ATTENUATION AND PROPAGATION VELOCITY OF ULTRASOUND IN ORGANIC LIQUIDS AND BIOLIQUIDS
Dynamics universality of critical attenuation in benzonitrile-isoctane and nitroethane-isoctane binary mixtures

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Ultrasound velocity and absorption as a function of temperature and frequency are reported for the benzonitrile-isoctane and nitroethane-isoctane critical binary mixtures. Experimental data were compared with the scaling functions $I(\omega^*)$ of Ferrell-Bhattacharjee dynamic scaling theory, Kroll-Ruhland renormalization group theory and Shiwa-Kawasaki mode coupling theory. The adiabatic coupling constant $g$ was calculated and compared with experimental value.

INTRODUCTION

Ultrasonic studies of the velocity and absorption provide valuable information about the dynamics of the relaxation process near the consolute point of the critical mixtures. Measured absorption grows rapidly when temperature approaches the critical value. This growth depends on frequency of ultrasonic wave. The lower frequency the quicker growth of absorption. This anomaly is a consequence of the coupling of acoustic field with the concentration fluctuations in critical mixtures.

Propagation of ultrasonic wave in critical mixtures is described by few theoretical models: mode-coupling theory developed by Shiwa and Kawasaki [1], Kroll-Ruhland [2, 3] and Onuki [4] renormalization-group theory, and Ferrell-Bhattacharjee [5, 6] dynamic scaling theory. All theories leads to the same equation for absorption coefficient per wavelength:

$$\alpha_{i0} = \pi A(\varepsilon) I(\omega^*), \quad (1)$$

yet they differ in the form of expression for temperature dependent critical amplitude $A(\varepsilon)$ and frequency dependent scaling function $I(\omega^*)$. All critical mixtures belong to the same universality class of $n = 1$ (scaling order parameter) and $d = 3$ (dimension of the system). It follows from Eq. 1 that measured absorption in all critical mixtures for different temperatures and frequencies should scale along universal curve — scaling function. Hence, it is very important to experimentally verify equations of above theories.

EXPERIMENTAL TECHNIQUE

Solutions were prepared by weight using Aldrich chemicals (99% purity) without further purification. The values of critical temperature $T_c$ and critical concentration $x_c$ for both mixtures are presented in Tab. 1.

<table>
<thead>
<tr>
<th></th>
<th>$T_c$ °C</th>
<th>$x_c$ isoctane</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzonitrile-isoctane</td>
<td>18.71</td>
<td>0.465</td>
</tr>
<tr>
<td>nitroethane-isoctane</td>
<td>30.05</td>
<td>0.431</td>
</tr>
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</table>

Measurements of absorption coefficient and velocity were made by pulse method using Matec apparatus. A block diagram and detailed description is to be found in paper [9].

RESULTS AND ANALYSIS

All thermodynamical quantities necessary to calculate the value of critical amplitude $A(\varepsilon)$ and characteristic frequency $\omega_D$ ($\omega^* = \omega/\omega_D$) describing concentration fluctuations are well known for both mixtures.

FIGURE 1. Dependence of $\alpha_{i0}/f^2$ on $f^{-1.06}$ in benzonitrile-isoctane and nitroethane-isoctane critical mixtures.
We started theory verification from linear dependence between $\alpha(T_c)/f^2$ and $f^{-1.06}$ predicted by Ferrell-Bhattacharjee (see Fig. 1):

$$\frac{\alpha(T_c)}{f^2} = \left[ \frac{\pi^2 \alpha_b^2 u_{c_{pb}}}{2 \sqrt{T_c} \epsilon_{c_{pc}}} \left( \frac{\omega}{\pi} \right)^\frac{\alpha}{2} \right] f^{-(1+\alpha/2)} + \frac{\alpha_b}{f^2} = S f^{-1.06} + b \tag{2}$$

where $\alpha_b/f^2$ describes the classical absorption, $c_{pc}$ and $c_{pb}$ indicate the critical and regular part of the specific heat respectively, $u$ is the velocity, $\alpha, \gamma, \nu$ are critical exponents. Eq. 2 is a valuable tool to determine adiabatic coupling constant $g$ from slope $S$ and classical absorption from intercept $b$. This acoustic value could be compared with theoretical value calculated from expression derived by Tanaka et al. [10] (Tab. 2).

Next step is to plot the reduced attenuation $\alpha_b/\pi A(\epsilon)$ versus reduced frequency $\omega^*$. All thermodynamic quantities necessary to calculate $A(\epsilon)$ and $\omega^*$ are well known for both mixtures [9, 11]. Fig. 2 presents results of absorption measurements for both mixtures for different frequencies and temperatures. Solid line represents Ferrell-Bhattacharjee scaling function whereas dashed line — Kroll-Ruhland scaling function. Both functions are in good agreement with experimental data in the whole reduced frequency range. Though the mathematical formulas are different, the shape of both scaling function is almost the same. Fig. 2 confirms also correctness of calculated critical amplitude value and reduced frequency value. Hence acoustic measurements in critical mixtures could be a precious method to determine differ thermodynamic parameters such as correlation length $\xi$.

### Table 2. Adiabatic coupling constant calculated from acoustic measurements $g_{ac}$ and theoretical expression $g_{th}$

<table>
<thead>
<tr>
<th></th>
<th>$g_{ac}$</th>
<th>$g_{th}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzonitrile-isoctane</td>
<td>±0.682</td>
<td>−0.668</td>
</tr>
<tr>
<td>nitroethane-isoctane</td>
<td>±0.356</td>
<td>−0.348</td>
</tr>
</tbody>
</table>

**REFERENCES**

Acoustic Waves Reflection and Refraction on a Liquid - Magnetoacoustic Material Boundary

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Longitudinal acoustic wave incidence on flat boundary of liquid and antiferromagnetic with “light plane” anisotropy is investigated. It is shown by refraction law analysis that two critical angles are appearing. The sliding wave radiation into a volume is possible near the phase transition point. The effective possibility to control the refraction angles and the waves types transformation by the field is shown in addition.

