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PHASE VELOCITY OF A PRESSURE WAVE ON THE AXIS OF AN ACOUSTIC FIELD OF A CIRCULAR RING IN AN ACOUSTIC BAFFLE

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This paper is concerned with the so-called local velocity of a harmonic pressure wave of a circular ring vibrating with a constant velocity amplitude. The ring is placed in an infinite rigid acoustic baffle. The local propagation velocity was calculated on the axis conducted from the center of the ring perpendicularly to its surface.

The propagation velocity changes from infinity for $z = 0$ (singular point) to a constant value, c_0, for z equal to about 10 times the external radius of the ring.

1. Introduction

Because this paper is a continuation of paper [4] we will not repeat the complete reasoning presented previously. Only several fundamental formulae and definitions will be given.

In a case of an arbitrary harmonic pressure wave, i.e. a wave with an arbitrary amplitude, $A(x_i)$ $i = 1, 2, 3$, and wave front $f(x_i)$, we have

$$p(x_i, t) = A(x_i)e^{i[\omega t - f(x_i)]}. \tag{1}$$

The condition of wave propagation acquires the form:

$$\omega t - f(x_i) = \text{const}. \tag{2}$$

Differentiating both sides of equation (2) with respect to time we obtain:

$$\omega - |\text{grad} f| c = 0 \tag{3}$$

where the so-called local velocity of wave propagation:

$$c = \frac{\omega}{|\text{grad} f|} \tag{4}$$

depends on the position in the acoustic field. It is constant only for a plane wave and an elementary spherical wave, as in both cases we have:

$$|\operatorname{grad} f| = k_0 = \frac{\omega}{c_0} \tag{5}$$

where c_0 is the material constant — propagation velocity from d'Alambert's equation [1] [2].

Paper [4] has dealt with the local velocity of propagation of an acoustic pressure wave in the near field of a circular piston in a rigid baffle. The wave propagated along the axis of symmetry of the field, marked as the z-axis. It has been proved there that this velocity changes from $2c_0$ on the source, to c_0 for all greater distances from the source (piston), and practically at a distance equal to 5 radii of the piston, c differs from c_0 by less than 1%.

The second case considered was the local velocity in an acoustic field of a cylinder for a zero order wave. Here the ratio c/c_0 depends on the value of k_0r, where r is a polar variable, i.e. the distance from the axis of the cylinder (source). As opposed to the first case, here c is lower than c_0 and with the increase of k_0r increases from zero (this value does not have physical sense) to c_0, and for $k_0r \approx 5$ c differs from c_0 by less than 1%.

This paper discusses an acoustic system, in which the local velocity can be arbitrarily great and theoretically decreases from ∞ to c_0. Such a system is ensured by a circular ring placed in an infinite rigid baffle. The field is considered on the z-axis, which is the axis of symmetry of the system and is drawn from the source (ring) perpendicularily to its surface. It will be proved that when $z \to 0$, then the local velocity approaches infinity.

2. Calculation of the phase velocity on the axis of the near field of a circular ring

The formula used for the acoustic pressure on axis z, directed as it has been given in the introduction, is given in accordance to Stenzel [3], [5]. Denoting the internal and external radius of the ring by a_1 and a_2, respectively, the velocity amplitude on the ring by u_0 and the rest density of the medium by ϱ_0, we obtain:

$$p = 2\,u_0\varrho_0c_0\sin\left[\frac{k_0}{2}\left(\sqrt{z^2+a_2^2}-\sqrt{z^2+a_1^2}\right)\right]e^{i\left[\omega t+\frac{\pi}{2}-\frac{k_0}{2}\left(\sqrt{z^2+a_2^2}+\sqrt{z^2+a_1^2}\right)\right]} \tag{6}$$

The condition of wave propagation (phase stability when z and t are changed) has the following form:

$$\omega t+\frac{\pi}{2}-\frac{k_0}{2}\left(\sqrt{z^2+a_2^2}+\sqrt{z^2+a_1^2}\right) = \text{const.} \tag{7}$$

Differentiating both sides of equation (7) with respect to time, we have:

$$\omega - \frac{k_0}{2}\left(\frac{z}{\sqrt{z^2+a_2^2}} + \frac{z}{\sqrt{z^2+a_1^2}}\right)\frac{dz}{dt} = 0. \tag{8}$$

Taking into consideration that:

$$\frac{dz}{dt} = c(z) \tag{9}$$

and

$$k_0 = \frac{\omega}{c_0} \tag{10}$$

we obtain

$$\frac{c}{c_0} = \frac{2\sqrt{z^2+a_1^2}\,\sqrt{z^2+a_2^2}}{z\sqrt{z^2+a_1^2}+\sqrt{z+a_2^2}}. \tag{11}$$

It is much more convenient to use formula (11) in a form expressed by the relative distance, z/a_2, and the radii ratio $-$ n, according to formula

$$a_1 = na_2, \quad n < 1. \tag{12}$$

Then we have

$$\frac{c}{c_0} = \frac{2\sqrt{n^2+\left(\frac{z}{a_2}\right)^2}\cdot\sqrt{1+\left(\frac{z}{a_2}\right)^2}}{\frac{z}{a_2}\left(\sqrt{n^2+\left(\frac{z}{a_2}\right)^2}+\sqrt{1+\left(\frac{z}{a_2}\right)^2}\right)} \tag{13}$$

When $n = 0$, the ring changes into a circular piston and then ($a_2 = a$)

$$\frac{c}{c_0} = \frac{2\sqrt{1+\left(\frac{z}{a}\right)^2}}{\frac{z}{a}+\sqrt{1+\left(\frac{z}{a}\right)^2}} \tag{14}$$

in accordance to the result in the paper [4].

When z/a_2 in formula (13) approaches zero, for $n \neq 0$, then $c/c_0 \to \infty$, and thus in the centre of the circular ring, on the baffle, the propagation velocity of the pressure wave has to be infinitely great. This result is only apparently surprising, because the rigidity of the baffle is tantamount to the infinite value of wave resistance. The baffle itself has such a resistance. However, when also the propagation velocity in the medium, in which the wave propagates, approaches infinity when $z/a_2 \to 0$, then we have the continuity of the boundary condition ensured. On the other hand, when $z/a_2 \to \infty$, we have $c/c_0 \to 1$.

Fig. 1 presents values of c/c_0 for various n, including the case of an infinitely thin ring, i.e. when $n = 1$. This case has been considered separately, because substituting $n = 1$, i.e. $a_2 = a_1$, in formula (6) gives the acoustic pressure equal to zero. Thus formula (6) can not be used in such a case. However, further on it will be proved than the result obtained with a different method is the same as if we substituted $n = 1$ in formula (13).

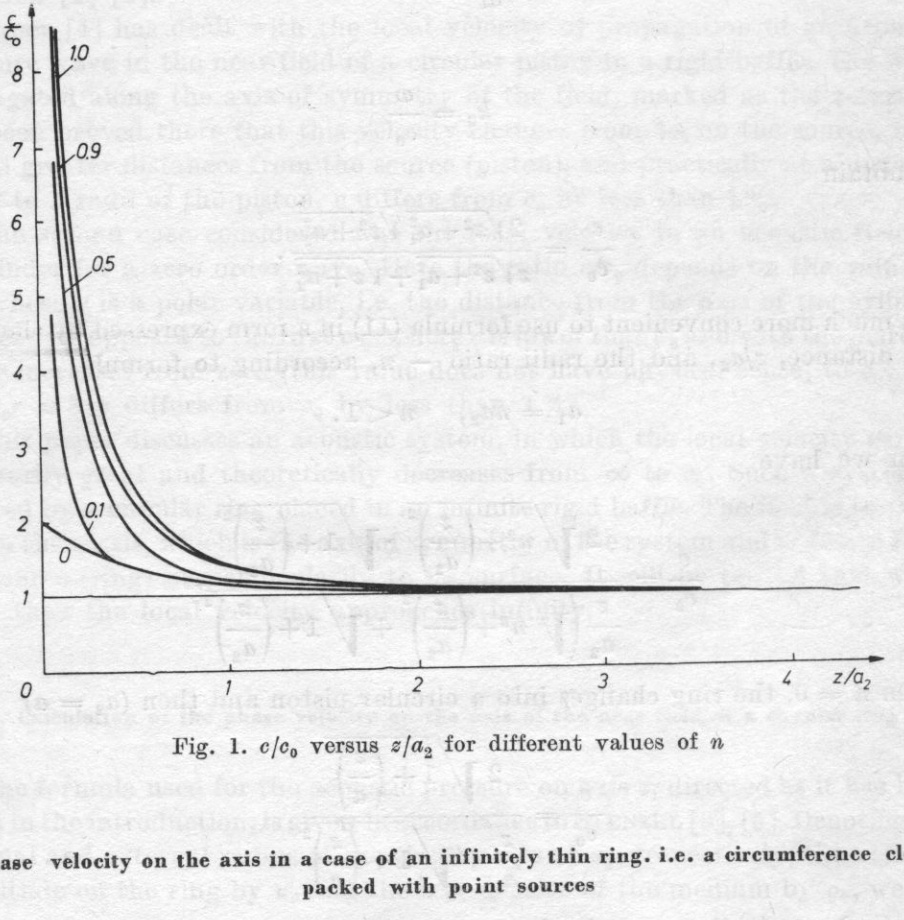

Fig. 1. c/c_0 versus z/a_2 for different values of n

3. Phase velocity on the axis in a case of an infinitely thin ring. i.e. a circumference closely packed with point sources

Even though the case of the near field of an infinitely thin ring is one of the simplest examples of an acoustic field, it has not been mentioned in literature. Only the formula for the far field has been given [1], [2]. Therefore, we will begin with the calculation of the near field.

According to Fig. 2 we will mark the radius of the ring by a and the velocity amplitude on the ring, calculated formally as the productiveness of the source per unit of arc length, by u_0, and the acoustic pressure on the z-axis will have the following form [1], [2], [4]:

$$p = \frac{k_0 \varrho c_0}{2\pi} u_0 e^{i(\omega t + \pi/2)} \int\limits_L \frac{e^{-ik_0 r}}{r} a d\varphi \tag{15}$$

where L is the length of the circumference of the circle (ring.). As r is a constant value, and we integrate over variable φ from 0 to 2π, then we have

$$p = k_0 \varrho c_0 u_0 e^{i(\omega t + \pi/2 - k_0 r)} \frac{a}{r}. \tag{16}$$

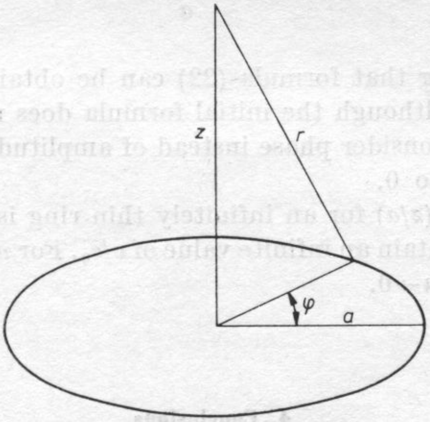

Fig. 2. The geometry of an infinitely thin ring

Naturally, also

$$r = \sqrt{z^2 + a^2}, \tag{17}$$

thus formula (16) will have the following form:

$$p = k_0 \varrho c_0 u_0 \frac{e^{i(\omega t + \pi/2 - k_0 \sqrt{z^2+a^2})}}{\sqrt{z^2+a^2}} \tag{18}$$

The condition of wave propagation is

$$\omega t + \frac{\pi}{2} - k_0 \sqrt{z^2 + a^2} = \text{const}. \tag{19}$$

Differentiating both sides of (19) with respect to time we obtain

$$\omega - k_0 \frac{z}{\sqrt{z^2+a^2}} \frac{dz}{dt} = 0 \tag{20}$$

and taking into consideration that

$$\frac{dz}{dt} = c, \quad k_0 = \frac{\omega}{c_0} \tag{21}$$

finally we acquire the following formula for an infinitely thin ring

$$\frac{c}{c_0} = \frac{\sqrt{1+\left(\frac{z}{a}\right)^2}}{\frac{z}{a}}. \tag{22}$$

It is worth mentioning that formula (22) can be obtained from formula (13) by accepting $n = 1$, although the initial formula does not suit this case. This happens, because we consider phase instead of amplitude, which for $a_2 = a_1$ in formula (6) is equal to 0.

The curve $c/c_0 = f(z/a)$ for an infinitely thin ring is shown in Fig. 1. Also there for $z/a = 0$ we obtain an infinite value of c/c_0. For $n = 1$ the curve ascends most steeply when $z/a \to 0$.

4. Conclusions

An acoustic antenna in the shape of a circular ring radiates a pressure wave, which propagates along axis z (axis of symmetry of the field) with a variable velocity dependent on the position, i.e. on variable z. For $z = 0$ this velocity exhibits a singularity – it is infinite. This means that the central point, $z = 0$, does not vibrate. This corresponds to the boundary condition on the baffle. In a point arbitrarily close to $z = 0$, but at a finite value of z, the local propagation velocity of a wave can be arbitrarily great. For every z this velocity has the greatest value for an infinitely thin ring ($n = 1$) and the smallest value for a circular piston ($n = 0$).

When z increases (as well as z/a_2, where a_2 is the external radius of the ring), then the propagation velocity of a pressure wave decreases to the material velocity, c_0.

These effects practically occur only at relatively small distances from the plane, i.e. up to the value of $z/a_2 \approx 4$, at greater distances they are imperceptible. However, they can play a significant role in large antennas in the shape of a circular ring not only for acoustic waves.

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ACOUSTICAL WAVE PROPAGATION IN A CYLINDRICAL LAYER SYSTEM IN VISCOUS MEDIUM

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A problem is considered of an acoustical wave propagating along a hollow, infinite elastic cylinder filled with air and surrounded by a viscoelastic tissue. Such a case approximately corresponds to a biopsy performed with the application of a needle introduced to such tissues as liver, kidney, muscles, and the like.

In the problem under consideration it was proved, that the volume viscosity is significant, whereas shear viscosity can be neglected.

Basic equations were formulated in terms of displacement potentials, as well as the boundary conditions. This led to a characteristic equation of the problem which were solved numerically.

It was proved that a boundary wave propagates along the needle with a velocity and attenuation not much smaller than in the surrounding tissue. Part of the energy is transfered from the needle into the tissue where the energy is dissipated. Distributions of the radial and axial stress components and radial displacement components were found.

Introduction

The numerical solution of a problem of acoustical wave propagation along a hollow cylinder filled with air and submerged in a absorbing liquid concerns an effect observed during the conduction of a biopsy controlled ultrasonically. It was observed, that under certain physical conditions a wave is produced which propagates along the needle, reaches the point of the needle and returns, giving an image of the needle point on the screen of the echoscope. This problem has been worked on under certain physical limitations in papers [1], [2], [3]. These papers proved, that the velocity of the propagating wave is close to the wave velocity in the biological structure surrounding the needle. Previous papers concerned the wave propagation in perfectly elastic media. Now we assume, that the biological structure surrounding the needle is an viscoelastic medium.

As it results from paper [4], such biological structures as muscle, kidney, liver, on which a biopsy is performed, have viscous properties. The propagation of an acoustical wave in a viscoelastic medium was considered in work [5]. It analysed a plane case. Now a needle used for puncturing a given biological structure will be approximated by a perfectly elastic hollow cylinder, infinitly long (Fig. 1).

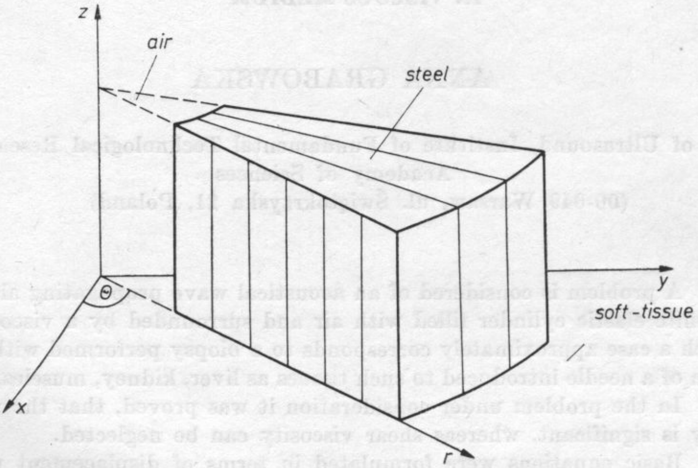

Fig. 1. A circular sector of a hollow cylinder filled with air and surrounded by a viscoelastic medium

The analyzed wave is a progressive one. We also assume, that the viscoelastic biological medium surrounding from the outside the hollow cylinder is an infinitely extended medium.

