHABAN determined the complex adiabatic compressibility of a medium with strong concentration fluctuations [16]. From the fluctuation dissipation theorem, he calculated the change in the fluctuation distribution caused by the acoustic wave. His considerations gave the following final results [17]:

$$v = v_0 \left\{ 1 - \frac{Mv_0}{2\pi\tau_1} [|T - T_c| + a|\bar{x} - \bar{x}_c|^3]^{-0.2} \left[F_2(\omega\tau) - \frac{b - \tan^{-1}b}{12} \right] \right\}, \quad (7)$$

$$\frac{\alpha}{f^2} = M [|T - T_c| + a|\bar{x} - \bar{x}_c|^3]^{-2} F_1(\omega\tau) + L, \quad (8)$$

where

$$F_1(\omega\tau) = \int_0^\infty \frac{z^4 \frac{3}{4} \left[\frac{1}{z^2} + 1 + \left(z - \frac{1}{z^3} \right) \tan^{-1} z \right] dz}{\left\{ (\omega\tau)^2 + 4z^4 \frac{9}{16} \left[\frac{1}{z^2} + 1 + \left(z - \frac{1}{z^3} \right) \tan^{-1} z \right]^2 \right\} (1+z^2)^2},$$

$$F_2(\omega\tau) = \int_0^\infty \frac{2z^6 \frac{9}{16} \left[\frac{1}{z^2} + 1 + \left(z - \frac{1}{z^3} \right) \tan^{-1} z \right]^2 dz}{\left\{ (\omega\tau)^2 + 4z^4 \frac{9}{16} \left[\frac{1}{z^2} + 1 + \left(z - \frac{1}{z^3} \right) \tan^{-1} z \right]^2 \right\} (1+z^2)^2},$$

$$\tau = \frac{\tau_1}{2\pi} [|T - T_c| + a|\bar{x} - \bar{x}_c|^3]^{-1/8}, \quad (9)$$

v_0 is the acoustic wave velocity at $\omega\tau \ll 1$, x_c is the critical concentration of the mixture, M and L are constants weakly dependent on temperature and concentration and independent of frequency. It follows from theoretical calculations that $b \cong 5$. Expressions (7) and (8) are valid with the condition $\omega\tau < 340$ [18].

Both in FIXMAN's and CHABAN's theories, the constants A and C and M and τ are represented by means of the parameters of the mixture, however, it is quite difficult to determine some of them, e.g. the correlation length or the diffusion constant. Therefore, these constants are most frequently determined from the condition of best agreement between theory and experiment. This method was also assumed in the present paper.

The parameters of the curves of the "best fit" were determined by using the least squares method, i.e. by minimizing the expression

$$\chi_r^2 = \sum_{j=1}^n \frac{[\hat{y}_j - f(x_1 \dots x_m)]^2}{\sigma_j^2}, \tag{10}$$

where \hat{y}_j is an experimentally determined quantity, n is the number of measurements, m is the number of constants to be determined, σ_j^2 is the squared mean error of the j th measurement and $\nu = n - m$ is the number of degrees of freedom.

The function $Im[f(d)]$ and $F_1(\omega\tau)$, their derivatives and the parameters of the curves of the "best fit" were computed on a Sinclair ZX-81 minicomputer, where the following analytical form of the function $Im[f(d)]$ was assumed:

$$Im[f(d)] = \frac{1}{2} \pi d^{3/2} \left[1 + \sqrt{\frac{(\Delta_1)^5}{\Delta}} \sin\left(\frac{5\vartheta_1 - \vartheta}{2}\right) + \sqrt{\frac{(\Delta_2)^5}{\Delta}} \sin\left(\frac{5\vartheta_2 - \vartheta - 2\pi}{2}\right) \right], \tag{11}$$

where

$$\Delta = \frac{1}{d^2} \sqrt{d^4 + 16}, \quad \vartheta = \tan^{-1} \frac{4}{d^2},$$

$$\Delta_1 = \left(\frac{1}{4} + \frac{1}{4} \Delta - \frac{1}{2} \sqrt{\Delta} \cos \frac{\vartheta}{2} \right)^{1/2}, \quad \Delta_2 = \left(\frac{1}{4} + \frac{1}{4} \Delta + \frac{1}{2} \sqrt{\Delta} \cos \frac{\vartheta}{2} \right)^{1/2},$$

$$\vartheta_1 = \tan^{-1} \left(\frac{\sin \frac{\vartheta}{2}}{\cos \frac{\vartheta}{2} - \frac{1}{\sqrt{\Delta}}} \right), \quad \vartheta_2 = \tan^{-1} \left(\frac{\sin \frac{\vartheta}{2}}{\cos \frac{\vartheta}{2} + \frac{1}{\sqrt{\Delta}}} \right) + \pi.$$

The values of the function $F_1(\omega\tau)$ were calculated by means of the Simpson quadrature, by transformation of the variables $x = \tan \alpha$.

$$F_1(\omega\tau) = \frac{3}{8} \int_0^{\pi/2} \frac{(\sin 2\alpha)^3 g(\alpha) d\alpha}{4(\omega\tau)^2 \cos^6 \alpha \sin^2 \alpha - 9g^2(\alpha)},$$

$$g(\alpha) = \frac{1}{2} \sin 2\alpha - \alpha \cos 2\alpha.$$

The derivatives of the functions $Im[f(d)]$ and $F_1(\omega\tau)$ were approximated by the difference quotient

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

Since both in CHABAN's and FIXMAN's theories there are nonlinear dependencies, therefore the fitting process must be carried out by successive approximations. This process should be stopped when the value of χ^2 reaches a minimum with the predescribed magnitude of the measurement error.