At passage of a flat monochromatic elastic wave with the certain polarization through border of two firm mediums generally there are three waves on each side of the border. Most simple is the case of isotropic medium contacting to a liquid, as the distribution of longitudinal wave only is possible in it [1]. On the other hand, it is known, that in magneto-ordered substances at the approach to a point of orientational phase transition (OPT) Magnetoelastic (ME) interaction effectively grows, causing strong renormalization of speeds of elastic waves [2]. Materials, in which this effect is observed, we shall name magnetoacoustic ones (MAM). Among those are antiferromagnetics with anisotropy of “an easy plane” (AFEP) in OPT area on an external magnetic field \(H\), the OPT point is defined by a condition of \(H=0\). For example, experimentally observable reduction of speed of a transverse sound in AFEP of hematite \(\alpha-Fe_2O_3\) was 50% [3].

Let longitudinal elastic wave (LW) falls from a liquid 1 \((y > 0)\) in the MAM 2 \((y < 0)\) with an angle of to normal of border \((y=0)\). While reflection it is transformed only to a longitudinal wave with the same reflection angle \(\alpha\) meaning, but at passage on second medium it will be transformed in longitudinal (LW2) and transverse (TW2) one with refraction angles of \(\beta\) and \(\gamma\) accordingly.

Let’s quote used in the further expressions for transverse and longitudinal speeds with the account of ME connection [5]:

\[
\sin^2 \beta = \frac{4\zeta\sin^2 \alpha + b - \sqrt{(4\zeta\sin^2 \alpha + b)^2 - 16\zeta^2\sin^4 \alpha}}{8\zeta\sin^2 \alpha},
\]

\[
\sin^2 \gamma = \frac{4\zeta\sin^2 \alpha - c + \sqrt{(4\zeta\sin^2 \alpha - c)^2 + 16\alpha(1 - \zeta)\sin^4 \alpha}}{8\zeta\sin^2 \alpha},
\]

where \(b = \frac{s_{1T}}{s_{2T}} c = \frac{s_{1L}}{s_{2L}}\). At limiting transition \(\zeta \to 0\) the ratios (4), (5) are passing into the usual Snellius law.

In a liquid practically always \(s_{1L} < s_{2T}, s_{2L}\) and the analysis of the formulas (3) – (5) shows, that there are two critical fall angels \(\alpha_{crT}\) and \(\alpha_{crL}\), since which at \(\alpha\)
$a > a_{cr} = \arcsin b^{1/2}$ longitudinal magnetoacoustic wave (MAW) is distributed along the division border of mediums, and then at $a > a_{2cr}$, $a_{cr} = \arcsin \left[c/(1-\zeta)^{1/2}\right]$ the same occurs for transverse MAW. Thus threshold meaning of an angle of complete internal reflection from firm border at $a > a_{2cr}$ becomes controlled by external magnetic field. Let’s note also, that for fall angle $\alpha = \arcsin \sqrt{c/2} = 14^\circ.65$, when $\gamma = 45^\circ$, the refraction angle of transverse wave does not depend on an external field ($\tilde{s}_{2l} = s_{2l}$). For a longitudinal wave it can be changed over a wide range.

From boundary conditions the amplitude factor of reflection of a falling longitudinal wave can be determined

$$R_l = \frac{u_{l10}}{u_{l20}} = \frac{A - B}{A + B}, \quad (6)$$

and also amplitudes factors of its transformation in past longitudinal and cross waves:

$$T_l = \frac{u_{l12}}{u_{l10}} = \frac{C}{A + B}, \quad (7)$$

$$T_l = \frac{u_{l11}}{u_{l10}} = \frac{D}{A + B}, \quad (8)$$

$A = [(\lambda_2 + 2\mu_2) \cos^2 \beta \tilde{s}_{2l}^{-1} \sin \gamma - \mu_2 \tilde{s}_{2l}^{-1} \sin 2\gamma \sin \beta \cos \alpha ]$; $B = \lambda_2 \tilde{s}_{2l}^{-1} \sin \beta \sin \gamma + \cos \beta \cos \gamma$; $C = 2\lambda_2 \tilde{s}_{2l}^{-1} \cos \alpha \sin \gamma + \mu_2 \tilde{s}_{2l}^{-1} \sin 2\gamma \sin 2\alpha$, $D = 2\lambda_2 \tilde{s}_{2l}^{-1} \cos \alpha \sin \beta + (\lambda_2 + \mu_2 \cos^2 \beta) \tilde{s}_{2l}^{-1} \sin 2\alpha$.

At $\alpha > \alpha_{cr}$, longitudinal MAW, being distributed along the border, is non-uniform: its speed $\tilde{s}_{2l}$ and depth of infiltration $\Lambda_{2l}$ ($u_{l2l} \approx e^{\lambda_{2l}}$) in the MAM begins to depend on a fall angle $\alpha$:

$$\tilde{s}_{2l} = \frac{s_{l2}}{\sin \alpha}, \quad (9)$$

$$\Lambda_{2l} = \frac{s_{l2}}{\omega \sqrt{\sin^2 \alpha - b}} \quad (10)$$

At $\alpha > \alpha_{cr}$, transverse wave, being distributed along the border, also becomes non-uniform, thus $\Lambda_{2l}^{\alpha}$ is determined by expression (9) with replacement of $s_{2l} \rightarrow \tilde{s}_{2l}$, and

$$\Lambda_{2l} = \frac{s_{2l}\tilde{s}_{2l}}{\omega \sqrt{1 - \zeta \cos^2 2\gamma}} \quad (11)$$

The analysis of expressions (4), (5) shows, that because of strong deformation of return speeds surfaces of a sound in the MAM by a threshold way at some $\zeta > \zeta^*$ there is one more interesting effect - radiation of a sliding wave in a volume. A critical angle $\alpha_r$ for this phenomenon is determined by a ratio

$$\alpha_r = \arcsin \left(\frac{b}{4\chi(1 - \chi)}\right), \quad (12)$$

where $\chi = (\zeta n)^{1/2}$, also depends on affinity of the MAM to a point its OPT. It is easy to show, that the minimal meaning $\alpha_r$ depends on $\chi = 0.5$. Parameter $\zeta$ is equal to $\zeta = 1/(4\alpha)$ and $\alpha_r = \arcsin (b^{1/2})$. Thus, always $\alpha_{cr1} \leq \alpha_r \leq \alpha_{cr1}$. At $\zeta = [2-b(1-b)]^{1/2}/4$ $\alpha_r = 90^\circ$. At further increase of parameter of ME connection $\zeta$ the critical angle decreases, achieving at $\zeta = 1$ meanings $\alpha_r = 19.8^\circ$ for structure of water - hematite. At $\alpha = \alpha_{cr}$, expression (4) subradical expression is zeroed and at $\alpha > \alpha_{cr}$ it becomes negative. Thereof $sin\beta$ becomes formally complex, and it physically means that sliding wave is leaving the border in volume of a liquid with attenuation growing in process distance from the border. Let’s note, that the given attenuation is non-dissipative (without absorption of energy by the medium) and characterizes structure of excited new oscillatory process, which also remains concentrated near to border.