The aim of the paper was to develop basic equations, to solve numerically the characteristic equation, and to determine the parameters characterizing the wave motion in this system.

Basic equations

The theory of elasticity assumes, that the components of the stress tensor are linear functions of the strain. This assumption (Hook's law) is in force, when the purely elastic forces are significantly greater then the forces depending on the strain velocity (viscous forces).

In a case when these forces are comparable and the stress components are also linear functions of the components of the strain velocity, we can say, that the given body has also viscous properties and we call it a viscoelastic body (Voigt's body for example). We approximate a biological medium by a mode of the Voigt body. Such a body, in a case of isotropy, is characterized by four material constants $\lambda', \mu', \lambda'', \mu''$, where λ' and μ' determine the elastic properties of the body, and λ'' and μ'' – the viscous properties.

The constitutive equation for a viscoelastic body is:

$$\tau_{ij} = \left(2\mu' + 2\mu'' \frac{\partial}{\partial t}\right) \varepsilon_{ij} + \left(\lambda' + \lambda'' \frac{\partial}{\partial t}\right) \varepsilon_{ij}\varepsilon_{kk} \quad i, j = x, y, z \tag{1}$$

where τ and ν are the stress and strain, respectively.

Placing (1) in the equations of motion:

$$\varrho_c \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial \tau_{ij}}{\partial x_j} \quad i, j = x, y, z \tag{2}$$

where $\vec{u}$ – displacement we obtain the displacement equation for an isotropic viscoelastic body:

$$\varrho_c \frac{\partial^2 \vec{u}}{\partial t^2} = \left[(\lambda' + \mu') + (\lambda'' + \mu'') \frac{\partial}{\partial t}\right] \operatorname{grad} \operatorname{div} \vec{u} + \left(\mu' + \mu'' \frac{\partial}{\partial t}\right) \nabla^2 \vec{u} \tag{3}$$

In a case of harmonic motion with a frequency f, which we assume in the paper as:

$$\vec{u}(x, y, z, t) = \vec{u}(x, y, z) e^{j\omega t} \tag{4}$$

and applying equation (3) we reach:

$$-\varrho_c \omega^2 \vec{u} = (\lambda_c + \mu_c) \operatorname{graddiv} \vec{u} + \mu_c \nabla^2 \vec{u} \tag{5}$$

where

$$\lambda_c = \lambda' + j\omega\lambda'', \quad \mu_c = \mu' + j\omega\mu'', \quad \omega = 2\pi f. \tag{6}$$

The displacement equation (5) has the same form as the displacement equation in the theory of elasticity. The difference is only in two parameters, λ_c and μ_c, which now are complex and depend on frequency according to equation (6), while in an perfectly elastic medium these parameters were real numbers. So a perfectly elastic isotropic body is characterized by two Lamé constants, while a viscoelastic isotropic body – by four constants. λ' and μ' determine the elasticity of volume and the shape elasticity, respectively. λ'' and μ'' – the volume and shape viscosity, respectively. Equation (5) is solved in the same way as in the theory of elasticity [6]. A cylindrical coordinate system is chosen (r, θ, z) (Fig. 1). In our case of a deformation axially symmetrical in respect to axis z, the displacements, deformations and stresses are independent on the angle θ. For the vibrations of a viscoelastic medium we have a displacement equation:

$$(\lambda + \mu) \operatorname{grad} \operatorname{div} \vec{u} + \mu \nabla^2 \vec{u} = \varrho_c \ddot{\vec{u}}. \tag{7}$$

Coefficients λ and μ are:

$$\lambda = \lambda' + \lambda'' \frac{\partial}{\partial t}, \quad \mu = \mu' + \mu'' \frac{\partial}{\partial t} \tag{8}$$

where λ' and μ' determine the elastic properties, and λ'' and μ'' – the viscous properties of the body.

We assume, that the displacement vector, $\overline{u}_c$, in a viscoelastic medium has the following form:

$$\vec{u}_c(r, z, t) = \operatorname{grad} \Phi_c + \operatorname{rot} \vec{W}^c, \tag{9}$$

Putting the relationship (9) in the displacement equation (7), shows that equation (7) will be fulfilled if the scalar Φ_c and the vector $\vec{W}^c$ potentials are the solutions of equations:

$$\nabla^2 \Phi_c = \frac{\varrho_c}{\lambda + 2\mu} \frac{\partial^2 \Phi_c}{\partial t^2} \tag{10}$$

$$\nabla^2 \vec{W}^c - \frac{1}{r} \vec{W}^c = \frac{\varrho_c}{\mu} \frac{\partial^2 \vec{W}^c}{\partial t^2} \tag{11}$$

where

$$\lambda = \lambda' + \lambda'' \frac{\partial}{\partial t}, \quad \mu = \mu' \pm \mu'' \frac{\partial}{\partial t}. \tag{12}$$

In a case of a deformation axially symmetrical in respect to axis z, only one component, W^c_θ, of vector $\vec{W}^c$ differs from zero. Therefore, equation (11) can be rewritten:

$$\nabla^2 W^c_\theta - \frac{1}{r} \vec{W}^c_\theta = \frac{\varrho_c}{\mu} \frac{\partial^2 W^c_\theta}{\partial t^2}. \tag{13}$$

We bring equation (13) to a scalar wave equation, defining scalar quantity Ψ_c, in the following way:

$$\Psi_c\colon W^c_\theta = -\frac{\partial \Psi_c}{\partial r} \tag{14}$$

Placing dependence (14) in equation (13) we obtain:

$$\nabla^2 \Psi_c = \frac{\varrho_c}{\mu} \frac{\partial^2 \Psi_c}{\partial t^2} \quad \text{where } \mu = \mu' + \mu'' \frac{\partial}{\partial t} \tag{15}$$

We rearrange equation (15):

$$\left(\mu'+\mu''\frac{\partial}{\partial t}\right)\nabla^2\Psi_c = \varrho_c\frac{\partial^2\Psi_c}{\partial t^2},$$

$$\mu'\nabla^2\Psi_c+\mu''\nabla^2\frac{\partial}{\partial t}\Psi_c = \varrho_c\frac{\partial^2\Psi_c}{\partial t^2}. \tag{16}$$

Let:

$$\Psi_c(r,z,t) = \Psi_0(r)e^{-jpz+j\omega t}$$

$$(\mu'+j\omega\mu'')\nabla^2\Psi_c = -\varrho_c\omega^2\Psi_c$$

$$(\mu'+j\omega\mu'')\left[\frac{\partial^2\Psi_0}{\partial r^2}+\frac{1}{r}\frac{\partial\Psi_0}{\partial r}-p^2\Psi_0\right] = -\varrho_c\omega^2\Psi_0$$

$$\frac{\partial^2\Psi_0}{\partial r^2}+\frac{1}{r}\frac{\partial\Psi_0}{\partial r}+\left[\frac{\varrho_c\omega^2}{\mu'+j\omega\mu''}-p^2\right]\Psi_0 = 0 \tag{17}$$

We introduce a denotation:

$$\frac{\varrho_c\omega^2}{\mu'+j\omega\mu''}-p^2 = l_t^2 \tag{18}$$

We accept the solution of the Bessel equation (17) in the following form:

$$\Psi_c(r,z,t) = BH_0^{(2)}(l_t r)e^{-jpz+j\omega t} \tag{19}$$

Analogically we solve equation (10), so we assume the solution of eq. (10) to have the following form:

$$\Phi_c(r,z,t) = \Phi_0(r)e^{-jpz+j\omega t}$$

and we reach the Bessel equation:

$$\frac{\partial^2\Phi_0}{\partial r^2}+\frac{1}{r}\frac{\partial\Phi_0}{\partial r}+\left[\frac{\varrho_c\omega^2}{\lambda'+2\mu'+j\omega(\lambda''+2\mu'')}-p^2\right]\Phi_0 = 0 \tag{20}$$

We denote:

$$\frac{\varrho_c\omega^2}{\lambda'+2\mu'+j\omega(\lambda''+2\mu'')}-p^2 = l_d^2. \tag{21}$$

Then the solution of equ. (20) is Φ_c in the form:

$$\Phi_c(r,z,t) = \mathrm{C}\mathrm{H}_0^{(2)}(l_d r)e^{-jpz+j\omega t}. \tag{22}$$

Equ. (10) and (15) describe the following wave:

$$\begin{aligned}\Phi_c(r,z,t) &= \mathrm{C}\mathrm{H}_0^{(2)}(l_d r)e^{-jpz+j\omega t}\\ \Psi_c(r,z,t) &= \mathrm{B}\mathrm{H}_0^{(2)}(l_t r)e^{-jpz+j\omega t}\end{aligned} \tag{23}$$

where

$$l_d^2 = \frac{\varrho_c\omega^2}{\lambda_c+2\mu_c}-p^2, \quad l_t^2 = \frac{\varrho_c\omega^2}{\mu_c}-p^2,$$

$$\lambda_c = \lambda'+j\omega\lambda'', \quad \mu_c = \mu'+j\omega\mu'', \tag{24}$$

$$H_0^{(2)}(z) = J_0(z)-jY_0(z)$$

p — is the sought propagation constant. Factors $e^{j\omega t}e^{-jpz}$ characterize a harmonic, absorbed, plane wave propagating in direction z. Let $p = \mathrm{Re}(p)+j\mathrm{Im}(p)$. Then:

$$e^{j\omega t}e^{-jpz} = e^{j\omega t}e^{-j\,\mathrm{Re}(p)z}e^{-j^2\,\mathrm{Im}(p)z} = e^{j\omega t}e^{-j\,\mathrm{Re}(p)z}e^{\mathrm{Im}(p)z}$$

Hence we obtain $e^{j\omega t}e^{-jpz} = e^{j\omega t}e^{-j^{\omega/cz}-\alpha z}$, when

$$c = \omega/\mathrm{Re}(p), \quad \alpha = -\mathrm{Im}(p) \tag{25}$$

where c — wave phase velocity, α — absorption coefficient.

The components of the displacement vector $\vec{u}^c$ can be noted with the application of the potentials Φ_c and Ψ_c:

$$u_r^c = \frac{\partial\Phi_c}{\partial r}+\frac{\partial^2\Psi_c}{\partial z\partial r}, \quad w_z^c = \frac{\partial\Phi_c}{\partial z}-\frac{\partial\Psi_c}{r\partial r}-\frac{\partial^2\Psi_c}{\partial r^2}. \tag{26}$$

The radial and axial stress are expressed by potentials Φ_c and Ψ_c in the following way:

$$\tau_{rr}^c = \lambda_c\left(\frac{1}{r}\frac{\partial\Phi_c}{\partial r}+\frac{\partial^2\Phi_c}{\partial r^2}+\frac{\partial^2\Phi_c}{\partial z^2}\right)+2\mu_c\frac{\partial}{\partial r}\left(\frac{\partial\Phi_c}{\partial r}+\frac{\partial^2\Psi_c}{\partial r\partial z}\right), \tag{27}$$

$$\tau_{rz}^c = \mu_c\frac{\partial}{\partial r}\left(2\,\frac{\partial\Phi_c}{\partial z}+\frac{\partial^2\Psi_c}{\partial z^2}-\frac{\partial^2\Psi_c}{\partial r^2}-\frac{1}{r}\frac{\partial\Psi_c}{\partial r}\right). \tag{28}$$

The radial and axial stresses, as well as the components of the displacement vector $\vec{u}^s$ in an elastic cylinder were defined in paper [3] by scalar potentials

Φ_s and Ψ_s, defined by the following equations:

$$\begin{aligned}\Phi_s(r, z, t) &= [A_1 J_0(k_d r) + A_2 Y_0(k_d r)]e^{-jpz+j\omega t}\\ \Psi_s(r, z, t) &= [B_1 J_0(k_t r) + B_2 Y_0(k_t r)]e^{-jpz+j\omega t}\end{aligned} \tag{29}$$

where

$$k_d^2 = \frac{\omega^2}{c_d^2} - p^2, \qquad k_t^2 = \frac{\omega^2}{c_t^2} - p^2 \tag{30}$$

and $J_0(z)$ and $Y_0(z)$ denote Bessel functions of the zero order first and second kind, respectively.

The components of the displacement vector $\vec{u}^s$, the radial and axial stresses are expressed by potentials Φ_s and Ψ_s as follows:

$$u_r^s = \frac{\partial \Phi_s}{\partial r} + \frac{\partial^2 \Psi_s}{\partial z \partial r}, \qquad w_z^s = \frac{\partial \Phi_s}{\partial z} - \frac{\partial \Psi_s}{r \partial r} - \frac{\partial^2 \Psi_s}{\partial r^2},$$

$$\tau_{rr}^s = \lambda_s\left(\frac{1}{r}\frac{\partial \Phi_s}{\partial r} + \frac{\partial^2 \Phi_s}{\partial r^2} + \frac{\partial^2 \Phi_s}{\partial z^2}\right) + 2\mu_s \frac{\partial}{\partial r}\left(\frac{\partial \Phi_s}{\partial r} + \frac{\partial^2 \Psi_s}{\partial r \partial z}\right) \tag{30a}$$

$$\tau_{rz}^s = \mu_s \frac{\partial}{\partial r}\left(2\frac{\partial \Phi_s}{\partial z} + \frac{\partial^2 \Psi_s}{\partial z^2} - \frac{\partial^2 \Psi_s}{\partial r^2} - \frac{1}{r}\frac{\partial \Psi_s}{\partial r}\right)$$

Material Constants of a Viscoelastic Biological Medium

The viscoelastic constants will be determined from the relationship between $\lambda', \mu', \lambda'', \mu''$ and the velocities of longitudinal, c_d, and transverse, c_t, waves in soft tissue as well as the absorption coefficients α_d, α_t, for given frequencies, $\omega = 2\pi f$.

Therefore:

$$c_d = \omega/\mathrm{Re}(h), \qquad \alpha_d = -\mathrm{Im}(h) \tag{31}$$

where:

$$h = [\varrho_c \omega/(\lambda_c + 2\mu_c)]^{1/2}, \quad \lambda_c = \lambda' + j\omega\lambda'', \quad \mu_c = \mu' + j\omega\mu''$$

and

$$c_t = \omega/\mathrm{Re}(l), \; \alpha_t = -\mathrm{Im}(l) \tag{32}$$

where $l = (\varrho_c \omega/\mu_c)^{1/2}$.

Papers dealing with the propagation of ultrasonic waves in soft tissue give only quantities characteristic for a longitudinal wave. A transverse wave propagating in tissue is absorbed so quickly (1000 times quicker than a longitudinal wave), that practically it is not applied. Also the measurement of this wave is very difficult. Paper [4] states first results of experiments conducted on determing the velocity, c_t, of a transverse wave, the absorption coefficient a_t and the bulk elasticity μ' and viscosity μ'' coefficients of such structures as muscle, liver, kidney. For frequencies in a range from 2 to 14 MHz only the intervals of c_t, a_t, μ' and μ'' were determined [4]:

$$c_t \in [9 \div 10^2]\,\mathrm{m/s}, \quad a_t \in [2\cdot 10^5 \div 3\cdot 10^6]\,1/\mathrm{m},$$
$$\mu' < 10^6\ \mathrm{N/m^2}, \quad \mu'' \in [3\cdot 10^{-3} \div 4\cdot 10^{-3}]\ \mathrm{Ns/m^2}. \tag{33}$$

In order to determine μ' and μ'' from equations (31), (32) we assume that:

a) c_t is the geometric mean in the interval (33), therefore $c_t = 30$ m/s

b) a_t was measured in paper [4] in the frequency range 2–14 MHz. The absorption coefficient a_d for longitudinal waves in soft tissue rises in direct proportion to the frequency [7], the choice of the smallest coefficient a_t from the outerval (33) is accepted by analogy. Frequencies applied in biopsy are about 2.5 MHz, thus $a_t = 2\cdot 10^3$ 1/m.

c) $c_d = 1.5\ 10^3$ m/s.

d) $a_d = 0.37$ 1/cm = 3,25 dB/cm.