4. Investigation results and discussion

a) Ultra and hypersonic properties of pure nitromethane

Measurements over the frequency range 29-130 MHz showed that within the measurement error a/f^2 does not depend on frequency. At a frequency of about 4.1 GHz the value of a/f^2 decreases, and there is also a slight increase in the acoustic wave propagation velocity.

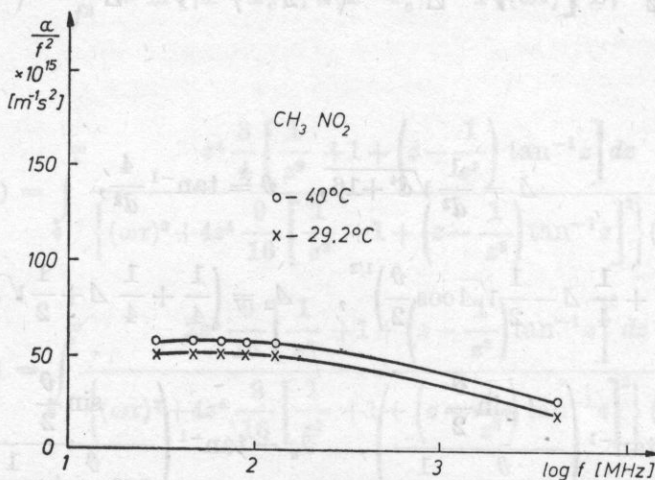


Fig. 1. The dependence of a/f^2 on $\log f$ in nitromethane for temperatures of 29.2°C and 40°C

The results of measurements of the quantity α/f^2 in pure nitromethane over the whole range of the frequencies investigated for two temperatures are shown graphically in Fig. 1. This figure indicates a slight increase in α/f^2 as temperature increases.

By using the formula

$$\tau = \frac{1}{\omega_n} \left[\left(\frac{\alpha'}{f^2} \right)_{f \rightarrow 0} / \left(\frac{\alpha'}{f^2} \right)_{f=f_n} - 1 \right]^{1/2}, \quad (12)$$

the acoustic relaxation time τ was estimated to be about $0.7 \cdot 10^{-10}$ s.

Subsequently, using the estimated value of the relaxation time τ , the value of the propagation velocity of hypersonic waves was determined at a frequency of about 4100 MHz for $T = 29.2^\circ\text{C}$, from the following relation:

$$\frac{v_0^2}{v^2} = 1 - \varepsilon \frac{\omega^2 \tau^2}{1 + (\omega \tau)^2}, \quad (13)$$

where

$$\varepsilon = \frac{A' v_0}{2\pi\tau}.$$

The experimental value of the propagation velocity of hypersonic waves for this temperature is 1350 m/s, while the one estimated according to the above method is about 1362 m/s. The above values of the velocity of hypersonic waves within the experimental error are sufficiently close to permit the relaxation process in nitromethane to be characterized by one relaxation time.

The respective values of some physical - chemical and acoustic quantities are given in Table 1. It follows from this table that the values of c_{opt}^* and c_{ac}^* coincide within the experimental error. The values of c_{opt}^* are found from data on the normal frequencies of the molecule vibration by means of the Planck - Einstein formula [1].

An increase in α_{ex}/f^2 and in the ratio η_v/η_s with increasing temperature indicates that there is oscillation relaxation. The investigations in [19] showed that in pure *n* - amyl alcohol there is structural relaxation. It can be expected that when in the mixture *n* - amyl alcohol - nitromethane acoustic dispersion is observed at frequencies lower than about 10^9 Hz, it will be caused by the relaxation of the concentration fluctuation.

b) *Ultra - and hypersonic properties of the critical mixture n - amyl alcohol - nitromethane*

The mixture *n* - amyl alcohol - nitromethane has an upper critical point. The critical parameters determined are respectively: $T_c = 27.8^\circ\text{C}$ and $x_c = 0.385$ (x_c - molar fraction of *n* - amyl alcohol). The critical temperature was determined visually from the vanishing boundary between phases and from the maximum intensity of the central component of scattered light.

Table 1

T [°C]	$A \cdot 10^{15}$ [$m^{-1}s^2$]	$\frac{\alpha_{ol}}{f^2} \cdot 10^{15}$ [$m^{-1}s^2$]	$\frac{\alpha_{exp}}{\alpha_{ol}}$	$\frac{\eta_v}{\eta_s}$	$\tau \cdot 10^{10}$ [s]	v_0 [m/s]	v_h [m/s]	$\Delta\nu$ [cm^{-1}]	c_p [$\frac{cal}{moldeg}$]	c_v [$\frac{cal}{moldeg}$]	c_{opt}^* [$\frac{cal}{moldeg}$]	c_{ao}^* [$\frac{cal}{moldeg}$]
29.2	39	6.5	8.2	9.4	0.7	1305	1350	0.15	24.6	16.2	4.8	4.2
40	40	6.3	8.9	10.6	0.8	1260	1296	0.13	—	—	—	—

Table 2

$n - C_t H_{11} OH$ in $CH_3 NO_2$	$\Delta\nu$ [cm^{-1}]	f_h [GHz]	v_0 [m/s]	v_h [m/s]	$\frac{I_c}{2I_{MB}}$	$\alpha f^2 \cdot 10^{15}$ [s^2/m]	$\Delta\nu_{MB} \cdot 10^3$ [cm^{-1}]	ρ [kg/m^3]
0.0	0.141	4.23	1340	1374	0.6	19.15	5	1124.1
0.1	0.132	3.96	1270	1285	0.7	28.04	6	1079.0
0.3	0.130	3.90	1248	1257	6.4	73.89	15	972.4
0.385	0.128	3.84	1232	1237	17.8	82.62	16	958.2
0.5	0.133	3.99	1240	1281	7.2	64.66	14	927.6
0.9	0.132	3.96	1243	1264	0.5	47.50	10	839.6
1.0	0.130	3.90	—	1237	0.3	20.02	4	814.8

Fig. 2 shows the dependence of the temperature of the separation of the components of the mixture for different concentrations.