It was computationally shown, that at $\alpha = \alpha_{cr} = 14.2^\circ$ for longitudinal MAW in hematite $\beta = 90^\circ$ and at $\alpha = \alpha_{cr} = 24.1^\circ$ ($\zeta = 0$) for transverse MAW $\gamma = 90^\circ$. Let’s note, that at $\alpha > 90^\circ$ the sharp increase of amplitude of the reflected wave is observed, which can be explained by heterogeneity of a wave in area $\alpha > \alpha_{cr}$ and localization of elastic energy near the border. For angles of fall in an interval $\alpha_{cr1} \leq \alpha \leq \alpha_{cr}$ the reduction of factors of reflection $R_l$, transition $T_l$ and transformation $T_l$ can be seen. It is possible to explain that by swapping of energy of a falling acoustic wave in a escaped wave with subsequent reradiating of it into volume.

References

Acoustic Relaxation in some Benzene Similar Compounds

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The acoustic investigations in the group of cyclic compounds and particularly research of the dependencies of acoustic parameters and the structure of the organic liquids demonstrated some interesting regularities in the group of these compounds. In this paper the results of research in five cyclic liquids: bromo-, chloro-, fluoro- and jodobenzene were discussed in comparison to the benzene. The acoustic relaxation observed in all the compounds was found to result from Kneser's processes (vibrational relaxation).

Based on investigations reported in this paper, as well as other, both experimental and literature data concerning a great number of compounds, one can draw a conclusion that almost all acoustic relaxation (Kneser-type) processes in liquids can be described using one relaxation time. It also seems that all vibrational degrees of freedom of the molecule take part in this process.

It is known that arising of differences in transition probabilities could be caused by additional attraction in interaction of molecules having the dipole moments. A high value of dipole moments of halogenobenzenes with adequate benzene could be responsible for the difference of transition probabilities and changes of the relaxation times.

**INTRODUCTION & THEORY**

Acoustical spectroscopy in the range to 10 GHz allows to provide the investigation of liquids where exists supraclascial absorption caused by vibrational relaxation so-called Kneser relaxation. Classical part of it described Stokesa - Kirchhoff very often redu-ced to the first part of the equation (1) because of a little thermal conductivity contribution [1, 2].

\[
\left( \frac{\alpha}{f^2} \right)_{\text{class}} = \frac{2\pi^2}{\rho c_0^3} \left[ \frac{4}{5} \kappa_T + \frac{1}{C_p} - \frac{1}{C_v} \right]
\]

where: \( f \) - frequency of an ultrasonic wave, \( \rho \) – density of liquid, \( c_0 \) – ultrasound velocity for the frequency below the range of vibrational relaxation, \( \kappa_T \) - coefficient of thermal conductivity, and \( C_p \) and \( C_v \) - molar thermal capacity for constant pressure and volume, respectively.

In the majority of cases, relaxation in liquids can be described with relaxation equation (2) with one relaxation time \( \tau \).

The character of kinetic and thermodynamic parameters dependence on temperature and pressure as well as coincidence of thermal capacity \( C_i \) calcula-

\[
\frac{\alpha}{f^2} = \frac{A}{1 + \omega^2 \tau^2} + B
\]

where: \( A \) and \( B \) represents the absorption for low and high frequency range.

\[\alpha \text{ from acoustic measurements and from equation of Planck-Einstein formula gives an evidence that acoustic relaxation observed in these compounds is caused by Kneser processes.}\]

**RESULTS & DISCUSSION**

In the figs. 1 & 2 there are presented the results of ultrasonic measurements of absorption \( \mu \) (3) and \( \alpha/f^2 \) in a function of frequency (in GHz range).

\[\mu = \frac{\pi R' C_i}{2 C_v (C_p - C_i)}\]  

where:

\[ R' = C_p - C_v, C_i \text{ – thermal capacity of vibrational degrees of freedom}\]

The other values dispersion \( D \), relaxation force \( \varepsilon \), relaxation times \( \tau \) and respectively frequencies \( f \) and absorption \( \mu_{\text{opt}} \) & \( \mu_{\text{ac}} \) calculated from optical and acoustical experimental results, \( A \) and classical absorption are presented in Table 1.
Figure 1. Comparison of relaxation curves $[\mu(f)]$ obtained by authors and before by other authors [9] for bromobenzene

Table 1.
The example of date obtained from acoustic spectroscopy for bromobenzene.

<table>
<thead>
<tr>
<th>No</th>
<th>Parameter</th>
<th>C$_6$H$_5$Br$\text{[3-4]}$</th>
<th>[5]</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>$f_{(\alpha/f^2)}$ [10$^{-9}$ s$^{-1}$]</td>
<td>4,59</td>
<td>5,39</td>
</tr>
<tr>
<td>2</td>
<td>$f_{\mu}$ [10$^{-9}$ s$^{-1}$]</td>
<td>4,85</td>
<td>5,70</td>
</tr>
<tr>
<td>3</td>
<td>$f_c$ [10$^{-9}$ s$^{-1}$]</td>
<td>5,43</td>
<td>6,38</td>
</tr>
<tr>
<td>4</td>
<td>$A[10^{-15}$ m$^{-2}$]</td>
<td>125,9</td>
<td>106,4</td>
</tr>
<tr>
<td>5</td>
<td>$\alpha/f^2$ [10$^{-15}$ m$^{-2}$]</td>
<td>12,4</td>
<td>12,4</td>
</tr>
<tr>
<td>6</td>
<td>$D$</td>
<td>1,120</td>
<td>1,119</td>
</tr>
<tr>
<td>7</td>
<td>$\varepsilon$</td>
<td>0,202</td>
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<tr>
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<td>$c_0$ [m s$^{-1}$]</td>
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<td>11</td>
<td>$\tau_{PS}$ [10$^{-12}$ s]</td>
<td>36,7</td>
<td>31,2</td>
</tr>
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<td>12</td>
<td>$\tau_{PT}$ [10$^{-12}$ s]</td>
<td>59,0</td>
<td>50,1</td>
</tr>
</tbody>
</table>

CONCLUSIONS

It is seen from the acoustical measurements that all processes observed in the investigated compounds are possible to describe with typical relaxation equation with one relaxation time $\tau$ and participation of all vibrational degrees of freedom what was already noticed for the other Kneser liquids [6]. There was also observed dependencies of relaxation time and the structure of these cyclic compounds.