With these assumptions, the following values of material constants (viscous and elastic) of soft tissue, were obtained for a frequency of $f = 2.5$MHz:

$$\begin{aligned} \lambda' &= 2.189\ 10^9\ \mathrm{N/m^2}, \quad \mu' = 5.854\cdot 10^5\ \mathrm{N/m^2} \\ \lambda'' &= 0.9056\ \mathrm{Ns/m^2}, \quad \mu'' = 0.0033\ \mathrm{Ns/m^2} \end{aligned} \tag{34}$$

It can be seen, that the volume viscosity coefficient λ'' is nearly three orders of magnitude greater than μ''. O'BRIEN in paper [6] showed, that μ'' has the same value for tissue and for water (soft tissue contains is 70% of water) and for water he accepted an approximation $\mu'' \ll \lambda''$. The same assumption can be applied for tissue. Then, comparing in (34) the elasticity coefficients λ' and μ', we can observe that μ' is 4 orders of magnitude smaller than λ'. In such a case we make an assumption: $\mu' \ll \lambda'$.

Summarizing the above assumptions we can define the tissue as a liquid characterized by coefficients:

volume viscosity: $\lambda'' = 0.9056$ Ns/m²,

elasticity of volume: $\lambda' = 2.189\cdot 10^9$ N/m².

In this liquid only a longitudinal wave propagates, because the absorption of a transverse wave in tissue is a 1000 times greater than the absorption of a longitudinal wave, what was proved in paper [4].

Therefore in the investigated case the displacement potential has the form:

$$\Phi^c(r, z, t) = \mathrm{C}H_0^{(2)}(l_d r)e^{-jpz}e^{j\omega t} \tag{35}$$

where

$$l_d^2 = \frac{\omega^2 \varrho_c}{\lambda_c} - p^2. \tag{35a}$$

The radial component of the displacement vector, expressed by potential Φ^c, is:

$$u_r^c = -\mathrm{C} l_d H_1^{(2)}(l_d r) e^{-jpz} e^{j\omega t}. \tag{36}$$

The normal and shear stresses in a viscoelastic liquid with a volume viscosity are:

$$\tau_{rr}^c = -\lambda_c \mathrm{C} H_0^{(2)}(l_d r)[l_d^2 + p^2] e^{-jpz} e^{j\omega t}, \qquad \tau_{rz}^c = 0. \tag{37}$$

Taking advantage of equations (29) and (30a), the radial and axial stresses, and the radial component u_r^s of the displacement vector in a elastic solid body are expressed by:

$$\begin{aligned}\tau_{rr}^s = \Big[& -A_1\{J_0(k_d r)(\omega^2 \varrho_s - 2\mu_s p^2) - \frac{k_d}{r} 2\mu_s J_1(k_d r)\} - \\ & - A_2\{Y_0(k_d r)(\omega^2 \varrho_s - 2\mu_s p^2) - \frac{k_d}{r} 2\mu_s Y_1(k_d r)\} - \\ & - B_1(2\mu_s jpk_t/r)\{J_1(k_t r) - k_t r J_0(k_t r)\} - \\ & - B_2(2\mu_s jpk_t/r)\{Y_1(k_t r) - k_t r Y_0(k_t r)\}\Big] e^{-jpz} e^{j\omega t},\end{aligned} \tag{38}$$

$$\begin{aligned}\tau_{rz}^s = \mu_s\{ & 2jpk_d A_1 J_1(k_d r) + 2jpk_d A_2 Y_1(k_d r) + B_1 k_t(p^2 - k_t^2) J_1(k_t r) \\ & + B_2 k_t Y_1(k_t r)(k_t^2 - p^2)\} e^{-jpz} e^{j\omega t},\end{aligned}$$

$$u_r^s = [-A_1 k_d J_1(k_d r) - A_2 k_d Y_1(k_d r) + B_1 jpk_t J_1(k_t r) + B_2 k_t jp Y_1(k_t r)] e^{-jpz} e^{j\omega t}$$

where

$$k_d^2 = \frac{\omega^2}{c_d^2} - p^2, \qquad k_t^2 = \frac{\omega^2}{c_t^2} - p^2,$$

c_d and c_t being the propagation velocities of the longitudinal and transversal waves, respectively, in the medium (issue).

Boundary conditions

The boundary conditions should be fulfilled, on the surface of the hollow cylinder with the internal and external radius, a and b, respectively. These conditions have the form of a continuity of radial and axial stresses, and the continuity of the radial component of the displacement vector, so:

$$\begin{aligned} &\tau_{rr}^{s} = \tau_{rr}^{c}, \quad \tau_{rz}^{s} = \tau_{rz}^{c}, \quad u_r^s = u_r^c \quad \text{for } r = a \\ &\tau_{rr}^{s} = 0, \quad \tau_{rz}^{s} = 0, \quad \text{for } r = b \end{aligned} \tag{39}$$

Placing relationships (36), (37), (38) in the system of equations (39) we obtain a system of 5 homogeneous equations with unknown complex amplitudes: A_1, A_2, B_1, B_2, C. If there is to be a non-trivial solution of the equation system, the determinant formed from coefficients standing by amplitudes A_1, A_2, B_1, B_2, C must disappear:

$$|b_{ij}| = 0 \quad i, j = 1, 5. \tag{40}$$

Determinant $|b_{ij}|$ is expressed by formula (40a). Terms b_{ij} $i, j = 1{,}5$ contain: the material constants characteristic for the needle and the biological structure, wave numbers k_d, k_t, l_d, the sought wave number p, which occurs explicitly in the equation, and is also included in k_d, k_t, l_d and in the arguments of the first and second kind Bessel functions.

The solution of the characteristic equation $|b_{ij}| = 0$ by means of analytical methods in order to obtain the complex wave number p — is impossible. The complicated form of the characteristic equation suggests the application of numerical methods. We look for such values of the wave number p, which corresponds to:

a) the zeroing of the determinant,
b) to a wave velocity close to the wave velocity in the surrounding liquid medium and absorption close to wave absorption in the surrounding unlimited liquid medium.

The signs of k_d, k_t and l_d in formulas (30) and (35a) have been chosen in such a way, that the wave propagating away from the media boundary is attenuated. The characteristic equation was solved numerically for the following data: $f = 2.5$ MHz, $a = 0.75$ mm, $b = 0.5$ mm.

The needle is made of steel with density $\varrho_s = 7.7$ g/cm³, Lame constants: $\lambda_s = 1.07 \cdot 10^{12}$ g/(cm s²) and $\mu_s = 8.03 \cdot 10^{11}$ g/(cm s²). The velocities of the longitudinal and transverse waves are $c_d = 5.9$ km/s, $c_t = 3.23$ km/s, respectively. A viscoelastic liquid was accepted as tissue. It was characterized by the following parameters: volume viscocity $\lambda'' = 0.9056$ Ns/m², elasticity $\lambda' = 2.189 \cdot 10^9$ N/m², density $\varrho_c = 1$ g/cm³. The velocity and absorption of the wave in this medium are $c = 1.5$ km/s, $\alpha = 0.37$ 1/cm, respectively.

Under these assumptions the acquired velocity of a wave propagating along a hollow cylinder immersed in a viscoelastic liquid was $c_x = 1.49741$ km/s, in other words samewhat smaller than the velocity of a longitudinal wave in an unlimited viscoelastic liquid, accepted at 1.5 km/s. The obtained absorption

$$\left|\begin{array}{lll}
\frac{2k_d\mu_s}{a}J_1(k_da) & \frac{2k_d\mu_s}{a}Y_1(k_da) & \frac{-2\mu_s jpk_t}{a}[J_1(k_ta)-k_taJ_0(k_ta)] \\
-\frac{2j\mu_s pk_t}{a}[Y_1(k_ta)-k_taY_0(k_ta)] & \lambda_c H_0^{(2)}(l_da)(l_d^2+\rho^2) & \\
-J_0(k_da)(\omega^2\varrho_s-2\mu_sp^2) & -Y_0(k_da)(\omega^2\varrho_s-2\mu_sp^2) & \\
2j\mu_sk_dpJ_1(-k_da) & 2j\mu_sk_dpY_1(k_da) & \mu_sk_tJ_1(k_ta)(p^2-k_t^2) \\
\mu_sk_tY_1(k_ta)(p^2-k_t^2) & 0 & \\
-k_dJ_1(k_da) & -k_dY_1(k_da) & jk_tpJ_1(k_ta) \\
k_tpY_1(k_ta) & l_dH_1^{(2)}(l_da) & \\
\frac{2k_d\mu_s}{b}J_1(k_db) & \frac{2k_d\mu_s}{b}Y_1(k_db) & \frac{-2j\mu_spk_t}{b}[J_1(k_tb)-k_tbJ_0(k_tb)] \\
\frac{-2j\mu_spk_t}{b}[Y_1(k_tb)-k_tbY_0(k_tb)] & 0 & \\
-J_0(k_db)(\omega^2\varrho_s-2\mu_sp^2) & -Y_0(k_db)(\omega^2\varrho_s-2\mu_sp^2) & \\
2jp\mu_sk_dJ_1(k_db) & 2jp\mu_sk_dY_1(k_db) & \mu_sk_tJ_1(k_tb)(p^2-k_t^2) \\
\mu_sk_tY_1(k_tb)(p^2-k_t^2) & 0 &
\end{array}\right| = |b_{ij}| \qquad (40a)$$

coefficient $a_x = 0.349$ 1/cm is also lower from the absorption coefficient of a longitudinal wave in an unlimited viscoelastic medium, accepted at $a = 0.370$ 1/cm.

As a consequence of solving the characteristic equation the following values of wave numbers k_d, k_t and l_d were obtained:

$$k_d = -0.36 - j\ 101,\ k_t = -0.39 - j\ 92.9,\ l_d = 16.3 - j\ 0.0037 \tag{41}$$

and the following values of the amplitudes of the displacement potentials:

$$A_2 = -j,\ B_1 = -j\ 0.0072,\ B_2 = -0.0072,\ C = -0.0011 - j\ 0.00073 \tag{42}$$

for an assumed amplitude value $A_1 = 1 + j0$.

Putting together the obtained numerically results (41) and (42), we receive the displacement potentials in the following form:

a) in a viscoelastic liquid:

$$\Phi^c = \mathrm{CH}_0^{(2)}\big((16.3 - j\ 0.0037)r\big)e^{-j104z}e^{-0.349z}e^{j5\pi10^6t}. \tag{43}$$

It results from formula (43), that the wave propagates also in direction z. The wave is attenuated along the z axis.

The second kind Hankel function $H_0^2(l_d r)$ represents a wave propagating in the direction of the increasing r. For $r \to \infty$ we have an asymptotic representation:

$$H_0^{(2)}(l_d r)\xrightarrow[r\to\infty]{}\left(\frac{2}{l_d r\pi}\right)^{1/2}\exp\left[-j\left(l_d r - \frac{\pi}{4}\right)\right]$$

$$= \left[\frac{2}{(16.3 - j\ 0.0037)r\pi}\right]^{1/2} e^{-j16.3r}\cdot e^{-0.0037r}e^{3\cdot5\pi10^6t}. \tag{44}$$

From this representation it can be seen, that the wave propagates also in direction r and is attenuated with the increase of r, because $\mathrm{Re}(l_d) > 0$ and $\mathrm{Im}(l_d) < 0$. In an ideal case (absorption in liquid is equal to zero) the real part, l_d, is zeroed and l_d is an imaginary quantity. Then the wave is attenuated with the increase of r, [3].

b) in an elastic solid body:

$$\Phi_s = [A_1J_0(-0.4\,r - j\ 101r) + A_2Y_0(-0.4r - j\ 101r)]e^{-j101z}\cdot e^{-0.349z}\times$$
$$\times e^{j5\pi10^6t} \tag{45}$$

$$\Psi_s = [B_1J_0(-0.4\,r - j\,93r) + B_2Y_0(-0.4\ r - j\ 93r)]e^{-j101z}\cdot e^{-0.349}\cdot e^{j5\pi10^6t} \tag{46}$$

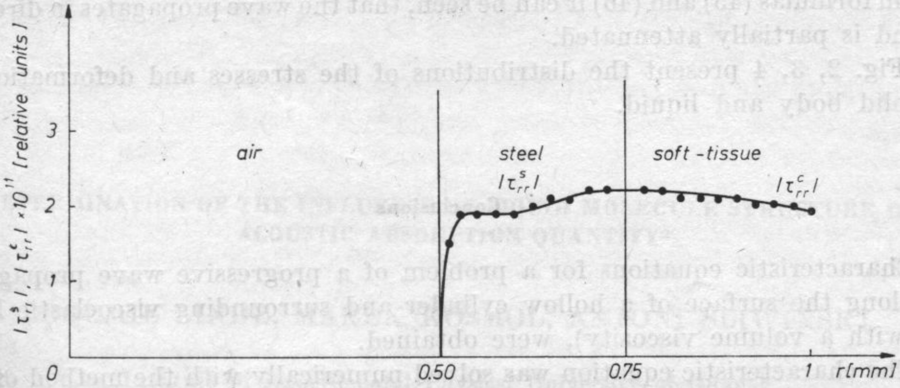

Fig. 2. Distributions of stress modules, τ_{rr}^s and τ_{rr}^c

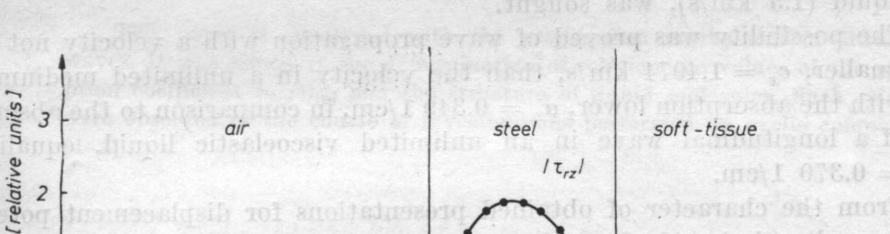

Fig. 3. Distributions of stress modulus τ_{rz}^s

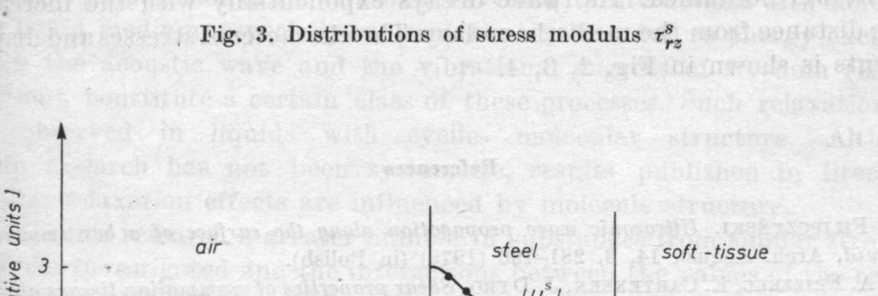

Fig. 4. Distributions of the displacement component modules u_r^s and u_r^c

From formulas (45) and (46) it can be seen, that the wave propagates in direction z and is partially attenuated.

Fig. 2, 3, 4 present the distributions of the stresses and deformations in a solid body and liquid.

Conclusions

1. Characteristic equations for a problem of a progressive wave propagating along the surface of a hollow cylinder and surrounding viscoelastic liquid (with a volume viscosity), were obtained.
2. The characteristic equation was solved numerically with the method of successive approximations and the zero crossing method. The wave velocity close to the velocity of a longitudinal wave characteristic for a viscoelastic liquid (1.5 km/s), was sought.