Fig. 3. shows the results of measurements of the light refractive index on concentration in the mixture *n* - amyl alcohol - nitromethane at a temperature of 29.2°C.

The measurements showed that *n* changes depending on composition in a rather linear way and does not "feel" the critical point. The light refractive indices of pure components of this mixture at 29.2°C differ slightly, therefore in practice, hardly any critical opalescence occurs in it, which permits the observation of the fine structure of the Rayleigh light scattering also in the direct neighbourhood of the temperature of the separation of the components.

In the experiment, chemically pure media were used, which were additionally cleaned chemically and distilled several times. The degree of purity was controlled by measuring the refractive index density and the boiling temperature. The cell filled with the mixture was sealed by welding so as to decrease the volume of the gas phase and to maintain the constant composition of the mixture in the course of optical measurements.

In order to gain essential information about the kinetics of the concentration fluctuation, acoustic investigations of the properties of the mixture *n* - amyl

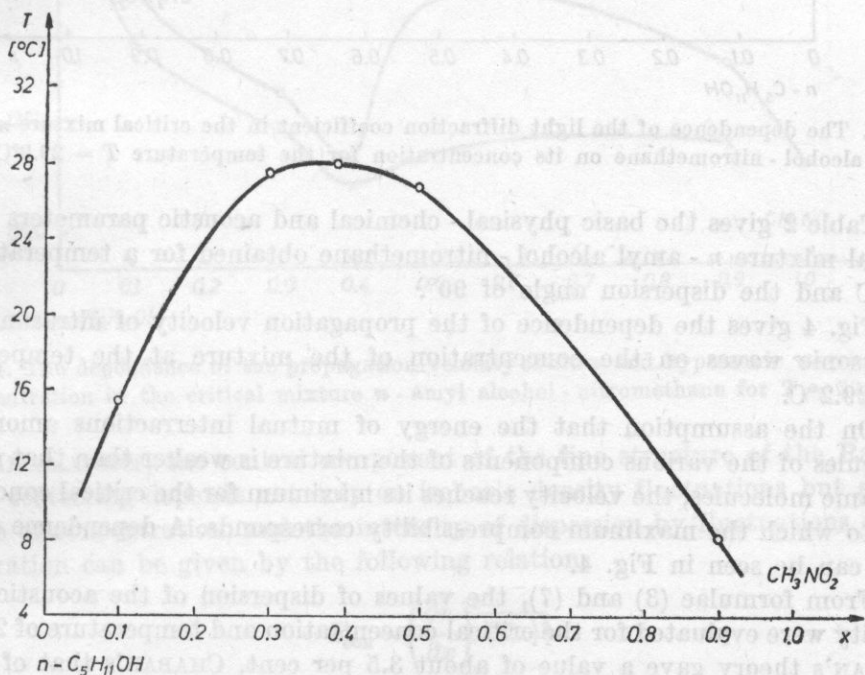


Fig. 2. The curve of the separation of the components of the system *n* - amyl alcohol - nitromethane. The concentration of the components expressed in molar fraction

alcohol - nitromethane were carried out for the following concentrations: $x = 0.1, 0.3, 0.385, 0.5, 0.9$ molar fraction of n - amyl alcohol.

The acoustic wave propagation velocity was determined for two frequencies: 28 HMz and about 3900 MHz. The amplitude coefficient of the absorption of acoustic waves was determined over the ultrasonic range 29.6-128.6 MHz by the pulse method, using the resonance excitation of piezoelectric transducers, and over the hypersonic range the fine structure of the Rayleigh light scattering.

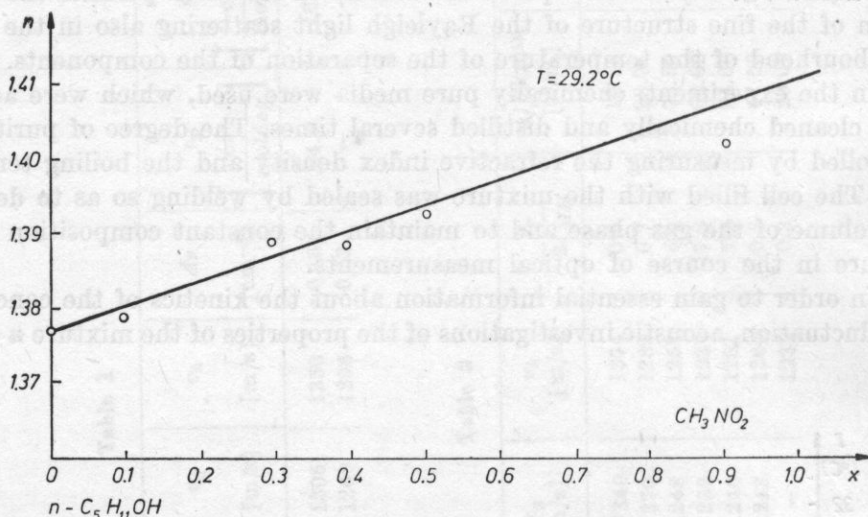


Fig. 3. The dependence of the light diffraction coefficient in the critical mixture n - amyl alcohol - nitromethane on its concentration for the temperature $T = 29.2^\circ\text{C}$

Table 2 gives the basic physical - chemical and acoustic parameters of the critical mixture n - amyl alcohol - nitromethane obtained for a temperature of 29.2°C and the dispersion angle of 90° .