REFERENCES

Ultrasonic Study of the Preferential Solvation in Aqueous Solutions of Chloracetamide and Zinc Chloride

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To investigate the effect of preferential solvation the ultrasonic velocities (3 MHz) and densities of ZnCl₂ and chloracetamide (CHAA) in water and its quasi-binary mixtures with the ratio (ZnCl₂ + CHAA): H₂O = 1:55 at 25°C have been measured. From these data various thermodynamical parameters such as adiabatic compressibility, molar volume and their excess functions have been calculated. All these parameters have been discussed to explain solute solvent interaction, especially the effect of complexation with preferential solvation with the creation of specific solvation ions "solvatomers". The creation of specific complexes and hydrolysis reaction in the CHAA - H₂O - ZnCl₂ system have a relaxational character which, within the measurements of ultrasonic absorption in the frequency range 2 - 50 MHz, have been observed. On the base of these properties the kinetic and dynamic parameters of the observed relaxation have been calculated.

CHARACTERISTIC OF THE STUDIED SOLUTIONS

Relatively, little attention has been focused on the problem of ion solvation in binary mixtures, although there have been some experimental studies carried out on such systems [1]. The theoretical attempt has been made also to describe ternary solutions containing electrolytes [2]. Recently, it has theoretical calculations and computer simulations been reported [3]. The most simulations of solvation in mixture were aimed at investigating equilibrium properties [4,5], and the dynamics of the solvation process [6].

An interesting aspect of binary mixed solvent/electrolyte systems is the possibility of enrichment of either of the two solvents in the solvation shells of the ions, leading to characteristic deviations of the solutions properties from a linear dependence upon the mixture composition [6-9]. The main aim of presented study was to investigate the possibility of complexation in the aqueous solutions of zinc chloride with the part of 2-chloracetamide. With regard of big complexing ability of zinc, there exist a theoretical possibility of attachment 2-chloracetamide to the inner coordination sphere of zinc through chloride atom. There can create here outer–sphere as well as inner-sphere complexes.

Measuring instruments and solutions preparation

The velocities of ultrasonic wave were measured by the method of pulse-echo-overlap using the MATEC apparatuses [9] and interferometic method. Measurements of absorption coefficient, α, were made by a pulse method with the piezoelectric broad-band transducers and electronic equipment of MATEC 7700. Density was measured by a microprocessor gauge. Concentration in mole fraction was defined as

\[ n_2 = \frac{n_2}{n_1 + n_2} \]

where \( n_2 \): mole fraction of ZnCl₂, \( n_1, n_2 \) – number of moles CHAA and ZnCl₂, respectively.

Results and analysis

One of the methods of determining the composition of molecular complexes developing in a solution is an investigation of the correlation between the excess functions of certain thermodynamic quantities and the composition of solution. The excess functions chosen for the purposes of this paper were excess mole volume \( V_m^{\text{excess}} \) (obtained from density \( \rho \) measurements) and excess mole compressibility \( -\frac{(\partial V_m/\partial \rho)_T}{(\partial V_m/\partial \rho)_T} \) excess (obtained from density and ultrasound velocity \( c \) measurements (Figure 1).

The shape of the curve shows a strong interaction between the components, which includes the emergence of molecular complexes. Still, the interaction is not the same throughout the range of concentration. In the range of the mole fraction of zinc chloride 0 – 0.5 we notice negative values of \( V_m^{\text{excess}} \), which proves a closer packing of molecules. The visible sharp minimum of \( V_m^{\text{excess}} \) at \( x_2 = 0.5 \) and minimum the value of \( -(\partial V_m/\partial \rho)_T^{\text{excess}} \) at \( x_2 = 0.4 \) demonstrates the emergence in the solution of these concentrations the outer-outer sphere complexes with the composition \([\text{Zn(CHAA)}(\text{H}_2\text{O})\text{Cl}]^+\). An altogether different interaction may be noticed at large concentrations of ZnCl₂. The maximum \( V_m^{\text{excess}} \) at \( x_2 = 0.6 \) and \( -(\partial V_m/\partial \rho)_T^{\text{excess}} \) at \( x_2 = 0.7 \) demonstrates the simultaneous presence in the solution of inner sphere...
complexes $\text{ZnCl}_4^{2-}$ and the solvatomers $[\text{Zn(CHA})(\text{H}_2\text{O})_5]^{2+}$.

Figure 2 present the results of the measurements in the form of correlation between the value $\alpha f^2$ ($\alpha$ - the coefficient of ultrasonic waves absorption) and frequency $f$. The results may be expressed with single period of relaxation time.

Basing on the numeric presentation the relaxation parameters: $(\alpha \lambda)_{\text{max}}$ and $\tau$ (relaxation time) were calculated (Figure 3).

The concentration characteristics of these quantities may provide evidence of the nature of the processes. The maximum of $\tau$ at $x_2 = 0.33$ and $x_2 = 0.67$ suggest the following reaction scheme describing the observed relaxation:

$$\text{Zn}^{2+} + \text{Cl}^{-} \rightleftharpoons \text{Zn}^{2+}(\text{CHAA})_x(\text{H}_2\text{O})_y\text{Cl}^{-}$$

and

$$2\text{Zn}^{2+} + 4\text{Cl}^{-} \rightleftharpoons \text{ZnCl}_4^{2-} + [\text{Zn(CHA)(H}_2\text{O})_3]^{2+}$$

REFERENCES

Ultrasonic Relaxation and Internal Rotation in Butyl Formate

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The acoustic spectra of liquid butyl formate have been investigated in the frequency range from 0.1 MHz to 150 MHz and at the temperatures from 20°C to 80°C. The ultrasonic spectra of pure butyl formate show a single relaxation term in the frequency range between 200 kHz and 2 MHz.