   The possibility was proved of wave propagation with a velocity not much smaller, $c_x = 1.4974$ km/s, than the velocity in a unlimited medium, and with the absorption lower, $a_x = 0.349$ 1/cm, in comparison to the absorption of a longitudinal wave in an unlimited viscoelastic liquid, equaling $a_d = 0.370$ 1/cm.
3. From the character of obtained presentations for displacement potentials it results, that aside from the propagation wave along the boundary of the media, also wave propagation takes place in the direction of the liquid medium where the energy is absorbed.
4. Distributions of radial and axial stresses, and radial components of displacement were obtained. The wave decays exponentially with the increase of the distance from the media boundary. The character of stresses and displacements is shown in Fig. 2, 3, 4.

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DETERMINATION OF THE INFLUENCE OF LIQUID MOLECULE STRUCTURE ON ACOUSTIC ABSORPTION QUANTITY*

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This paper is concerned with the propagation mechanism of ultrasonic waves. It was aimed at the determination of relation the values of the absorption coefficient $(\alpha/f^2)_{rel}$ and the structure of liquid molecules. Such relation were observed in the course of investigations performed on cyclic compounds [1–4].

Introduction

Acoustic relaxation processes take place due to interactions between an ultrasonic wave and the environment in which it propagates. Effects accompanying the propagation of an ultrasonic wave and its interactions with molecules of the liquid medium, especially molecular relaxation due to energy exchange between the acoustic wave and the vibrational degrees of freedom (Kneser relaxation), constitute a certain class of these processes. Such relaxation has been observed in liquids with cyclic molecular structure. Although hitherto research has not been systematic, results published in literature show that relaxation effects are influenced by molecule structure.

Within this research a greater number of substances from similar structure groups was investigated and the interactions between the values of the relaxation coefficients $(\alpha/f^2)_{rel}$ and the molecule structure of these substances was determined.

Many authors (BERGMANN and JAENSCH [5], PARTHASARATHY [6], RAO [7], LAGEMANN [8], SCHAAFFS [9] and SETTE [10]) very accurately determined relations between the propagation velocity of ultrasonic waves and liquid molecule structure, but there are no systematic papers concerned with the relationship between the absorption coefficient α/f^2 and molecule structure. Only three aut-

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* Work performed within the framework of the problem MR. I. 24.

hors have classified liquids in relation to the attenuation quantity: PINKERTON [11] on the basis of the a_{exp}/a_{cl} ratio, MICHAJŁOW [12] dividing the frequency measuring range into five relaxation ranges, and VERMA [13], who took into consideration the mechanism responsible for absorption. These approaches are not based on the dependences between sound attenuation and molecule structure. SZACHPARONOW and TUNIN [14] observed that in rigid molecules with active electrons π the absorption of ultrasounds, which is always caused by energy transition to vibrational degrees of freedom, is considerable and the relaxation time is about 10^{-10} s. This conclusion has been confirmed by investigations presented below.

On the basis of own investigations and data from literature, concerning ultrasound absorption in cyclic compounds, certain strict relations between $(\alpha/f^2)_{rel}$ and molecule structure of a given liquid can be established.

Research was performed on non-associated liquids without rotational isomers, in which structural relaxation processes do not occur, i.e. absorption of an ultrasonic wave mainly due to Kneser relaxation [15].

On the basis of the analysis of achieved results, investigated substances have been divided into five characteristic group according to: relations between $(\alpha/f^2)_{rel}$ and the number of substituents in molecules (groups I and II), the exchange of carbon atoms by nitrogen (group III), molecule enlargement caused by substituent exchanges (group IV) and changes caused by bond saturation in a ring (group V).

Apparatus

The amplitude absorption coefficient, α/f^2, of an ultrasonic wave was measured with the pulse method in two measuring set-ups covering frequency ranges from 10 to 180 MHz and from 400 to 1300 MHz.

A modernized ultrasonic spectrometer *US*-3 [3] was applied in the first range, while in the second range a system designed by LEŻNIEW [17], which employs the method of non-resonance excitation of a lithium niobate monocrystal in a resonance chamber, was used.

The principle of operation of this system, presented in Fig. 1, is as follows; the two-channel pulse generator – *1* switches on the oscilloscope time base – *2*, the pulse generator – *4* and modulates generator signals – *3*. A pulse with a determined carrier frequency leaves the high frequency generator and enters the coaxial quarter-wave resonator – R_1 through the coupling loop – P_1. A quarter of the length of an electromagnetic wave is saved in the resonator cavity. The resonance frequency could be smoothly changed with a slidable tuner in a range from 400 to 1300 MHz. A 5 mm in radius and 15 mm in length lithium niobate crystal *I* was inserted in the center of the resonant cavity, so one end was within the range of the variable electric field. When the field in the resonator was excited by pulses, a pulse of mechanical vibrations was generated on the surface of the crystal, propagated along it and entered the investigated liquid [18]. (The R_1 resonator together with the transducer were attached to the mobile part of the cathetometer, moved with a $5 \cdot 10^{-7}$ m accuracy, in order to regulate the acoustic path in the liquid). After passing through the liquid, the acoustic pulse enters transducer *II*, where it is again changed into an electric pulse, which is fed into the input of the receiving amplifier *7* through resonator R_2 and coupling loop P_2 and then, sent directly to oscilloscope *2*.

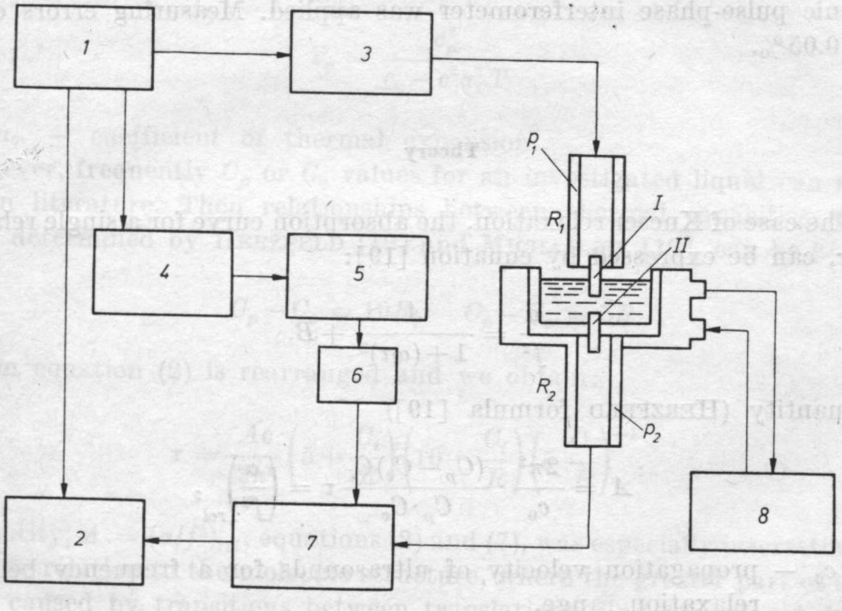


Fig. 1. Block diagram of a system for measuring absorption of ultrasonic waves in a frequency range 100–1300 MHz *1* – two-channel pulse generator, *2* – oscilloscope, *3* – high frequency generator G3-21, *4* – rectangular pulse generator G-920, *5* – generator of standard sygnals G4-44, *6* – damper, *7* – receiver *P5-3*, $P_{1,2}$ – coupling loops, $R_{1,2}$ – resonators, *I* and *II* – transducers from lithium niobate, *8* – ultrathermostat

The mentioned above pulse generator *4* (acts as a regulated delay line and cuts out the unnecessary initial part of the pulse, giving a more legible oscilloscope picture) switches on the calibrated pulse generator *5*. Generator *5* sends a pulse through a damper (regulated smoothly from 0 to 30 dB with a 0.1 dB accuracy) to oscilloscope *2*. This pulse is used in the absolute measurement of the amplitude absorption coefficient. Comparing amplitudes of two signals: ultrasonic, A_1, and calibrated, A_2, the value of the absorption coefficient, expressed in [s²/m], can be determined according to equation:

$$\frac{\alpha}{f^2} = \frac{\Delta A}{f^2 \Delta s \, 20 \log e}.$$

Every absorption measurement was repeated ten times for different lengths of the ultrasonic wave path in investigated liquids and, possibly, in various points of this path.

The temperature was stabilized with an *U-10* ultrathermostat with the accuracy of 0.1 K.

Estimated errors of determining the absorption coefficient are contained in a range from 3.5 % for the frequency of 400 MHz to 5 % for 1300 MHz.

Additional measurements of the propagation velocity of ultrasounds were performed in order to calculate classical absorption coefficients. An *UI-12* ultrasonic pulse-phase interferometer was applied. Measuring errors equaled about 0.05 %.

Theory

In the case of Kneser relaxation, the absorption curve for a single relaxation time, τ, can be expressed by equation [19]:

$$\frac{\alpha}{f^2} = \frac{A}{1+(\omega\tau)^2} + B. \tag{1}$$

The quantity (HERZFELD formula [19])

$$A = \frac{2\pi^2}{c_0} \cdot \frac{(C_p - C_v)C_i}{C_p \cdot C_v} \tau = \left(\frac{\alpha}{f^2}\right)_{rel}, \tag{2}$$

where c_0 – propagation velocity of ultrasounds for a frequency below the relaxation range,

C_p, C_v, C_i – thermal capacities at constant pressure, and volume, and thermal capacity of inertial degrees of freedom,

τ – acoustic relaxation time,

informs about the share of the relaxation process in the observed entire absorption, while B denotes the absorption due to: viscosity η, thermal conductivity $\varkappa$, and possibly other relaxation processes with relaxation times considerably shorter than τ. Therefore, it represents the classic part of the absorption coefficient, determined by Stokes [20]:

$$B = \left(\frac{\alpha}{f^2}\right)_{kl} = \frac{8\pi^2}{3\varrho c^3}\eta, \tag{3}$$

where ϱ is the density.

Relaxation time, τ, can be determined knowing the A quantity, thermal capacities, C_p and C_v, and the frequencies of vibrational degrees of freedom in molecules, ν_i, which enable the calculation of C_i according to the Planck-Einstein formula [21]:

$$C_i = R \sum_i g_i \left(\frac{h\nu_i}{kT}\right)^2 \exp\left(-\frac{h\nu_i}{kT}\right)\left[1-\exp\left(-\frac{h\nu_i}{kT}\right)\right]^{-2}, \tag{4}$$

where: g_i — degree of degeneration, ν_i — frequency of the i vibration, h, k and T — Planck and Boltzman constants, and temperature.

If C_v is unknown, then the relation between the propagation velocity of an acoustic wave, c, and specific heats, c_p and c_v, [22], can be applied:

$$c_v = \frac{c_p^2}{c_p + c^2 a_T^2 T} \tag{5}$$

where a_T — coefficient of thermal expansion.

However, frequently C_p or C_v values for an investigated liquid can not be found in literature. Then relationships between thermal capacities, C_p, C_v and C_i, determined by HERZFELD [19] and MICHAJŁOW [12], can be applied:

$$C_p - C_i \approx 10R, \quad C_p - C_v \approx 5R$$

and then equation (2) is rearranged and we obtain:

$$\tau = \frac{Ac}{2\pi^2}\left(5+\frac{C_i}{R}\right)\left(10+\frac{C_i}{R}\right)\left(5\ \frac{C_i}{R}\right)^{-1}. \tag{7}$$

The quantity, $A = (\alpha/f^2)_{rel}$, equations (2) and (7), was especially interesting due to its close relation to the molecule structure, where the greater part of absorption is caused by transitions between translational and vibrational degrees of freedom.

Investigated substances

42 aromatic and heterocyclic compounds were chosen for investigation. The necessary acoustical data for ten compounds can be found in literature, while as for the other 32 liquids — the authors performed required measurements.

Measurements proved that the entire research material can be divided into five groups according to relations between $(\alpha/f^2)_{rel}$ and the molecule structure:

Group I

Benzene, toluene, *p*-xylene, *o*-xylene, *m*-xylene, pseudoucumene, hemihexamethylbenzene.

Group II

Pyridine, α-picoline, β-picoline, γ-picoline, 3-4 lutidine, 2-4 lutidine, 2-5 lutidine, 3-5 lutidine, 2-6 lutidine, 2,4,6-collidine, 2,5,6-collidine, aniline, ethylaniline.

Group III

Benzene, pyridine, pyrimidine, naphthalene, quinoline.

Group IV

Toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, 3,4-lutidine, β-collidine, 2,5-lutidine, 2-methyl-5-ethylpyridine, toluene, acetophenone, toluene, benzyloamine, α-picoline, 2-ethylpyridine, γ-picoline, 4-ethylpyridine, naphthalene, bromonaphthalene, 2-methylnaphthalene.

Group V

Pyridine, piperdine, furane, tetrahydrofuran, pyrrole, pyrrolidine, naphthalene, decalin.

Picolines and xylenes, which were investigated first, were additionally purified, but it was stated that this process does not influence the measured value of the absorption coefficient and propagation velocity of ultrasounds. Apart from this it was found that for liquids with the absorption coefficient $\frac{\alpha}{f^2}$ less than 100×10^{-17} s^2/m, and such that the dispersion regions do not occur within the investigated frequency range, the acoustical parameters α and c are the same (within the experimental error) for well purified compunds as for ones only distilled and not submitted to any purification processes. Values, α and c, for these compounds, do not depend on the company they were produced by (Fluka, Schuchard, Koch. Light Laboratory, Reachim or Loba) or on the degree of purity, i.e. whether the compound was pure, analytically pure or pure special for spectroscopy. However, in compounds with higher attenuation small impurities play a significant role, which increases with the increase of the coefficient of ultrasound absorption.

Yet, all investigated liquids were dried and distilled at least once in order to eliminate possible larger solid impurities, water and compounds formed in photoreactions (with time nearly all investigated liquids become brown).

Table 1. Methyl alcohol C_2H_5OH

f MHz	10	17.75	30	45	59.5	410	500	600	850	1000	1100	1250
$\frac{\alpha}{f^2}\,\frac{s^2}{m}\,10^{-15}$	34.0	35.1	33.5	34.2	34.1	34.2	34.9	34.7	33.7	33.1	33.9	34.1

Before research was initiated the apparatus was calibrated and checked by performing control measurements for methyl alcohol. Calibration results are presented in Table 1. The α/f^2 values are constant in the investigated frequency range. This is in compliance with data stated by other authors.

All measurements were arried out at a temperature of 293 K in order to eliminate systematic errors of the apparatus.

Classic absorption coefficients were calculated additionally, because they are necessary to determine the α_{exp}/α_{cl} ratio. This ratio indicates whether acoustic dispersion will take place and which processes condition it, and so: if $\alpha_{exp}/\alpha_{cl} > 1$, then acoustical relaxation must occur (only it is of unknown origin and further detailed information about the liquid is necessary to determine what physical phenomenon is responsible for the relaxation process — in our case Kneser interactions); if $\alpha_{exp}/\alpha_{cl} = 1$, then dispersion can occur and it will be caused by shear viscosity relaxation; if $\alpha_{exp}/\alpha_{cl} < 1$, then we are in the dispersion region and viscosity relaxation, η_s, is responsible for the process.