Fig. 4 gives the dependence of the propagation velocity of ultrasonic and hypersonic waves on the concentration of the mixture at the temperature $T = 29.2^\circ\text{C}$.

On the assumption that the energy of mutual interactions among the molecules of the various components of the mixture is weaker than that among the same molecules, the velocity reaches its maximum for the critical concentration to which the maximum compressibility corresponds. A dependence of this type can be seen in Fig. 4.

From formulae (3) and (7), the values of dispersion of the acoustic wave velocity were evaluated for the critical concentration and temperature of 29.2°C . FIXMAN's theory gave a value of about 3.5 per cent, CHABAN's that of about 0.6 per cent, whereas the dispersion determined experimentally is about 0.4 per cent.

As was already mentioned, in pure nitromethane and *n*-amyl alcohol, over the frequency range 29.6-128.6 MHz, the quantity α/f^2 does not depend on frequency within the experimental error, and for hypersonic frequencies a deviation from the Stokes law can be observed.

The present paper demonstrates that the relaxation process in pure nitromethane is caused by the oscillation relaxation, while it was proved in paper [19] that the structural relaxation is responsible for the relaxation process in *n*-amyl alcohol.

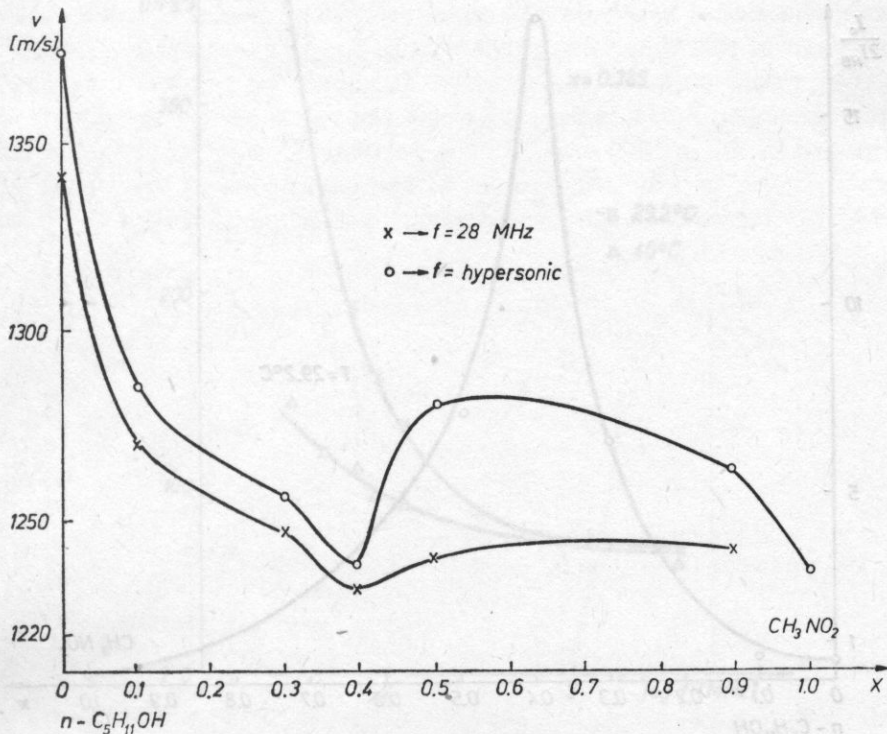


Fig. 4. The dependence of the propagation velocity of ultra- and hypersonic waves on concentration in the critical mixture *n*-amyl alcohol - nitromethane for $T = 29.2^\circ\text{C}$

In mixtures, the central component of the fine structure of the Rayleigh light scattering depends not only on isobaric density fluctuations but also on those of concentration, and the intensity of dispersion by fluctuations of concentration can be given by the following relation:

$$I_{\text{con}} \sim \left(\frac{\partial n}{\partial x} \right)^2 (\Delta x)^2.$$

In the mixture *n*-amyl alcohol - nitromethane, concentration fluctuations can be observed, which increase as the temperature and concentration

approach their values at the critical point. Therefore, $I_c/2I_{MB}$ reaches for this mixture its maximum values close to the critical parameters, which can be seen in Fig. 5, where the dependence of $I_c/2I_{MB}$ on the composition of the mixture is given for the temperature $T = 29.2^\circ\text{C}$.

A considerable increase in the value of the ratio $I_c/2I_{MB}$ as the mixture approaches the critical parameters indicates strong light scattering by concentration fluctuations and by isobaric density fluctuations, with the simultaneous decrease in the effect of adiabatic density fluctuations.