INTRODUCTION

In the past years ultrasonic methods as well as T-jump P-jump, nuclear magnetic resonanse (NMR), electron paramagnetic resonance and stopped flow techniques have been extensively used to study the kinetics of monomolecular reactions in liquids. Rotational barriers in a two-isomer system are most accurately measurable with the ultrasonic relaxation method, when the isomer is presented in unequal amounts. On the other hand, it is difficult to extend the NMR method to two-isomer systems where the ratios of the two isomers are much smaller than ca. 1/20. Therefore, in the study of rotational barriers the techniques of ultrasonic relaxation and NMR are largely complementary[1].

This work is part of a series dealing with internal rotation and low-frequency ultrasonic relaxation[2,3] behaviour in pure liquids. The kinetics and mechanisms of the processes occuring in liquid formate during thermal movement have been inadequately studied. The study of the kinetics of relaxation processes have proved useful, apart from their independent scientific and practical interest, for a more detailed understanding of the mechanism of the internal rotations in liquid formate.

In this paper we focus on the relaxation process caused by internal rotation in pure butyl formate(HCOO(CH_2)_3CH_3, synonyms: formic acid butyl ester). Butyl formate may also exist in two rotational isomers: cis(I) and trans(II). At room temperature there will be a fast dynamical equilibrium between these two isomers. The isomers (I) and (II) are presented in unequal amounts and their ratio varies with temperature. The relaxation processes associated with these processes are usually characterized by relaxation times ~1 ms and for exact estimating of the relaxation parameters low-frequency ultrasonic technique (f < 1 MHz) must be used.

RESULTS AND DISCUSSION

The acoustic spectra of liquid butyl formate have been investigated in the frequency range from 0.1 MHz to 150 MHz and at the temperatures from 20°C, 50°C and 80°C. The ultrasonic spectrum of the butyl formate has been measured by a cavity resonator method using two different specimen cells to cover frequency range between 100 kHz and 20 MHz and further developed versions of pulse-modulated wave transmission techniques in the frequency range from 20 MHz to 150 MHz. The procedure for the measurement of sound attenuation and velocity is described in our earlier work [4,5]. The temperature of all specimen cells was controlled to within 0.05 K. The error in the attenuation data was smaller than 5% at f <20 MHz and smaller than 2% at f > 20 MHz. Butyl formate was purchased from REAHIM(Erevan) and was subjected to additional distillation. Figures 1 and 2 show results of the ultrasonic absorption measurements and data analysis. As seen from these figures, as the temperature is increased, the relaxation frequency moves toward higher frequencies. Analyzing the data, we have found that the curves are described by identical relaxation processes of the form:

\[
\alpha = \sum_{i=1}^{n} \frac{A_i}{1 + (\omega \tau_i)^2} + B
\]

where \( f \) is the frequency, \( A \) is the relaxation amplitude, \( \tau \) is the relaxation time of the characteristic processes, and \( B \) is a contribution to attenuation of other factors which do not depend on the considered relaxation process, \( \omega=2\pi f \) is the cyclic frequency. The
Experimental data at each temperature were analyzed by using the least-squares method.

FIGURE 1. Ultrasonic attenuation as a function of frequency for butyl formate at 20°C; our data; Pancholy and Mathur[6].

The approximate results are the solid curves shown in Fig.(1-2). It is apparent that a single relaxation equation is required to adequately fit the experimental data obtained, and this holds for all of the ultrasonic relaxation spectra obtained in this study. For the temperature 80°C measurements in the frequency range between 1 MHz and 10 MHz was impossible. Therefore, in Table 1 values A and τ have uncertainty exceeding a standard value. The coefficients resulting from these calculations and sound velocity measured at 20 MHz are given in Table 1. The relaxation parameters A and τ are in qualitative agreement with[7] those of determined in this study. The experimental results were analysed for a low-

frequency relaxation process by using Eyring relations[8], the detail description in Ref.3. The energy differency $H_0$ between the activation enthalpies of “cis and trans” groups derived from equation (2) by least-square method yield $H_0 = 15.4$ kJ/mol. On the basis of the foregoing arguments and the experimental values of τ (see Table I) we determine $ΔH_2 = 40 ± 2$ kJ/mol. Thus relaxation should be assigned to the “cis and trans” internal rotation process. The values of both $ΔH_0$ and $ΔH_2$ for propyl and butyl formates within the limits of an experimental error coincide and are close to significances for methyl and ethyl formates, obtained other authors by an impulse method.

ACKNOWLEDGMENTS

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REFERENCES


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<th>$τ$ ns</th>
<th>$B$ $10^{-15}$m$^{-1}$s$^2$</th>
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Abstract
Intensive research work based on Sound velocity, density and viscosity measurements have been carried out to investigate the property of liquids and liquid mixtures. The density, Sound velocity and viscosity of the binary and ternary mixtures of 2 – E. E with DMSO, DMFA and DMA have been measured at 308.15k for entire range of molefraction. The various Physico-chemical parameters like Relative Association, Wada’s Constant, Ultrasonic relaxation time, Internal pressure, Acoustic Impedance and their excess values have been calculated. In the light of the above results the property changes, inter and intra molecular interactions of the above said liquid mixtures have been discussed.

INTRODUCTION
This paper is part of our general work concerning the study of some physical and physicochemical properties of binary and ternary liquid mixtures in order to gain information about molecular interactions between the molecules in these systems. Here we have taken 2 Ethoxy ethanol (2E-E), DMSO, DMFA and DMA because of the following reasons. 2-E-E is a versatile organic liquid used in chemical industries. It is miscible with a number of organic solvents. Among the dipolar aprotic solvents, dimethyl sulfoxide (DMSO), N, N’ – dimethyl formadide (DMF) and N, N’ – dimethyl acetamide (DMA) are the important industrial liquids that find applications in a variety of areas.