Results and their analysis

Group I

Table 2 presents measurement results for a series of benzene and naphthalen derivatives, namely: amplitude absorption coefficient, classic absorption coefficient calculated from formula (3), density, viscosity, propagation velocity of ultrasounds and α_{exp}/α_{cl} ratio. All liquids from this group, except benzene and toluene (methylbenzene) do not exhibit dispersion regions in the measured frequency range, but values of the classic absorption coefficient ($\alpha_{cl} < \alpha_{exp}$)

Table 2

Compound	$\left(\frac{\alpha}{f^2}\right)_{cl}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\varrho\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s [mPa·s]	$c\left[\frac{m}{s}\right]$	$\frac{\alpha_{exp}}{\alpha_{cl}}$	$\left(\frac{\alpha}{f^2}\right)_{exp}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
p-xylene $C_6H_4(CH_3)_2$	8.6	0.8655 53	0.648 78	1320.1	7.0	59.9
o-xylene $C_6H_4(CH_3)_2$	9.5	0.8845 53	0.804 78	1361.7	6.5	61.7
m-xylene $C_6H_4(CH_3)_2$	7.7	0.8685 53	0.615 78	1340.0	9.9	76.2
pseudocumene $C_6H_3(CH_3)_3$	11.85	0.8748 55	1.01 80	1368.9	4.1	48.1
hemihexamethylbenzene $C_6H_3(CH_3)_3$	11.25	0.8944	1.062	1405.7	4.8	54.1
mesitylene $C_6H_3(CH_3)_3$	8.97	0.8651 55	0.735 80	1355.7	7.27	65.1
isodurene $C_6H_2(CH_3)_4$	—	0.8906 58	—	1410.8	—	60.2

indicate that acoustic relaxation occurs and should be observed at higher frequencies. Measurements were conducted in a range from 1 MHz to 1.3 GHz. When acoustical relaxation processes take place, then observed dispersion regions usually cover two frequency decades (Fig. 2) and thus the acoustic relaxation time, τ_{ak}, can be estimated. (These quantities have been marked τ_{ak} to indicate that relaxation times were determined from acoustical investigations, solely).

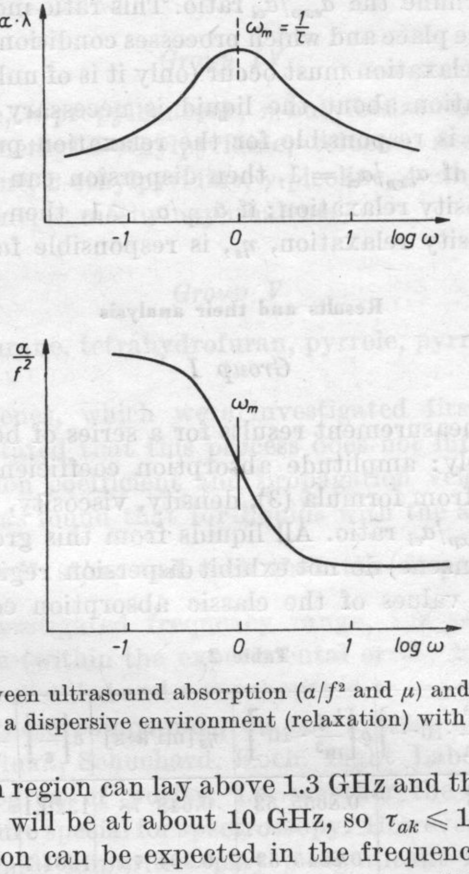


Fig. 2. Dependence between ultrasound absorption (α/f^2 and μ) and the logarithm of the acoustic wave frequency in a dispersive environment (relaxation) with a single relaxation time τ

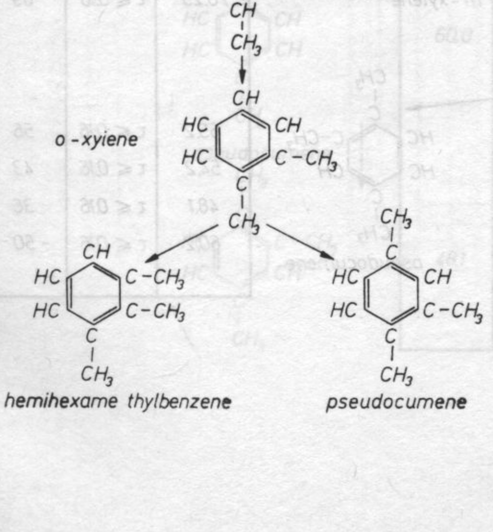
The closest dispersion region can lay above 1.3 GHz and then the inflexion point of the α/f^2 (f^2) curve will be at about 10 GHz, so $\tau_{ak} \leqslant 1.6 \times 10^{-11}$ s. Only the Kneser type relaxation can be expected in the frequency region investigated by the authors in these liquids. If this conclusion is valid, then the performed relaxation time τ should be concurrent with τ_{ak}. Relaxation times, τ, have been calculated from equation (2), making use of the frequency values of free vibrations of the molecule, ν_i, obtained from investigations in the infrared [24–29]. Calculated τ values are of the same order as τ_{ak}, estimated from acoustical measurements (Table 3). This confirms the hypothesis that the relaxation process can be caused by Kneser effects.

Performed investigations indicate that an increase of the number of methyl groups attached to the benzene ring causes a shortening of the relaxation time, so an addition of a group promotes the deactivation of the vibrational degrees

Table 3

Substance	C_p $\left[\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right]$	C_v $\left[\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right]$	C_i $\left[\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right]$	$\left(\frac{\alpha}{f^2}\right)_{exp} - \left(\frac{\alpha}{f^2}\right)_{cl} = A$ $\left[\frac{\mathrm{s}^2}{\mathrm{m}} \cdot 10^{-15}\right]$	τ $\mathrm{s} \cdot 10^{-11}$	τ_{ak} $\mathrm{s} \cdot 10^{-11}$
Benzene 10	134.7	92.9	52.7	841.5	—	28.0
Toluene 31	155.2	113.4	71.1	75.2	—	5.0
o-xylene	188.7 57	147.3	98.3	52.3	1.2	1.6
m-xylene	183.3 57	141.0	92.0	68.5	1.5	1.6
p-xylene	183.7 57	141.0	91.6	51.4	1.1	1.6
mesitylene	207.9 55	163.2	125.1	56.2	0.9	1.6
hemihexamethylbenzene	215.5 55	172.4	132.2	43.0	0.8	1.6
pseudocumene	213.8 55	167.8	130.5	36.3	0.6	1.6
sodurene	241.0 57	199.6	157.7	—	—	—

Table 4. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of benzene



$\frac{\alpha}{f^2}\left[\frac{s^2}{m} \cdot 10^{-15}\right]$	$\tau\ [s \cdot 10^{-10}]$	$A\left[\frac{s^2}{m} \cdot 10^{-15}\right]$
860.0	2.8	841
82.0	0.5	75
61.5	$\tau \leqslant 0.16$	52
54.2	$\tau \leqslant 0.16$	43
48.1	$\tau \leqslant 0.16$	36

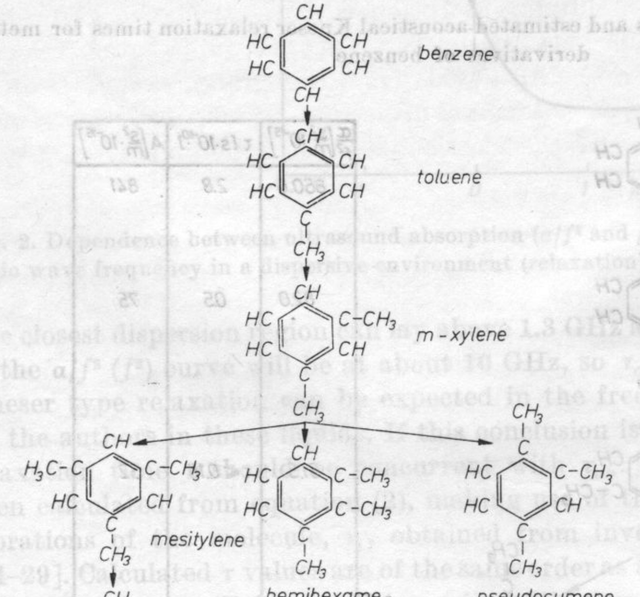
of freedom. (It has to be mentioned that this does not concern arbitrary compounds differing in the number of attached methyl groups, but those that are formed in a series from one another by adding a succeeding group (Tables 4–6) according to the KÖRNER principle).

It has been also found (as it can be seen in the tables) that with the addition of a succeeding methyl group the value of the amplitude absorption coefficient decreases. The addition of the first group causes a very big decrease of the value, while succeeding additions cause smaller drops (Figs. 3–5). The decrease of the absorption coefficient observed in experiments is in accordance with the Herzfeld formula (2):

$$\left(\frac{\alpha}{f^2}\right)_{rel} = A = \frac{2\pi^2\tau}{c} \cdot \frac{C_i(C_p - C_v)}{C_p \cdot C_v}$$

because the addition of a CH_3 group increases the quantity of oscillatory degrees of freedom, thus the thermal capacity, C_i, and thermal capacities, C_p and C_v,

Table 5. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of benzene



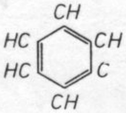
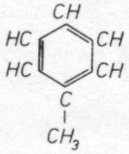
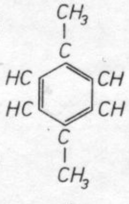
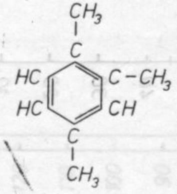
$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot10^{-15}\right]$	$\tau\,[s\cdot10^{-10}]$	$A\left[\frac{s^2}{m}\cdot10^{-15}\right]$
860.0	2.8	841
82	0.16	75
76.25	$\tau \leqslant 0.16$	69
65.2	$\tau \leqslant 0.16$	56
54.2	$\tau \leqslant 0.16$	43
48.1	$\tau \leqslant 0.16$	36
60.2	$\tau \leqslant 0.16$	~ 50

also increase, while the difference $C_p - C_v$ is a nearly constant quantity, so the second factor in the above equation decreases. The relaxation time τ, is shortened and the absorption coefficient has to decrease.

From the point of view of structure this can be explained as follows: the CH_3 group in the ring is a steric hinderence which undergoes a transformation in a collision of heavy and rigid rings with mobile electrons π, which transfer a large amount of energy. The energy transfer is significantly smaller during the collision of light and mobile CH_3 groups. Therefore, an increase of the number of groups decreases the probability of a collision of rings and the energy transfer from the ultrasonic wave to the internal degrees of freedom, what leads to the decrease of the absorption coefficient.

It can be noticed that the addition of succeeding methyl groups causes a decrease of the a_{exp}/a_{cl} ratio (Table 7), so the shear viscosity fraction in the attenuational effect increases.

Table 6. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of benzene

	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau\ [s\cdot 10^{-10}]$	$A\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
benzene 	860.0	2.8	84.1
toluene 	82.0	0.5	75
p -xylene 	60.0	$\tau \leqslant 0.16$	51
pseudocumene 	48.1	$\tau \leqslant 0.16$	36

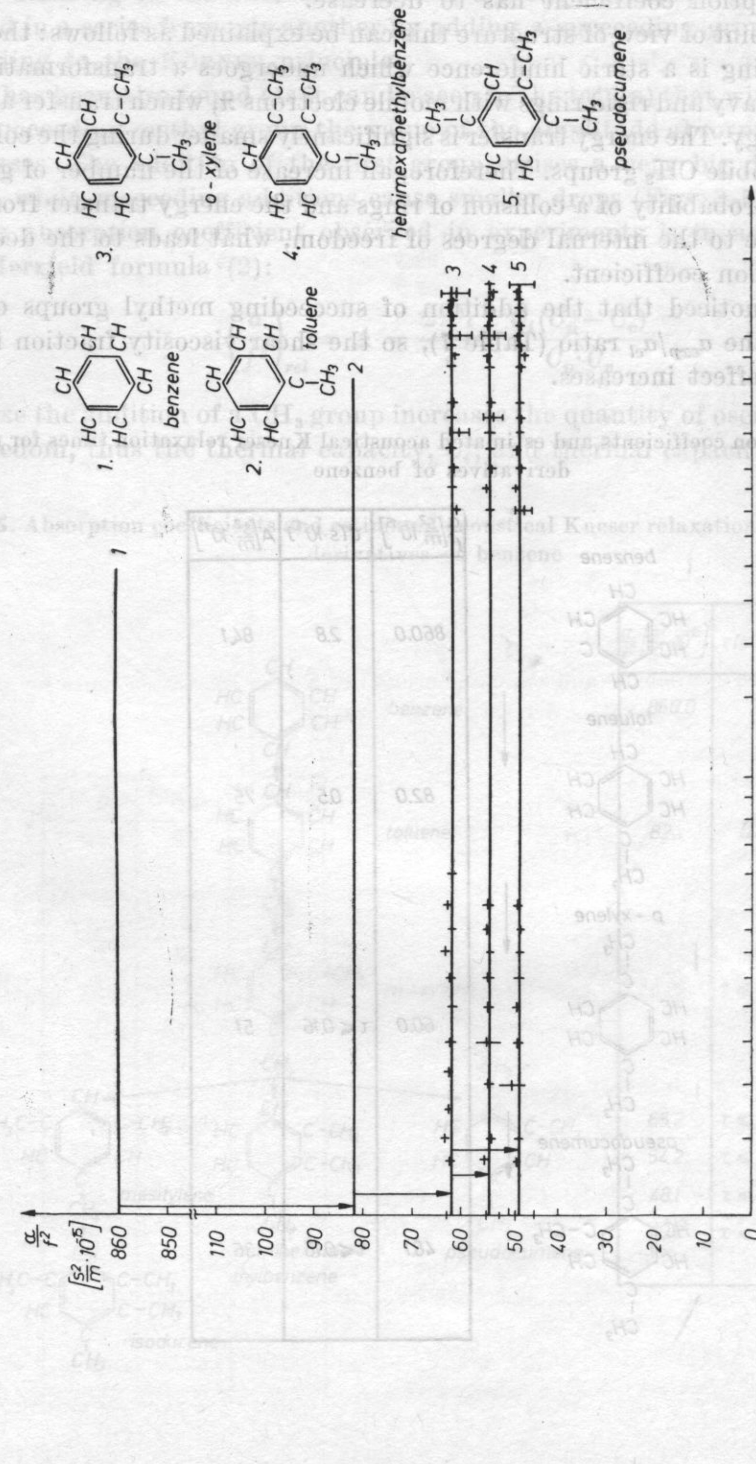


Fig. 3. $a/f^2(f)$ dependence for benzene and benzene methyl derivatives. Arrow ↓ marks the direction of changes of a/f^2 due to an addition of another CH_3 group

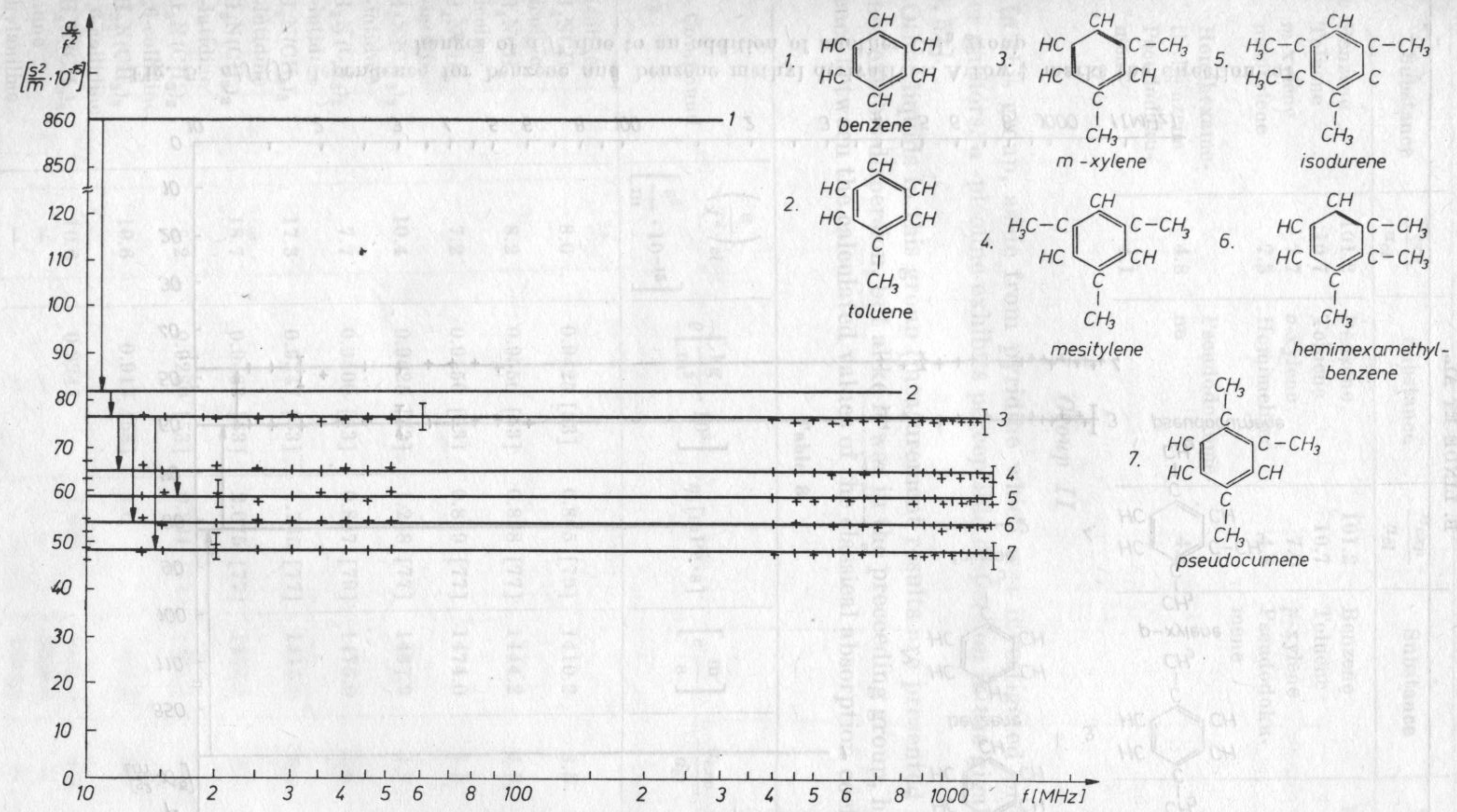


Fig. 4. $\alpha/f^2(f)$ dependence for benzene and benzene methyl derivatives. Arrow ↓ marks the direction of changes of α/f^2 due to an addition of another CH_3 group