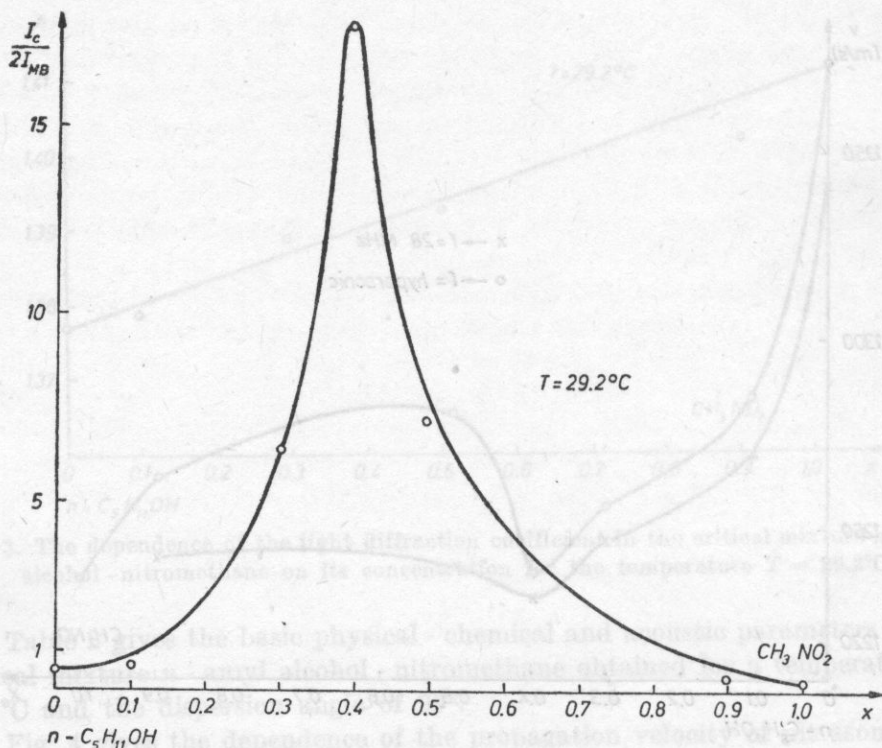


Fig. 5. The dependence of $I_c/2I_{MB}$ on concentration in the critical mixture n -amyl alcohol-nitromethane at the temperature $T = 29.2^\circ\text{C}$ (x - molar fraction of n -amyl alcohol)

In the mixture n -amyl alcohol-nitromethane considerable depolarised spectrum can be observed, which reaches its maximum values in the direct neighbourhood of the critical point, indicating that it is possible to observe and measure the scattering by the orientation fluctuations.

Experimental points representing the dependence of a/f^2 on frequency are plotted in Figs. 6-8 respectively for three concentrations and two temperatures. The solid lines in these figures were plotted on the basis of formulae (2) and (5) resulting from FIXMAN's theory.

The values of the parameters of the "best fit curves" are listed in Table 3. In Figs. 9-11 the solid curves were plotted from formulae (8) and (9), resulting from CHABAN's theory.

On the basis of this theory, the following values of the parameters of the curves of the "best fit" were obtained: $M = 2.751 \cdot 10^{-11} \text{ s}^2 \text{ deg}^2 \text{ m}^{-1}$, $\tau_1 = 2.166 \cdot 10^{-7} \text{ s}$, $L = 60.1 \cdot 10^{-15} \text{ s}^2 \text{ m}^{-1}$.

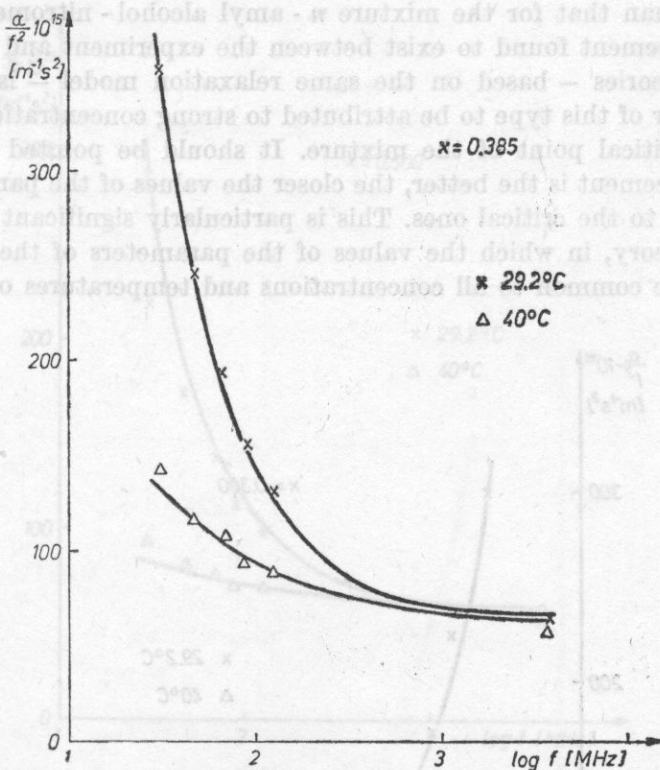


Fig. 6. The dependence of a/f^2 on $\log f$ in the mixture *n*-amy alcohol - nitromethane with the critical concentration $x = 0.385$ (x - molar fraction of *n*-amy alcohol) for two temperatures. The solid curves were plotted from formulae (2) and (5). x , Δ - experimental points

The quantity a in equation (9) was determined from the dependence of the separation temperature of the mixture on concentration. It is $a = 400 \text{ deg/}$ /molar fraction.

Figs. 12 and 13 give the dependence of the quantity a/f^2 on concentration for different frequencies for the mixture *n*-amy alcohol - nitromethane.

Figs. 12 and 13 indicate that in the mixture *n*-amy alcohol - nitromethane the quantity a/f^2 passes a maximum at $x_c = 0.385$. The value of this maximum

decreases as the frequency increases, and it almost vanishes at hypersonic frequencies.