In the present study the density, the speed of sound, the viscosity of the binary mixtures 2E-E with DMSO and ternary mixture 2E-E + DMFA + DMA have been measured at 308.15k for the entire mole fraction range.

EXPERIMENTAL SECTION
All chemicals were purchased from Merck Co. Their purities were 99.5% or better and no further purification has been done. The chemicals were stored over molecular sieves.

Liquid mixtures of various compositions were prepared by mole fraction using an electronic balance of ±0.01 mgm accuracy. The calculated mole fractions were accurate to ± 0.0001 units.

The densities of pure liquids, binary and ternary mixtures were measured at 308.15 K with specific gravity bottle method. The results of density are accurate to ± 0.0002 units. The speed of sound in the liquid mixtures has been measured by an Ultrasonic interferometer of frequency 2 MHZ. The speed of sound values are accurate to ± 2ms⁻¹. The viscosities were determined using Ostwald’s viscometer.

The flow time of the liquid in the viscometer has been measured with an accuracy of 0.01s.

Results and discussion
The excess molar volumes V^E were calculated form the density data by the relationship,

\[ V^E = V_M - \sum_i x_i V_i \] (1)

where \( V_i \) represents the molar volume and \( X_i \) the mole fraction of the ith component and \( V_m \) is the molar volume of the mixture and given as

\[ V_M = \left( \sum X_i M_i + X_2 M_2 \right) \] (2)

The adiabatic compressibility (β_a) is the property of a liquid which can be obtained from sound velocity and density measurements as

\[ \beta_a = \frac{1}{u^2 \rho} \] (3)

The excess adiabatic compressibility is calculated as

\[ \beta_a^E = \beta_a^m - \sum \phi_i \beta_{ai} \] (4)

where \( \phi_i \) is the volume fraction of the ith liquid which can be obtained as

\[ \phi_i = \frac{X_i V_i}{\sum_j X_j V_j} \] (5)

The excess viscosity is obtained as

\[ \eta^E = \eta_m - \sum X_i \eta_i \] (6)

Where \( \eta_i \) and \( \eta_m \) refer respectively to viscosities of pure components and of the mixture. The Internal pressure is given as,

\[ P_i = bRT \left( \frac{K \eta}{U} \right)^{1/2} \rho^{2/3} \frac{1}{M_{eff}^{7/6}} \] (7)
Where $P_1$ is the internal pressure, $b$ is the packing factor which is usually taken to be 2 assuming cubic packing, $R$ the gas constant and $m_{eff} = X_1m_1 + X_2m_2$, the effective molecular weight. The excess internal pressure is got as

$$P^E = P_m - \sum_i x_i P_i$$  \hspace{1cm} (8)

The rest of the parameters i.e., Relative association, Wada’s constant, Ultrasonic relaxation time and Free length and their excess values are calculated using the standard formulae available in the literature (1).

For the binary mixture of 2E-E with DMSO $V^E$ and $\beta_\lambda^E$ values are negative which indicates the specific hydrogen-bond type interactions between the hydroxy group of 2E-E and the sulphoxide group in DMSO, and dipole-dipole interactions. It has been observed that the free length increases linearly with increase in concentration. The variation of ultrasound velocity through the mixtures depends upon the value of free length as suggested by Eyring and Kinacid (2). With mixtures having dispersion and dipolar forces, the values of excess viscosity should be negative, whereas the existence of charge transfer and other specific interactions tend to make the $\eta^E$ values to be positive (3). Since in the present system of study specific interactions like dipole-dipole and hydrogen bonding exists, $\eta^E$ values are positive.

An increase in the temperature of the liquids results in a decrease in the values of the energy of activation (Gibb’s energy - $\Delta G$).

At constant temperature, relaxation time will depend on the energy difference between the activated and normal states. On increasing the temperature, the thermal fluctuations will increase and the energy required to bring the molecules to the activated state will increase. But the time for returning to the normal state will decrease, because the increased thermal agitations increase the rate of energy loss due to a large number of collisions (4). So, the relaxation time $\tau$ decreases with increase in temperature.

The Wada’s constant increases linearly with respect to the increase in concentration of 2-ethoxyethanol.

The excess internal pressure values show a positive deviation; this shows the absence of any cluster formation.

Relative Association $R_A$ is found to increase with mole fraction of dimethylsulphoxide. This suggests that 2-ethoxyethanol-DMSO interactions predominates in the breaking up of 2-ethoxyethanol associates. The former tends to increase, while the latter causes a decrease in $R_A$.

For the ternary mixture of 2-Ethoxy Ethanol + Dimethyl Formamide + Dimethyl Acetamide it is worth noting that the experiment was carried out for 18 different combinations of the mixture, which by itself is a tedious job.

Here it is observed that excess adiabatic compressibility values are negative for the entire composition range. The negative sign of excess values indicate a closer approach of molecules as a result of molecular interaction between dissimilar molecules. However, the less negative and more positive values of excess volume may be attributed to the decreased interactions of the amide group molecules in the 2-ethoxy ethanol environment.

With mixtures having dipolar and dispersion forces, values of $\eta^E$ should be negative, whereas, the existence of charge transfer and other specific interactions tend to make $\eta^E$ values to be positive. In the present system of study, specific hydrogen bond type interaction between the hydroxy group of 2-ethoxy ethanol and the amide group in DMFA and DMAC exists. And we also come across dipole-dipole interactions between the component molecules of the mixtures, since the dipole moment of 2-ethoxy ethanol is 2.08 D, while, dimethyl formamide and dimethyl acetamide have dipole moments, 3.8 D and 3.72 D respectively. The above mentioned interactions tend to make the $\eta^E$ values positive.

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Acoustic Waves Reflection and Refraction on a Dielectric – Magnetoacoustic Material Boundary

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A substantial sound speed change is possible in magnetoacoustic material under the effect of magnetic field. In our case two critical angles of incident wave are appearing when longitudinal and then transverse wave is sliding along the boundary, and a new critical angle when the sliding wave is radiated into the volume.