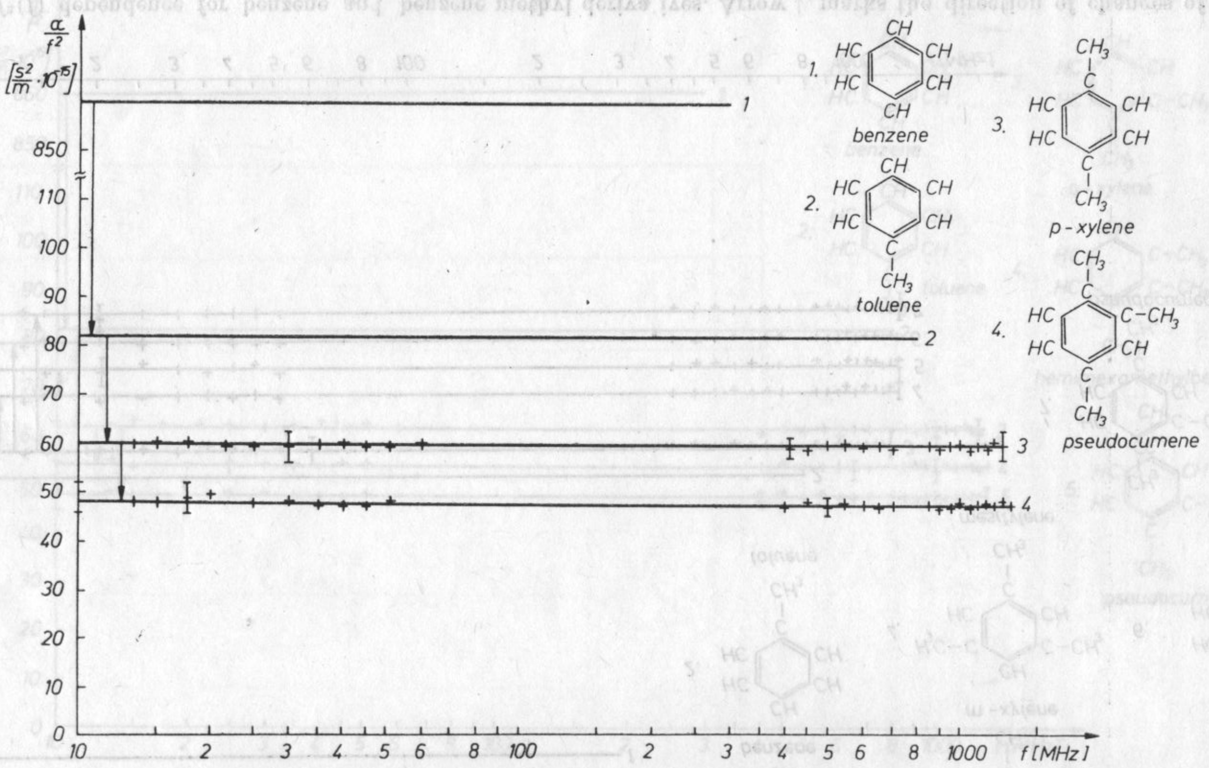


Fig. 5. $\alpha/f^2(f)$ dependence for benzene and benzene methyl derivatives. Arrow ↓ marks the direction of changes of α/f^2 due to an addition of another CH_3 group

Table 7

Substance	$\frac{a_{exp}}{a_{cl}}$	Substance	$\frac{a_{exp}}{a_{cl}}$	Substance	$\frac{a_{exp}}{a_{cl}}$
Benzene	101.2	Benzene	101.2	Benzene	101.2
Toluene	10.7	Toluene	10.7	Toluene	10.7
m-xylene	7.7	*o*-xylene	7.0	*p*-xylene	6.5
mesitylene	7.3	Hemimeliten	4.8	Pseudodokumene	4.1
Hemihexamethylbenzene	4.8	Pseudodokumene	4.1		
Pseudodokumene	4.1				

Group II

In this group, aside from pyridine which was investigated previously by other authors, α -picoline exhibits perceptible dispersion in the gigahertz range [30, 52].

Other liquids in this group (measurement results are presented in Table 8) do not exhibit dispersion, but alike it was in the preceding group, here the difference between the calculated values of the classical absorption coefficient and

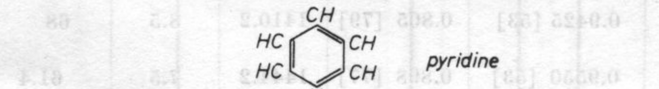
Table 8

Compound	$\left(\frac{\alpha}{f^2}\right)_{cl}$ $\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\varrho\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s[mPa·s]	$\left[c\ \frac{m}{s}\right]$	$\frac{a_{exp}}{a_{cl}}$	$\left(\frac{\alpha}{f^2}\right)_{exp}$ $\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
α-picoline $C_5H_4NCH_3$	8.0	0.9425 [53]	0.805 [79]	1410.2	8.5	68
β-picoline $C_5H_4NCH_3$	8.2	0.9550 [53]	0.898 [77]	1444.2	7.5	61.4
γ-picoline $C_5H_4NCH_3$	7.2	0.9556 [53]	0.839 [77]	1474.0	8.5	61.5
3,4-lutidine $C_5H_3N(CH_3)_2$	10.4	0.9625 [53]	1.248 [77]	1487.9	4.9	51.2
2,4-lutidine $C_5H_3N(CH_3)_2$	7.7	0.9400 [53]	0.887 [79]	1475.0	6.6	51.0
2,5-lutidine $C_5H_3N(CH_3)_2$	17.3	0.9347 [53]	1.745 [77]	1415.0	3.0	51.2
3,5-lutidine $C_5H_3N(CH_3)_2$	18.7	0.9463 [53]	2.075 [77]	1454.7	2.6	48.7
2,6-lutidine $C_5H_3N(CH_3)_2$	8.2	0.9280 [53]	0.831 [77]	1421.1	7.4	60.9
2,4,6-collidine $C_5H_2N(CH_3)_3$	10.6	0.917 [58]	1.0	1392.2	5.3	56.0
2,3,6-collidine $C_5H_2N(CH_3)_3$	10.6	0.9241	1.026	1401.0	4.3	45.9
Aniline	—	—	—	1656.0	—	70
Ethylaniline	—	—	—	1528.6	—	44

Table 9

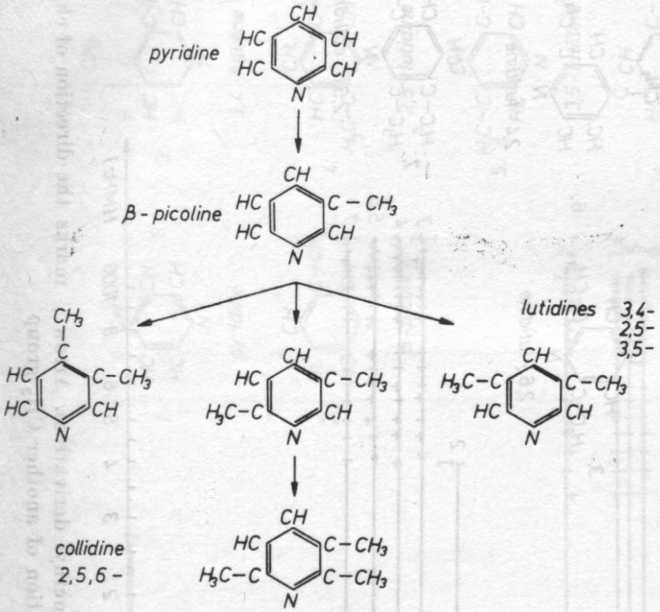
Substance	C_i $\left[\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}\right]$	$A = \left(\frac{\alpha}{f^2}\right)_{exp} - \left(\frac{\alpha}{f^2}\right)_{cl}$ $\left[\frac{\mathrm{s}^2}{\mathrm{m}}\cdot 10^{-15}\right]$	τ $[\mathrm{s}\cdot 10^{-11}]$	τ_{ak} $[\mathrm{s}\cdot 10^{-11}]$
Pyridine [10]	46.4	400.0	—	21.0
α-picoline	52.7	60.0	1.5	6.1
β-picoline	49.4	53.3	1.4	1.6
γ-picoline	44.8	54.0	1.6	1.6
2,4-lutidine	74.9	43.1	1.0	1.6
2,5-lutidine	59.4	34.6	0.8	1.6
2,6-lutidine	56.1	52.5	1.3	1.6
3,4-lutidine	68.6	40.6	1.0	1.6
3,5-lutidine	67.8	29.9	0.7	1.6
2,4,6-collidine	83.7	44.6	0.7	1.6
2,5,6-collidine	83.3	35.0	0.9	1.6

Table 10. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of pyridine



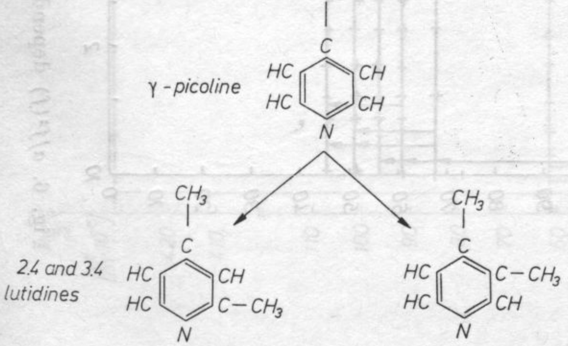
$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot10^{-15}\right]$	$\tau\,[s\cdot10^{-10}]$	$A\left[\frac{s^2}{m}\cdot10^{-15}\right]$
431	2.1	400
68.0	0.16	60
50.8	0.16	43
60.7	0.16	62
51.9	0.16	35
56.2	0.16	46
45.8	0.16	35

Table 11. Absorption coefficients and estimated acoustical Kneser relaxation times for methyl derivatives of pyridine



	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau\,[s\cdot 10^{-10}]$	$A\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
pyridine	431	2.1	400
β - picoline	61.4	$\tau \leqslant 0.16$	53
lutidines 3,4-	51.2	$\tau \leqslant 0.16$	41
2,5-	51.9	$\tau \leqslant 0.16$	35
3,5-	48.8	$\tau \leqslant 0.16$	30
collidine 2,5,6 -	45.8	$\tau \leqslant 0.16$	35

Table 12. Absorption coefficie nts and estimated acoustical Kneser relaxation times for methyl derivatives of pyridine



	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau\,[s\cdot 10^{-10}]$	$A\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
pyridine	431	2.1	400
γ - picoline	61.5	$\tau \leqslant 0.16$	54
2.4 and 3.4 lutidines	50.8	$\tau \leqslant 0.16$	43
	51.2	$\tau \leqslant 0.16$	41

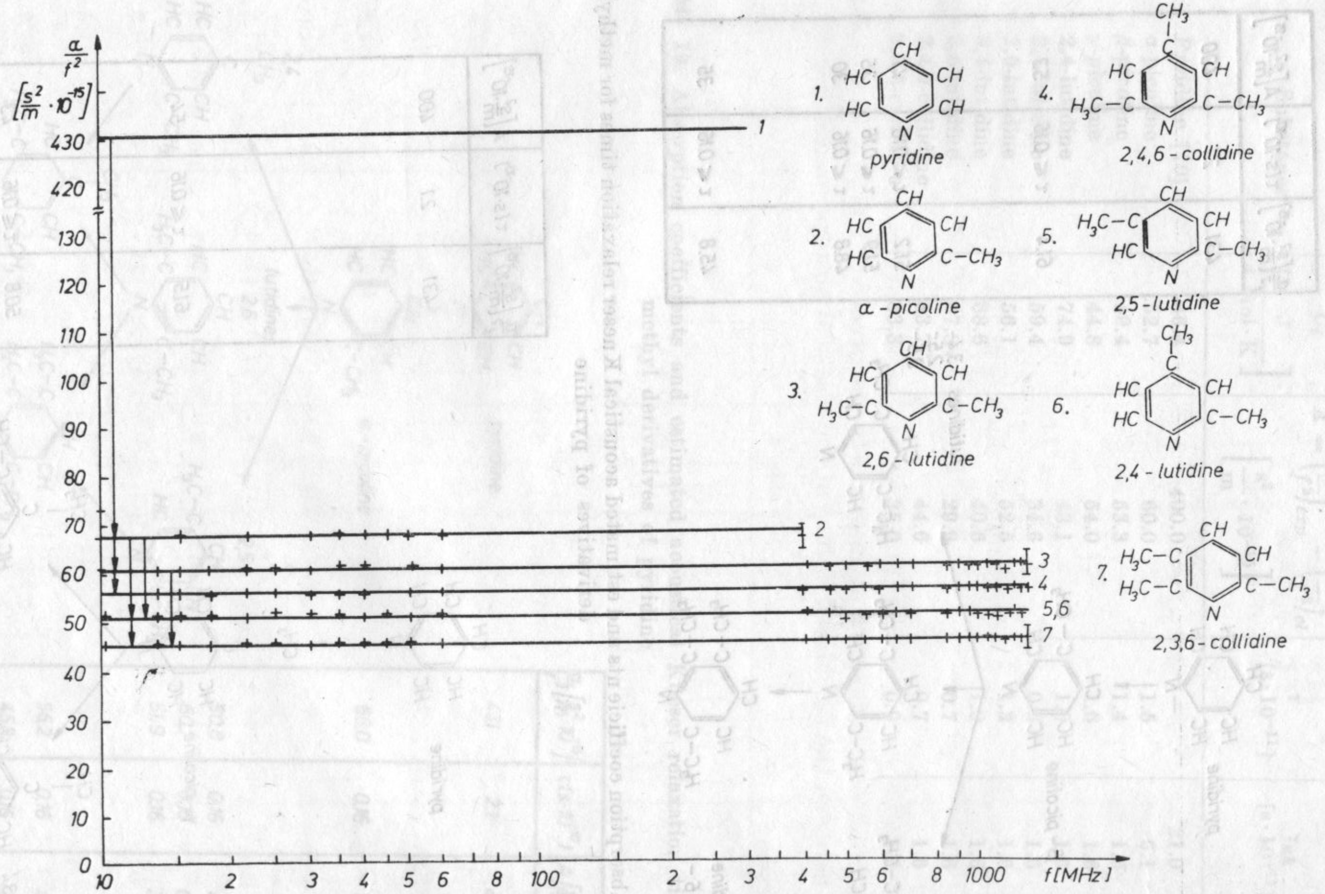


Fig. 6. $a/f^2(f)$ dependence for pyridine and pyridine methyl derivatives. Arrow ↓ marks the direction of changes of a/f^2 due to an addition of another CH_3 group