This effect cannot be explained by an increase in the shear viscosity, which increases slightly only in the direct neighbourhood of the critical point [20], or by relaxation processes occurring in the pure components of the mixture. It was shown experimentally that in the pure components of the mixture the quantity a/f^2 hardly depends on frequency and is lower by several orders of magnitude than that for the mixture *n*-amyl alcohol - nitromethane.

The agreement found to exist between the experiment and FIXMAN's and CHABAN's theories — based on the same relaxation model — is the basis for the behaviour of this type to be attributed to strong concentration fluctuations about the critical point of the mixture. It should be pointed out, however, that this agreement is the better, the closer the values of the parameters of the mixtures are to the critical ones. This is particularly significant in the case of CHABAN's theory, in which the values of the parameters of the curves of the "best fit" are common to all concentrations and temperatures of the mixture,

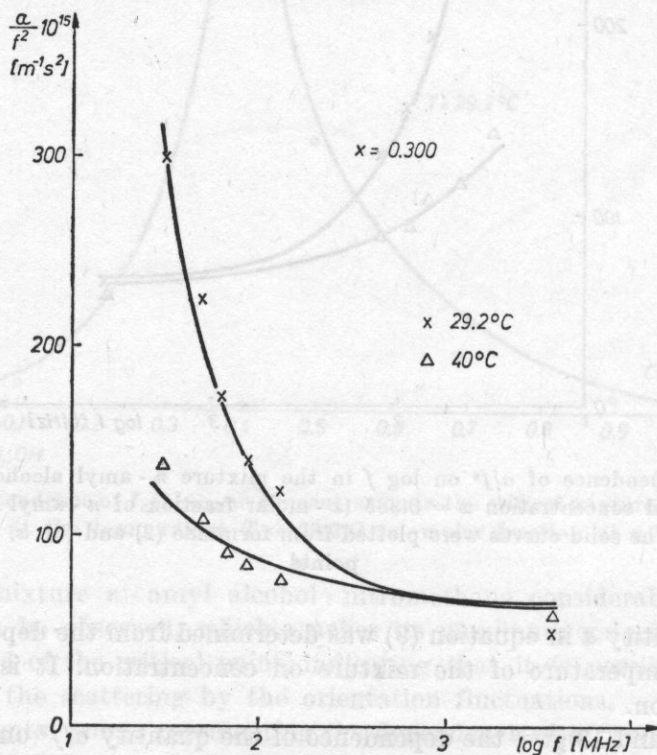


Fig. 7. The dependence of a/f^2 on $\log f$ in the critical mixture *n*-amyl alcohol - nitromethane with the concentration $x = 0.300$ (x - molar fraction of *n*-amyl alcohol) for two temperatures. The solid curves were plotted from formulae (2) and (5). x , Δ - experimental points

in contrast to FIXMAN's theory, where the constants A and C , dependent on concentration, must be selected for each concentration.

The attempts to generalize FIXMAN's theory [6, 21], i.e. a description of the absorption coefficient as function of concentration, based on the Flory-Huggins approximation, give very poor agreement between theory and experiment (with maxima usually displaced towards higher concentrations, and the simultaneous decrease in their value).

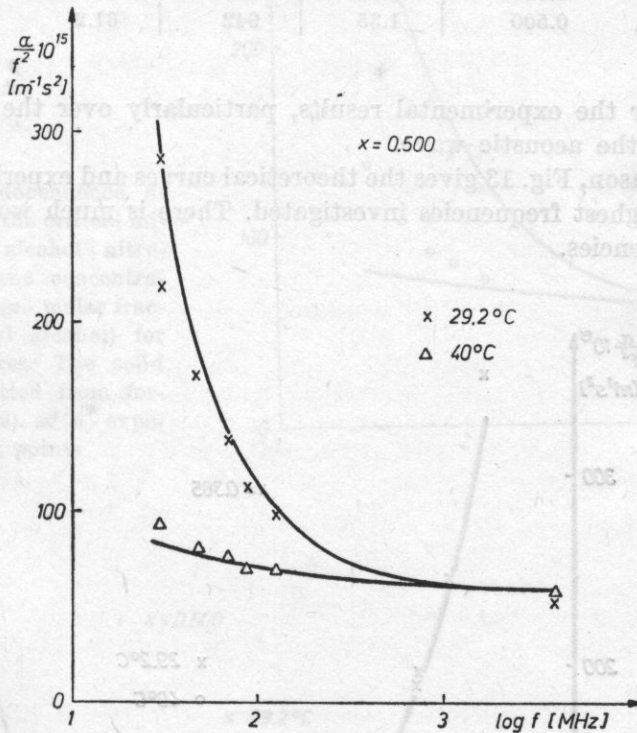


Fig. 8. The dependence of a/f^2 on $\log f$ in the critical mixture n - amyl alcohol - nitromethane with the concentration $x = 0.500$ (x - molar fraction of n - amyl alcohol) for two temperatures. The solid curves were obtained from formulae (2) and (5). x , Δ - experimental points

Neglecting the Flory - Huggins approximation would require that the additional quantity $(\partial\mu/\partial x)_{p,T}$ should be determined from the total intensity of the central component of the scattered light.

At the present stage of investigations, CHABAN's theory is more convenient than FIXMAN's, as it permits - while requiring determination of a smaller number of parameters - the acoustic parameters of critical mixtures to be described with greater complexity.