At passage of a flat monochromatic elastic wave with the certain polarization through border of two solid mediums generally there are three waves on each side of the border. Most simple is the case of isotropic medium contacting to a liquid, as the distribution of longitudinal wave only is possible in it and their polarization are only longitudinal or only transverse. We shall consider here the reflection of elastic waves on border of dielectric-antiferromagnetic. Let’s note, that in magetoordered crystals at the approach to a point of orientational phase transition (OPT) magnetoelastic interaction effectively grows, causing, change of a spectrum of long-wave transverse acoustic fluctuations from linear to square-law in the OPT point [1]. Thus even for magnetic isotropic on elastic and magnetoelastic properties near OPT the anisotropy of dynamic elastic modules appears, causing the reduction of a longitudinal sound speed and especially of a transverse sound speed.

If using expressions for free energy of dielectric and magnetoacoustic material (MAM), it is not difficult to receive the wave equations for mechanical shifts. Their solutions in form of flat harmonic non-fading waves are the following expressions for transverse longitudinal magnetoacoustic wave (MAW) speeds [3]:

$$\tilde{s}_{2l} = S_{2l} \sqrt{1 - \zeta \cos^2 2\alpha} ,$$  \hspace{1cm} (1)

$$\tilde{s}_{2t} = S_{2l} \sqrt{1 - \n \sin^2 2\alpha} ,$$  \hspace{1cm} (2)

where \(\alpha\) angle is counted from a negative direction of an axis \(y\) counter-clockwise, \(s_{2l}\), \(s_{2t}\) are speeds of transverse and longitudinal sound far from OPT respectively, \(n = \frac{s_{2t}}{s_{2l}}\).

Let the longitudinal acoustic wave falls from dielectric \((y > 0)\) on border of MAM \((y < 0)\) with angle \(\gamma\) to normal of the border \((y=0)\). It derivates two reflected - longitudinal and transverse waves - and two refracted - longitudinal and transverse MAW. The directions of waves spread are determined by Snellius ratio

$$\frac{\sin \alpha}{s_{ul}} = \frac{\sin \beta}{s_{ul}} = \frac{\sin \gamma}{s_{Ut}} = \frac{\sin \delta}{s_{Utl}} ,$$  \hspace{1cm} (3)

and also can be found on the basis of this expression graphically, proceeding from geometrical construction of surfaces of return phase speeds of all waves.

From the equations (3) we find expressions for angles of waves transformation:

$$\sin^2 \beta = a \sin^2 \alpha ,$$  \hspace{1cm} (4)

$$\sin^2 \gamma = \frac{4 \zeta n \sin^2 \alpha + b - \sqrt{(4 \zeta n \sin^2 \alpha + b)^2 - 16 \zeta n \sin^4 \alpha}}{8 \zeta n \sin^2 \alpha} ,$$  \hspace{1cm} (5)

$$\sin^2 \delta = \frac{4 \zeta n \sin^2 \alpha - 1 + \sqrt{(4 \zeta n \sin^2 \alpha - 1)^2 - 16 \zeta (1 - \zeta) n \sin^4 \alpha}}{8 \zeta n \sin^2 \alpha} ,$$  \hspace{1cm} (6)

where \(a = \frac{s_{ul}^2}{s_{ul}}, \ b = \frac{s_{ul}^2}{s_{Ut}}, \ c = \frac{s_{Utl}^2}{s_{Utl}}\).

Using boundary conditions, which determine a continuity of elastic shifts and pressures, makes it possible to determine the reflection factor of a falling longitudinal wave \(R_{ll} = \frac{u_{l0}}{u_{l10}}\), the transformation factor of it at reflection in a transverse wave \(R_{lt} = \frac{u_{lt}}{u_{l10}}, \ a\)
and also factor of its transformation at refraction in transverse MAW \( T_a = \frac{u_{l,a}}{u_{t,a}} \). All these four parameters can be determined by a Gauss method from the linear equations system appropriate to boundary conditions

\[
\begin{align*}
\mu_1 s_{1l}^{-1} \sin 2\alpha R_a - \mu_2 s_{1l}^{-1} \cos 2\alpha R_a + \mu_1 (1 - \zeta) s_{2l}^{-1} (\gamma) \sin 2\gamma T_a + \\
\left( \lambda_1 + 2\mu_1 \cos^2 \alpha \right) s_{1l}^{-1} R_a + \mu_1 s_{1l}^{-1} \sin 2\beta R_a - \\
- (\lambda_2 + 2\mu_2 \cos^2 \gamma s_{2l}^{-1} (\gamma) T_a + \mu_2 s_{2l}^{-1} (\delta) \sin 2\delta T_a = - (\lambda_1 + 2\mu_1 \cos^2 \alpha) s_{1l}^{-1}, \\
\sin \alpha R_a - \cos \beta R_a - \sin \gamma T_a - \cos \delta T_a = - \sin \alpha, \\
\cos \alpha R_a + \sin \beta R_a + \cos \gamma T_a - \sin \delta T_a = \cos \alpha.
\end{align*}
\]

We shall not show the decision (7) for \( R_a, R_n, T_a, T_n \) because it is cumbersome. Numerically system (7) was solved for quartz - hematite structure at a various degree of affinity of last to the OPT point.

The analysis of (5), (6) shows, that there can be two critical fall angles \( \alpha_{1,2\nu} \) and \( \alpha_{2,2\nu} \), since which at \( \alpha > \alpha_{1,2\nu} = \arcsin k / \sqrt{c} \) longitudinal MAW starts spreading along the mediums division border, and then at \( \alpha > \alpha_{2,2\nu} = \arcsin [c / (1 - \zeta) k / \sqrt{c}] \) the transverse MAW behaves similarly. A threshold meaning of complete internal reflection angle of a wave from the MAM border becomes controllable by external magnetic field.