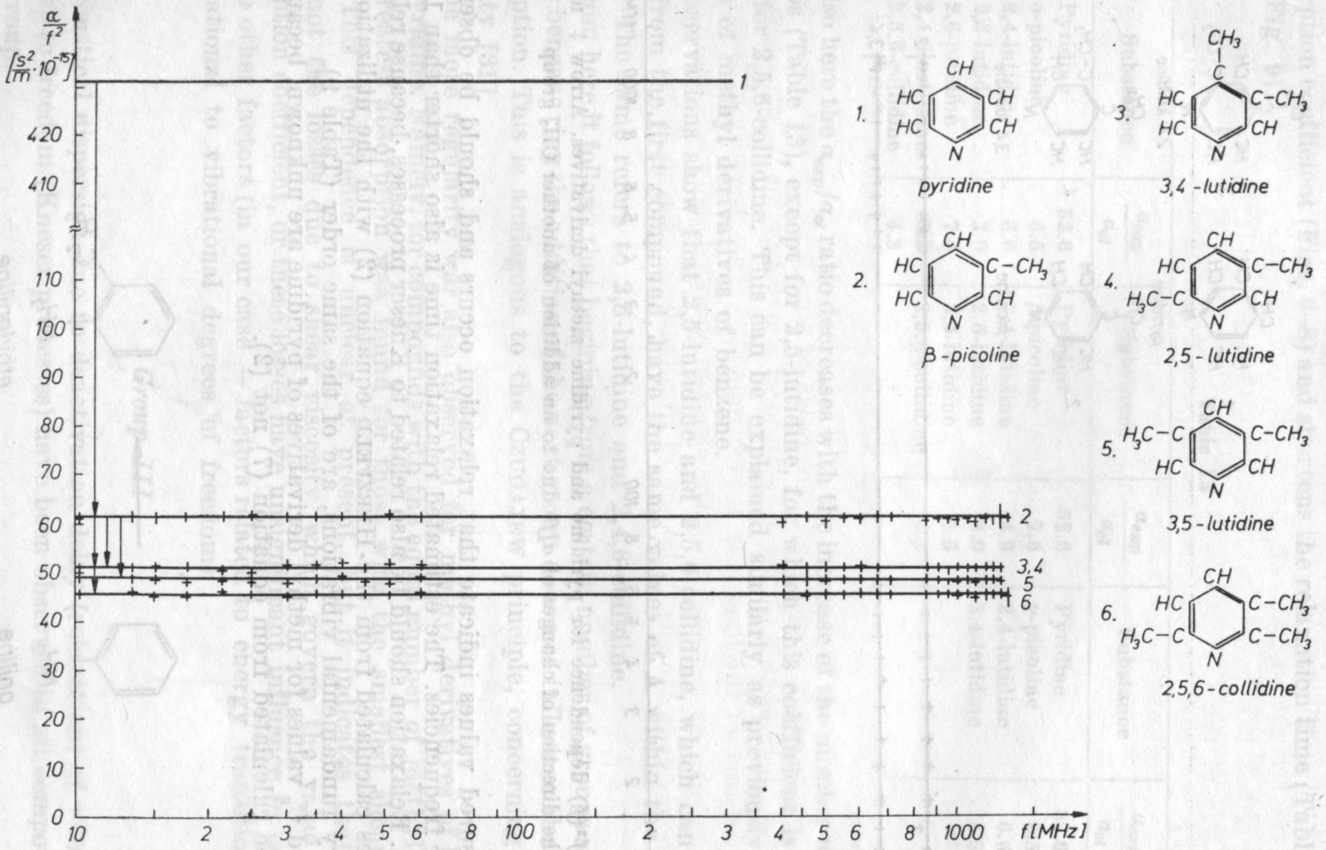


Fig. 7. $\alpha/f^2(f)$ dependence for pyridine and pyridine methyl derivatives. Arrow ↓ marks the direction of changes of α/f^2 due to an addition of another CH_3 group

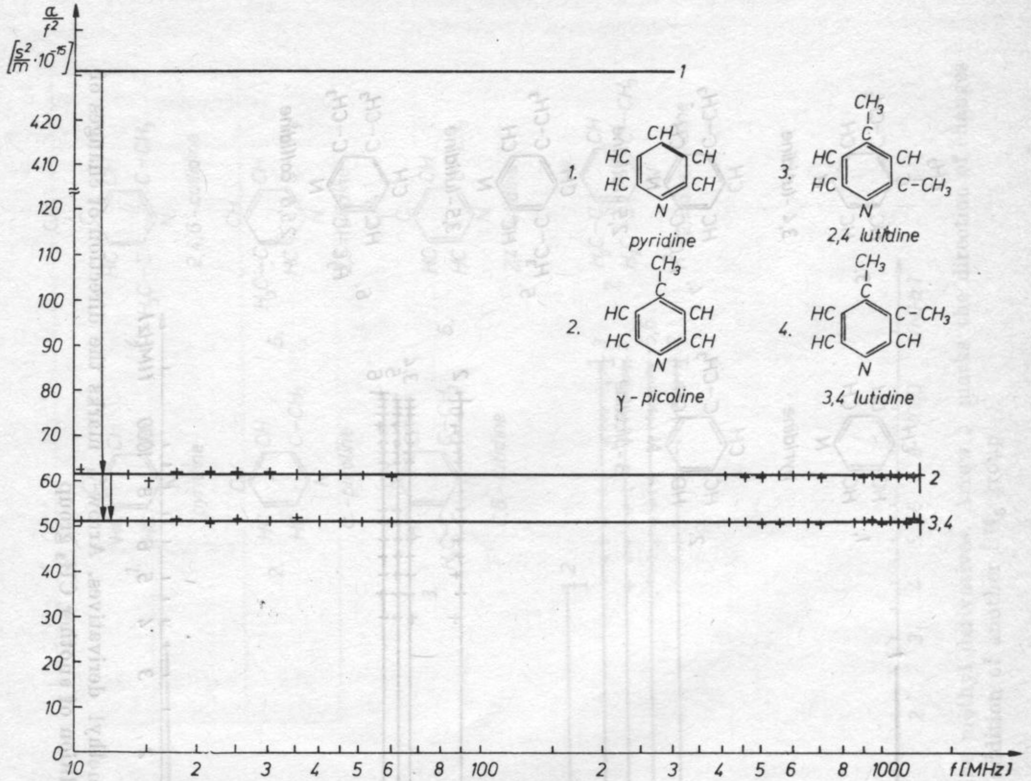


Fig. 8. $a/f^2(f)$ dependence for pyridine and pyridine methyl derivatives. Arrow ↓ marks the direction of changes of a/f^2 due to an addition of another CH_3 group

the measured values indicate that relaxation occurs and should be observed at higher frequencies. The estimated relaxation time is also shorter than $1.6 \times \times 10^{-11}$ s. Relaxation should be also related to Kneser processes, because relaxation times calculated from the HERZFELD equation (2) with the utilization of oscillatory fundamental vibrations, are of the same order (Table 9).

C_p and C_v values for methyl derivatives of pyridine are unknown, because τ had to be calculated from equation (7) not (2).

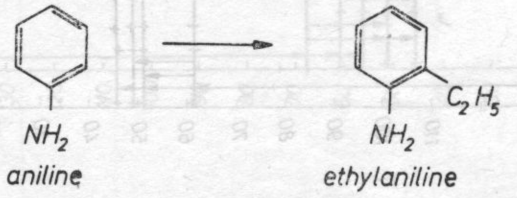


Fig. 9

Liquids belonging to this group exhibit similar dependences between acoustical quantities and the structure as liquids from the first group, namely: the addition of a methyl group causes a decrease of the value of the amplitude absorption coefficient (Figs. 6–8) and shortens the relaxation time (Tables 10–12 and Fig. 9).

Table 13

Substance	$\frac{a_{exp}}{a_{cl}}$	Substance	$\frac{a_{exp}}{a_{cl}}$	Substance	$\frac{a_{exp}}{a_{cl}}$
Pyridine	52.6	Pyridine	52.6	Pyridine	52.6
α-picoline	8.5	β-picoline	7.5	γ-picoline	8.5
2,4-lutidine	6.6	3,4-lutidine	4.9	2,4-lutidine	6.6
2,5-lutidine	3.0	2,5-lutidine	3.0	3,4-lutidine	4.9
2,6-lutidine	7.4	3,5-lutidine	2.6		
2,4,6-collidine	5.3	2,5,6-collidine	4.3		
2,5,6-collidine	4.3				

Also here the a_{exp}/a_{cl} ratio decreases with the increase of the number of methy groups (Table 13), except for 2,5-lutidine, for which this coefficient is smaller than for 2,5,6-collidine. This can be explained similarly as previously for the group of methyl derivatives of benzene.

Observations show that 2,5-lutidine and 2,5,6-collidine, which can be formed from the first compound, have the same values of A within the limit of error. The same refers to 2,3-lutidine and 2,4,6-collidine.

From here it follows that begining from a certain number of groups attached to the benzene ring the addition of the next group does not influence the $(a/f^2)_{rel}$ absorption. This is analogous to the CZUGAJEW principle, concerning optical activity [31].

One more regularity war also observed for methyl derivatives of benzene and pyridine. Namely, for compounds with the equal number of methyl groups the greatest absorption was found for those with the smallest shear viscosity. This dependence is unclear at present, but it indicates that either it is not the losses due to shear viscosity which govern the value of the absorption coefficient, or these losses have unsignificant influence in comparison to other factors (in our case — factors related to energy transition from translational to vibrational degrees of freedom).

Group III

Acoustical dispersion due to deactivation delay (relaxation) of vibrational degrees to freedom (Kneser processes) have been observed in all compounds in this group.

Only one compound, pyrimidine, has been investigated by the authors [30].

The comparison of compounds in this group leads to the following conclusions: an interchange of a carbon to a nitrogen decreases absorption and shortens the relaxation time. This may seem contradictory to what was said previously, that a steric hindrance in the ring, such as a CH_3 group, decreases damping and shortens the relaxation time; so the detachment of one hydrogen should cause a reverse effect. It appears that a lone pair of electrons from the nitrogen atom replaces one of the C-H bonds in benzene (Fig. 10).

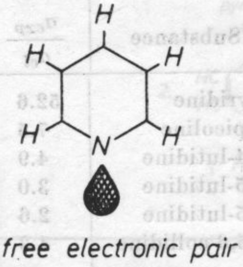


Fig. 10. Pyridine with a cloud from the lone pair of electrons from nitrogen

The fundamental property of molecules of this type — this pairs proton receptivity accompanied by the formation of a pyridine ion — gives evidence of the existance of the lone pair of electrons [32]. This was also confirmed by rentgenographic measurements of the electron charge density distribution [33], which clearly indicate the existance of "protruding" charge clouds (Fig. 11).

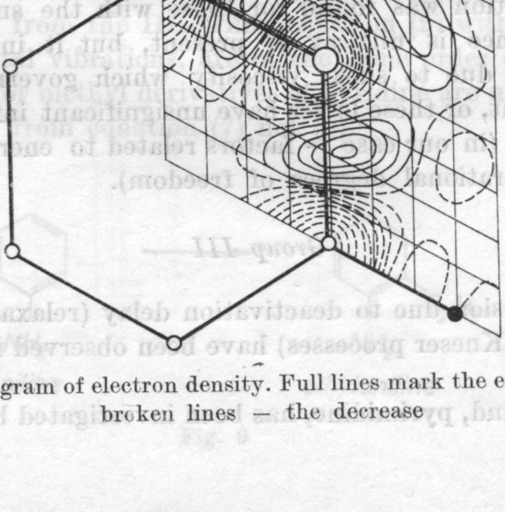


Fig. 11 Differential diagram of electron density. Full lines mark the electron density increase, broken lines — the decrease

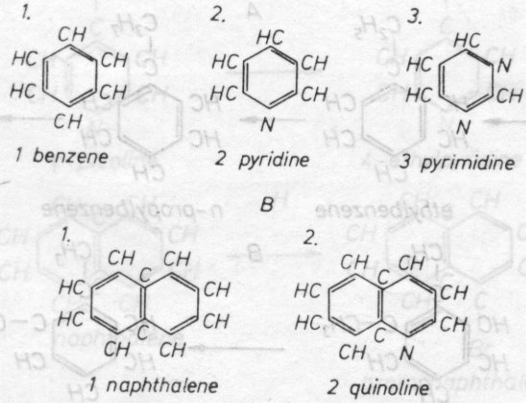
Such a steric hindrance is far smaller than the larger CH_3 group, so changes in absorption and the relaxation time should be smaller. This conclusion is confirmed by acoustical data obtained for the entire group of compounds (Table 14.) From benzene to toluene (group I) absorption decreases about ten times and, the relaxation time about six times, while in a series from benzene to pyridine the analogical quantities decrease two and less than two times, respectively.

The ratios of absorption and the relaxation time for naphthalene and quinoline are even smaller, because the influence of the cloud, which results from two lone electrons, is probably negligible in such large compounds.

Table 14

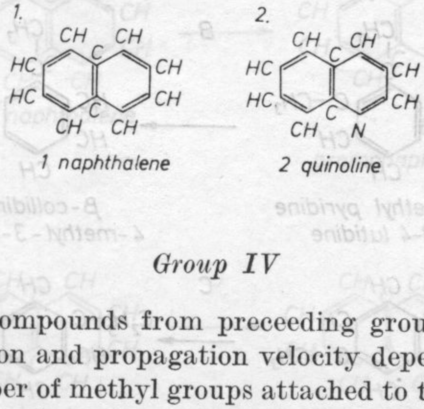
substance	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau_{ak}\,[s\cdot 10^{-11}]$	references
A1	860	2.8	21, 34, 35, 36, 37
A2	431	2.1	23, 34, 37, 38
A3	120	1.2	
B1	275	0.6	39
B2	163	0.3	14

A



1 benzene 2 pyridine 3 pyrimidine

B



1 naphthalene 2 quinoline

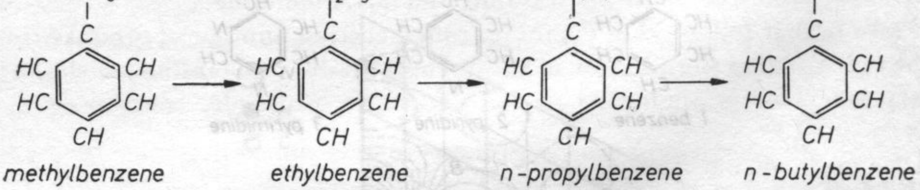
Group IV

Investigations of compounds from preceeding groups showed that values of acoustical attenuation and propagation velocity depend on the steric hindrance, i.e. on the number of methyl groups attached to the ring and on whether a methyl group or an electron cloud formed the hindrance. This indicated that the enlargement of a group attached to the ring should give similar effects.