In the case of the mixture n - amyl alcohol - nitromethane, the dependence of the quantity a/f^2 on concentration, determined from CHABAN's theory,

Table 3

Concentration in molar frac- tions of <i>n</i> -amyl alcohol	$A \cdot 10^3$ [s ^{3/4} m ⁻¹]	C [s ^{-1/2} deg ⁻¹]	$B \cdot 10^{15}$ [m ⁻¹ s ²]
0.385	2.07	574	66.6
0.300	1.72	567	65
0.500	1.35	942	61.2

describes better the experimental results, particularly over the higher frequency range of the acoustic wave.

For this reason, Fig. 13 gives the theoretical curves and experimental results only for the highest frequencies investigated. There is much worse agreement at lower frequencies.

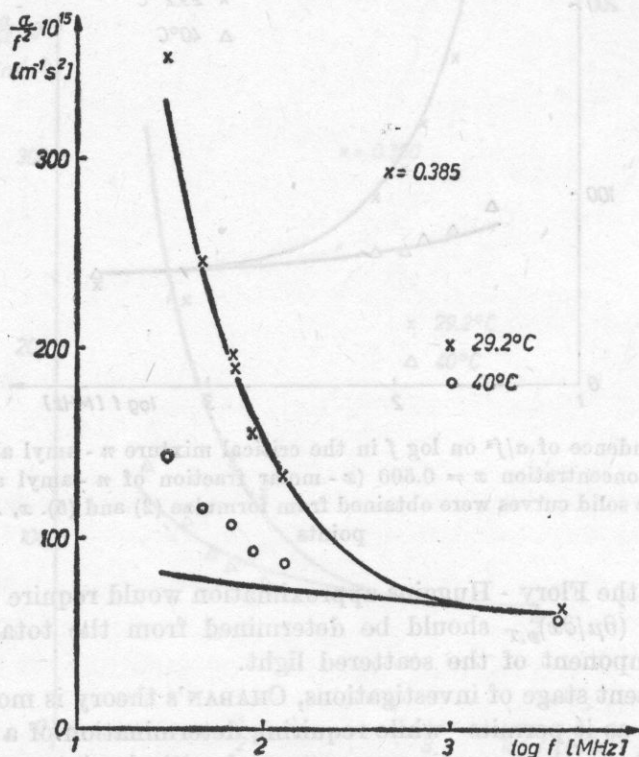


Fig. 9. The dependence of a/f^2 on $\log f$ in the mixture *n*-amyl alcohol - nitromethane with the critical concentration $x = 0.385$ (x - molar fraction of *n*-amyl alcohol) for two temperatures. The solid curves were plotted from formulae (8) and (9). x , o - experimental points

Fig. 10. The dependence of α/f^2 on $\log f$ in the critical mixture *n*-amyl alcohol-nitromethane with the concentration $x = 0.300$ (x - molar fraction of *n*-amyl alcohol) for two temperatures. The solid curves were plotted from formulae (8) and (9). x , o - experimental points

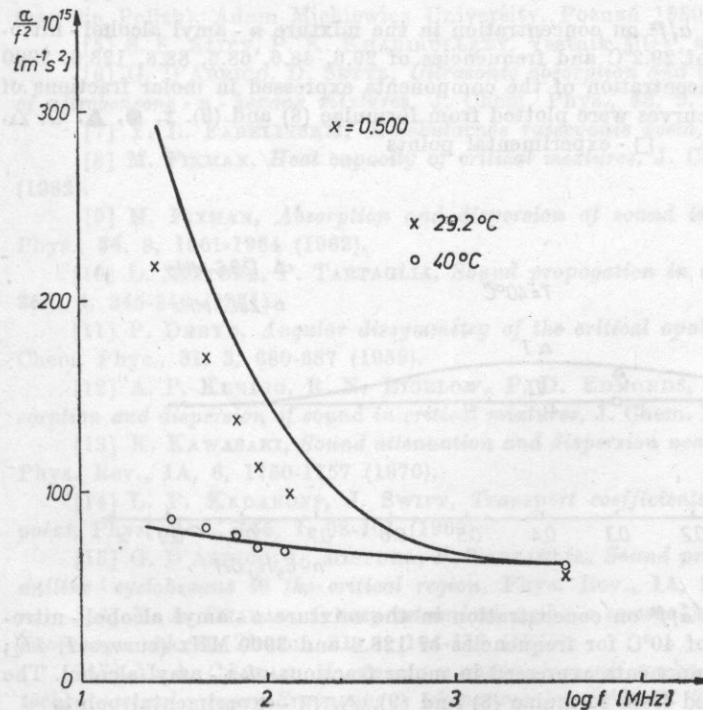
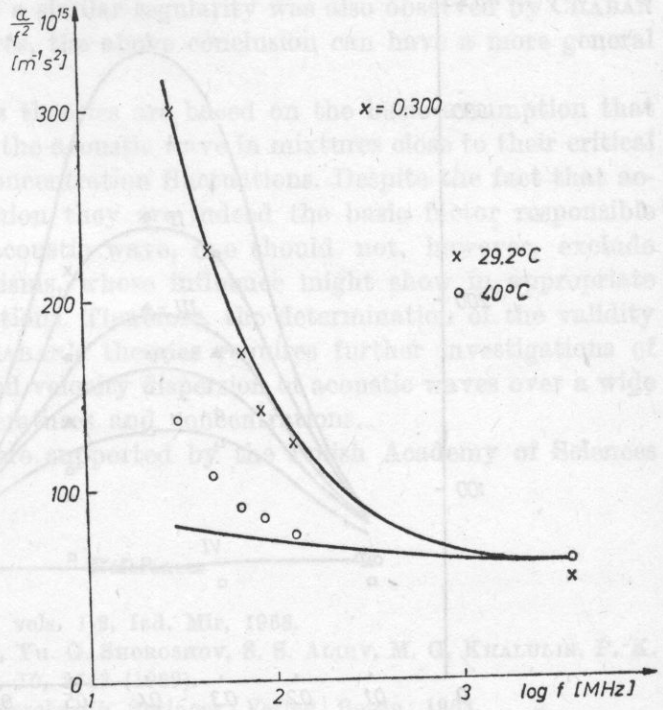