At \( \alpha > \alpha_{1,2\nu} \) longitudinal MAW, being spread along the border, is non-uniform: its speed \( s_{2l} \) and depth of infiltration \( \Lambda_{2l} (n_{2l} \sim e^{iRL_{2l}}) \) in the MAM begin to depend on fall angle \( \alpha \) as follows:

\[
\begin{align*}
\tilde{s}_{2l} &= \frac{s_{2l}}{\sin \alpha}, \\
\Lambda_{2l} &= \frac{s_{2l}}{\omega \sqrt{s_{2l}^{-1} \sin^2 \alpha - s_{2l}^{-2}},}
\end{align*}
\]

At \( \alpha > \alpha_{2,2\nu} \) transverse MAW, being spread along the border, also becomes non-uniform, thus \( \tilde{s}_{2l} \) is determined similarly to \( s_{2l} \):

\[
\tilde{s}_{2l} = \frac{s_{2l}}{\sin \alpha},
\]

and depth of infiltration

\[
\Lambda_{2l} = \frac{s_{2l}}{\omega \sqrt{\left[ 1 - \zeta \cos^2 2\alpha \right] s_{2l}^{-1} \sin^2 \alpha - s_{2l}^{-2}},}
\]

The analysis of (5), (6) expressions shows, that because of strong deformation of return speeds surfaces of a sound in the MAM by a threshold way at some \( \zeta > \zeta^* \) there is one more interesting effect - radiation of a sliding wave into the volume. A critical angle \( \alpha^* \) thus is determined by a ratio

\[
\alpha_{1,2\nu}' = \arcsin \frac{b}{4(1 - \chi)},
\]

where \( \chi = (\zeta n)^{1/2} \), also depends on affinity of the MAM to a point its OPT. At \( \zeta' = [2 - b - 2(1 - b)^2] / (4n) \) \( \alpha_{1,2\nu}' = 90^\circ \) is received, and at the further increase of magnetoelastic connection parameter \( \zeta' \) a critical angle \( \alpha_{1,2\nu}' \) decreases. At \( \alpha > \alpha_{1,2\nu}' \) in (5) expression under a square root zeroes and at \( \alpha > \alpha_{1,2\nu}' \) becomes negative. Formally we receive, that \( \sin \gamma \) becomes complex, and it physically means that sliding wave leaves the border into dielectric volume with attenuation growing in process of distance from border. Let's note, that the given attenuation is non-dissipative (without absorption of energy by the medium) and characterizes structure of the arisen new oscillatory process, which also remains concentrated near to border \( y = 0 \). For structure quartz - hematite \( \beta_{a,w}=55^\circ, \alpha_{1,2\nu}=55^\circ, \alpha_{2,2\nu}=0,1\), at \( \zeta = 1, \alpha_{1,2\nu}'=55^\circ \).

The task of the fall of transverse wave on division border was solved similarly. The results of researches have appeared qualitatively close to mentioned above, but with some specific features.

Thus, there is an essential opportunity of controlling the reflection and refraction waves factors and their mutual transformation with the help of a magnetic field. Thus close to OPT the radiation of sliding waves in volume appears in a threshold way. Depending on ratio of elastic constants of structure substances, the complete internal reflection of waves from the MAM, controlled by a field, is possible.

References

Hysteresis of changes of ultrasonic wave attenuation in a ferrofluid caused by the magnetic field

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The ferrofluids change their structure under the influence of an external magnetic field and do not return to the initial state after the magnetic field removal. It is supposed that the cluster formed in the fluid subjected to a magnetic field remains after the field has been removed. The resulting dependence of the ferrofluid properties on its magnetic history has been studied by analysis of changes in the ultrasonic wave absorption coefficient.

INTRODUCTION

Ferrofluid (magnetic fluid) is a colloidal suspension of magnetic particles covered with a surfactant layer in a carrier fluid [1]. The structure of a magnetic fluid is changed under the influence of a constant external magnetic field. Colloidal particles forms aggregates (clusters) which tend to join into a chain-like structure as long as hundreds of nanometers [2]. The structure does not return to initial condition after turn off the magnetic field. Probably, the clusters remain in magnetic fluid. One of the methods of studying changes in ferrofluid structure is the method based on changes in ultrasonic wave absorption under the influence of an external magnetic field. The process of cluster formation depends on the rate of external magnetic field changes [3, 4]. In this paper the authors study the behavior of the ultrasonic wave coefficient as a function of a constant external magnetic field for varying rates of such changes (different ‘sweep’ times) and directions. On the basis of these measurements the changes of magnetic fluid structure was investigated.

MEASURING METHOD

Measurements of changes of ultrasonic wave absorption coefficient were conducted by a pulse method using the MATEC apparatus [5]. A slowly changing magnetic field was obtained in an electromagnet controlled by a system with a programmable current source. It permitted an automatic sweep of the range of magnetic field studied at a given time.

EXPERIMENTAL RESULTS

The studied medium was a ferrofluid EMG-605, produced by Ferrofluid Corporation. It consist of magnetite Fe₃O₄ particles of mean radius 10 nm, covered with a 2 nm thick layer of oleic acid, and suspended in water. The basic properties of this magnetic fluid, such as the saturation magnetization, viscosity, initial susceptibility and volume fraction are equal to: 20 mT (at 27°C), < 5 cP (at 25°C), 0.54, 3.5 %, respectively.

Measurement were conducted at an ultrasonic wave frequency of 3.6 MHz when the direction of ultrasonic wave propagation was perpendicular to the direction of the external magnetic field. The magnetic field in the range 0 – 90 kA/m was swept with a rate (different sweep times) varying from 1.5 kAm⁻¹s⁻¹ (the sweep time — 2 min) to 15 Am⁻¹s⁻¹ (20 min). The magnetic field increases and decreases on the same rate. Figure 1 shows the dependence of ultrasonic wave absorption coefficient on the intensity of the external magnetic field for 4 different sweeping times, when the ferrofluid temperature was 30°C. The graphs show that with increasing magnetic field intensity the absorption coefficient increases, and the character of the changes strongly depends on the rate of magnetic increase (the sweep time). With decreasing magnetic field intensity the character of absorption coefficient changes is different, process form and disintegrate aggregates is distinct. The structure does not return to initial condition after turn off the magnetic field. It shows hysteresis of changes of ultrasonic wave absorption coefficient. Probably, the small clusters remain in magnetic fluid. The maxims of changes of the ultrasonic wave absorption coefficient, when magnetic field intensity decreasing, show about it [6].

SUMMARY

Magnetic fluid is a substance which properties depend on its magnetic history. The established hysteresis of the ultrasound wave absorption coefficient proves that the structural changes in a ferrofluid are irreversible.
FIGURE 1. Dependence of changes $\Delta \alpha$ in the absorption coefficient of an ultrasonic wave as a function of magnetic field intensity $H$ for different sweeping times when $H \perp k$ and $T = 30^\circ C$.

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