Fig. 11. The dependence of α/f^2 on $\log f$ in the critical mixture *n*-amyl alcohol-nitromethane with the concentration $x = 0.500$ (x - molar fraction of *n*-amyl alcohol) for two temperatures. The solid curves were plotted from formulae (8) and (9). x , o - experimental points

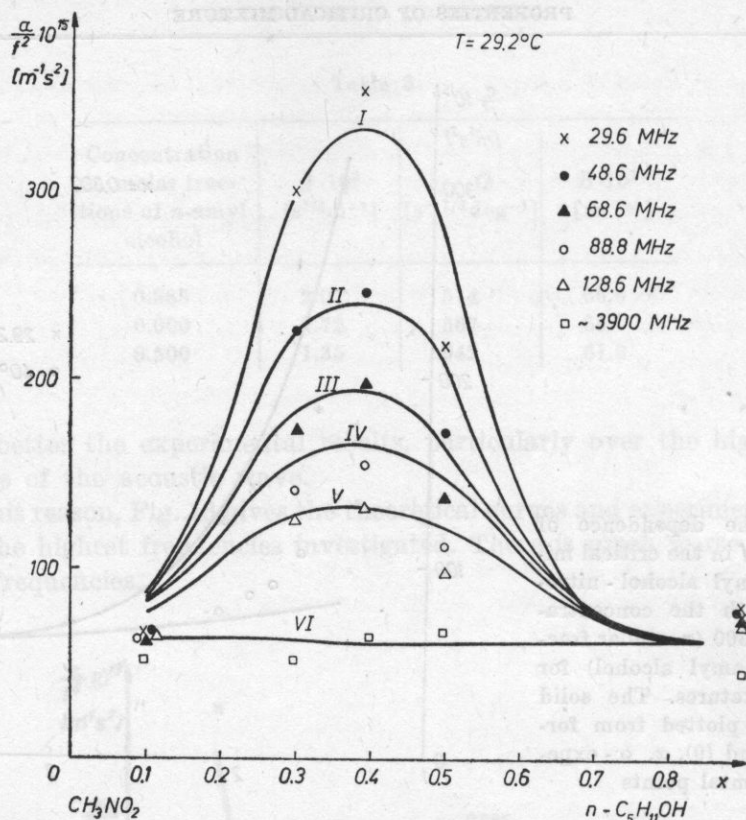


Fig. 12. The dependence of a/f^2 on concentration in the mixture *n*-amyl alcohol - nitromethane at a temperature of 29.2°C and frequencies of 29.6, 48.6, 68.6, 88.8, 128.6, 3900 MHz (curves I-VI); the concentration of the components expressed in molar fractions of *n*-amyl alcohol. The solid curves were plotted from formulae (8) and (9). x, ●, ▲, ○, △, □ - experimental points

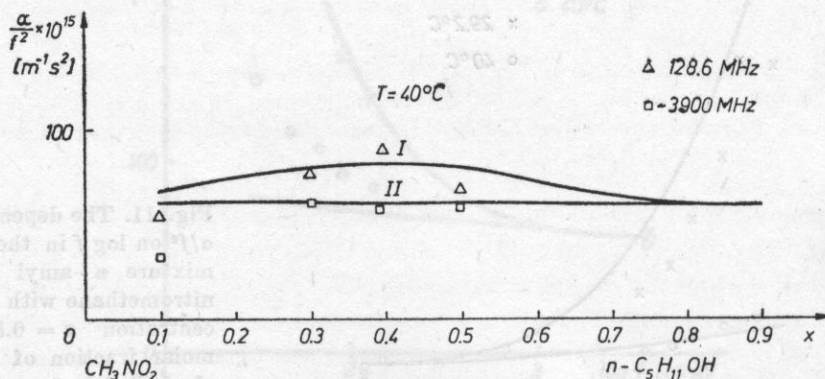


Fig. 13. The dependence of a/f^2 on concentration in the mixture *n*-amyl alcohol - nitromethane at a temperature of 40°C for frequencies of 128.6 and 3900 MHz (curves I, II); the concentration of the components expressed in molar fractions of *n*-amyl alcohol. The solid curves were plotted from formulae (8) and (9). △, □ - experimental points

In view of the fact that a similar regularity was also observed by CHABAN [17] in other critical mixtures, the above conclusion can have a more general nature.

FIXMAN's and CHABAN's theories are based on the basic assumption that the anomalous behaviour of the acoustic wave in mixtures close to their critical point is caused by strong concentration fluctuations. Despite the fact that according to the current opinion they are indeed the basic factor responsible for this behaviour of the acoustic wave, one should not, however, exclude the effect of other mechanisms, whose influence might show in appropriate mixtures under some conditions. Therefore, the determination of the validity range of FIXMAN's and CHABAN's theories requires further investigations of the absorption coefficient and velocity dispersion of acoustic waves over a wide range of frequencies, temperatures and concentrations.

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