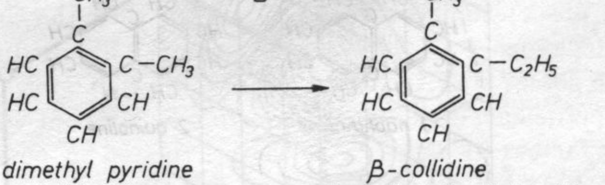
Table 15

Compound	$\left(\frac{\alpha}{f^2}\right)_{cl}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\varrho\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s[mP·s]	$c\left[\frac{m}{s}\right]$	$\frac{\alpha_{exp}}{\alpha_{cl}}$	$\left(\frac{\alpha}{f^2}\right)_{exp}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	References
A1						82	[40, 41] [42, 43]
A2						55	[44, 45]
A3						56	[45,50]
A4						55	[45]
B1	10.4	0.9625	1.248	1487.9	4.9	51.2	
B2		0.9	—	1486.1	—	42.3	
C1	17.3	0.9347	1.745	1415.0	3.0	51.2	
C2				1388.0		50.6	
D1					10.7	82.0	
D2				1593.4		40.5	
E1	8.0	0.9425	0.805	1410	8.5	68	
E2				1383.6		46.1	
F1					10.7	82	
F2				1486.2		31	
G1	7.2	0.9556	0.839	1474.0	8.5	61.5	
G2	8.6	0.936	0.91	1439.4	4.0	34.2	
H1 and I2						275	
H2	41.8	1.4839	6.2	1380.2	3.4	142.7	
I2	13.4	1.0123	1.8	1518.7	7.3	97.3	

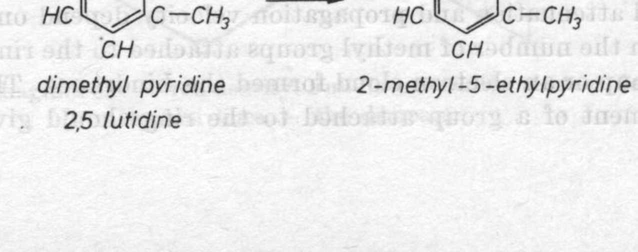
A



B



C



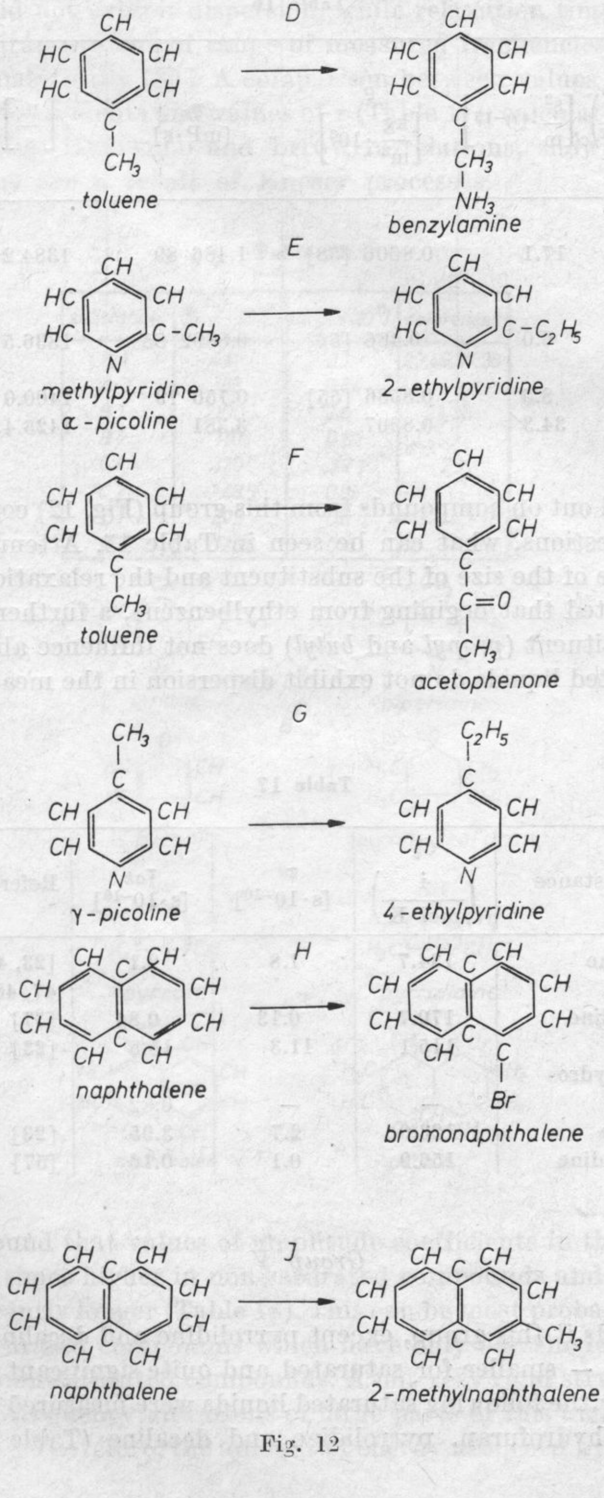

D
toluene
benzylamine
E
methylpyridine
α-picoline
2-ethylpyridine
F
toluene
acetophenone
G
γ-picoline
4-ethylpyridine
H
naphthalene
bromonaphthalene
J
naphthalene
2-methylnaphthalene

Fig. 12

Table 16

Compound	$\left(\frac{a}{f^2}\right)_{cl}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	ϱ $\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s [mP·s]	$c\left[\frac{m}{s}\right]$	$\frac{a_{exp}}{a_{cl}}$	$\left(\frac{a}{f^2}\right)_{exp}$ $\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
Piperidine $C_5H_{11}N$	17.1	0.8606 [58]	1.486 89	1384.2	5.0	78.4
Tetrahydrofuran C_4H_8O	6.0	0.486 [56]	0.8892 85	1336.5	18.3	99.1
Pyrrolidine C_4H_9N	8.5	0.8586 [55]	0.756 79	1400.0	5.2	43.5
Decaline	34.3	0.8967	3.381	1425.4	3.5	120.0

Research carried out on compounds from this group (Fig. 12) confirmed mentioned above suggestions, what can be seen in Table 15. Attenuation decreases with the increase of the size of the substituent and the relaxation time is shortened. It was stated that begining from ethylbenzene, a further increase of the size of the substituent (*propyl* and *butyl*) does not influence absorption.

All investigated liquids do not exhibit dispersion in the measured frequency range.

Table 17

Substance	C_i $\left(\frac{i}{mol\cdot K}\right)$	τ $[s\cdot 10^{-10}]$	τ_{ak} $[s\cdot 10^{-10}]$	References
Pyridine	134.7	1.8	2.1	[23, 46, 47, 48]
Piperidine	170.7	0.13	0.84	[57]
Furan	115.1	11.3	15.5	[23]
Tetrahydrofuran	–	–	0.82	
Pyrrole	123.0	2.7	3.95	[23]
Pyrrolidine	156.9	0.1	0.16	[57]

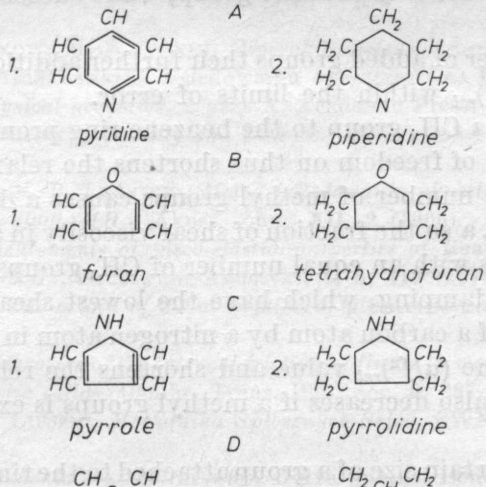
Group V

All compounds it this group, except pyrrolidine and decaline, exhibit acoustical dispersion – smaller for saturated and quite significant for unsaturated compounds. Only the following saturated liquids were measured by the authors: piperidine, tetrahydrofuran, pyrrolidine and decaline (Table 18).

Pyrrolidine did not exhibit dispersion, while relaxation times for piperidine and tetrahydrofuran are out of range of measured frequencies [30]. They can be determined analytically [30]. A comparison between values of τ_{ak} estimated from acoustic measurements and values of τ (Table 17), calculated from formula (6) with simplifying **Herzfeld** and **Litowitz** relations, shows that observed dispersion regions are a result of Kneser processes.

Table 18

substance	$\frac{\alpha}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\tau_{ak}[s\cdot 10^{-10}]$	references
A 1	431	2.1	23,46,37,38
A 2	85	0.84	
B 1	2100	12.6	23,38
B 2	110	0.82	
C 1	370	3.2	23
C 2	43.5	0.16	
D 1	275	0.6	14
D 2	120.5	0.16	



It was also found that values of amplitude coefficients in the low frequency range are many times higher in non-saturated compounds and their relaxation times are significantly longer (Table 18). This can be most probably explained by the fact that saturated compounds which have only one single bond are much more rigid than non-saturated compounds. A not very rigid structure of a molecule permits low frequency vibrations of large parts of this molecule in relation to each other [14]. Therefore, the amount of energy absorbed by such a molecule is smaller and given up to the surroundings more rapidly. This is also valid for compounds in which absorption is influenced by two factors: Kneser effects and rotary isomeric transition [15]. (In transitions from benzene to cyclohexane [23] and from naphthalene to decaline [39, 49], absorption and relaxation time values are significantly lower than in benzene and naphthalene, although in cyclohexane and decaline aside from Kneser absorption also absorption due to *cis-trans* isomeric transition occurs.)

Conclusions

Investigations performed on a series of cyclic compounds have led to the determination of certain dependences between the amplitude absorption coefficient, $(\alpha/f^2)_{rel}$, and the structure of the liquid, namely:

1. The addition of a CH_3 group to a benzene ring causes a decrease of the amplitude absorption coefficient. The value of $(\alpha/f^2)_{rel}$ decreases quite significantly with the addition of the first group, while succeeding additions cause smaller changes.
2. At a certain number of added groups their further addition does not influence the value of $(\alpha/f^2)_{rel}$ within the limits of error.
3. Every addition of a CH_3 group to the benzene ring promotes deactivation of oscillatory degrees of freedom on thus shortens the relaxation time.
4. An increase of the number of methyl groups causes a decrease of the value of the α_{exp}/α_{cl} ratio, a so the fraction of shear viscosity in absorption increases.
5. Among compounds with an equal number of CH_3 groups those are characterized by greatest damping, which have the lowest shear viscosity.
6. The replacement of a carbon atom by a nitrogen atom in a benzene ring causes a decrease of the $(\alpha/f^2)_{rel}$ value and shortens the relaxation time.
7. The $(\alpha/f^2)_{rel}$ value also decreases if a methyl groups is exchanged by a larger one.
8. After reaching a certain size of a group attached to the ring, a further increase of size does not influence the $(\alpha/f^2)_{rel}$ value.

Investigations performed with different compounds [51] also indicate strict relations between absorption and the structure of liquid molecules. Therefore, further research with a wide rang of compounds seems highly advisable.

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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 (^{0}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
$\alpha/f^2 \cdot 10^{15}$ (s^2/m)	19.15	28.04	73.89	82.62	64.66	47.50	20.02
$\Delta\nu_{MB} \cdot 10^3$ (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.

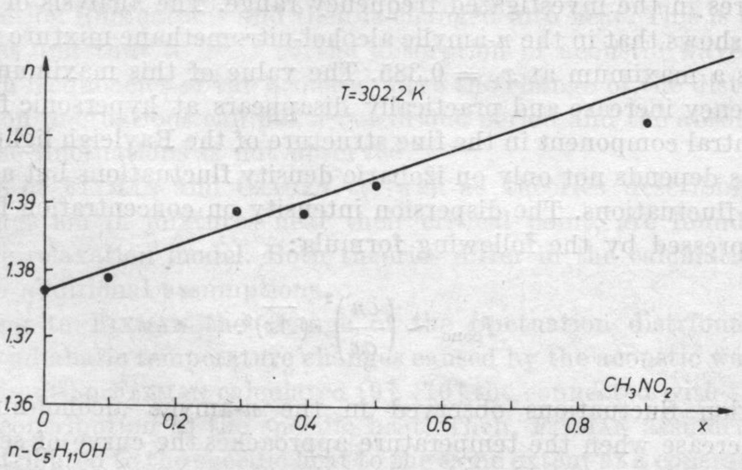

Fig. 1. Refractive index in terms of concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 29.2$°C

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:

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

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 $T = 29.2°C$.

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 mixwtures 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.

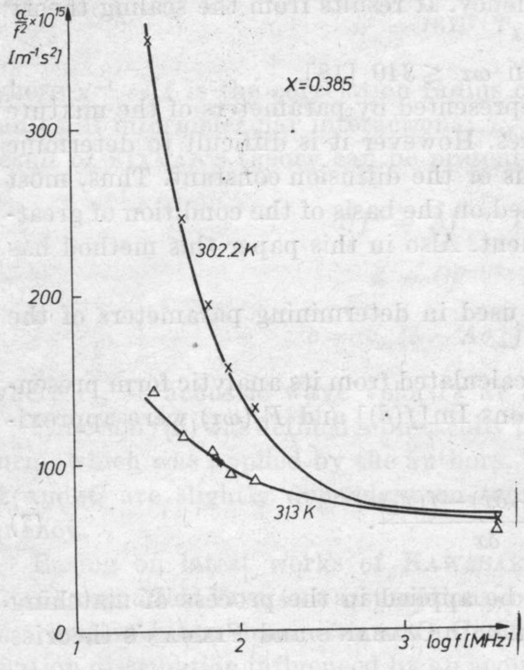

Fig. 2. α/f^2 versus $\log f$ in the n-amylic alcohol-nitromethane mixture with critical concentration $x = 0.385$ (x – molar fraction of n-amylic alcohol) at two temperatures. Full lines obtained from formulae (2) and (2a); ×, △ – experimental points

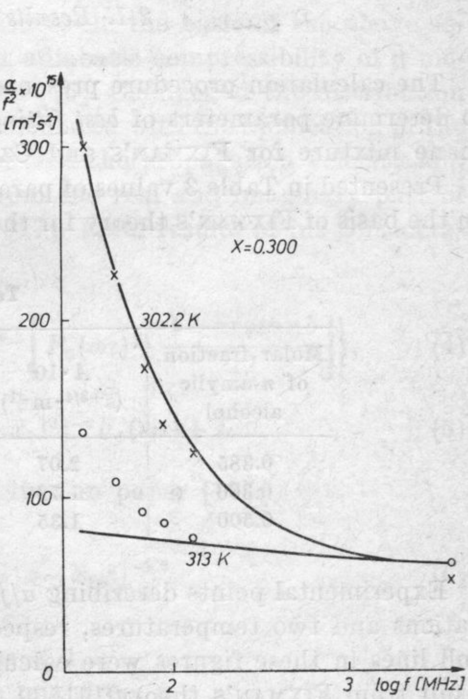

Fig. 3. α/f^2 versus $\log f$ in the n-amylic alcohol-nitromethane mixture with concentration $x = 0.300$ (x – molar fraction of n-amylic alcohol) at two temperatures. Full lines obtained from formulae (2) and (2a); ×, △ – experimental points

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

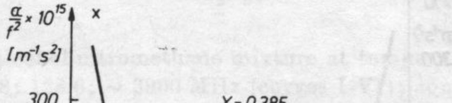

Fig. 5. α/f^2 versus $\log f$ in the n-amylic alcohol-nitromethane mixture with concentration $x = 0.385$ (x – molar fraction of n-amylic alcohol) at two temperatures. Full lines obtained from formulae (5) and (6); ×, ○ – experimental points

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 a/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

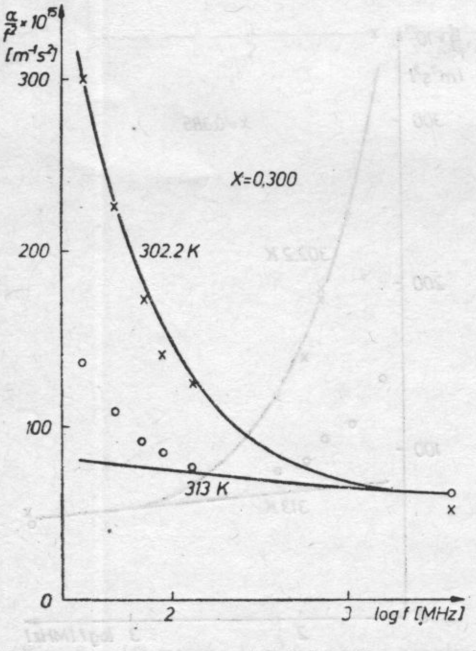

Fig. 6. a/f^2 versus $\log f$ in the *n*-amylic alcohol-nitromethane mixture with concentration $x = 0.300$ (x — molar fraction of *n*-amylic alcohol) at two temperatures. Full lines obtained from formulae (5) and (6); ×, ○ — experimental points

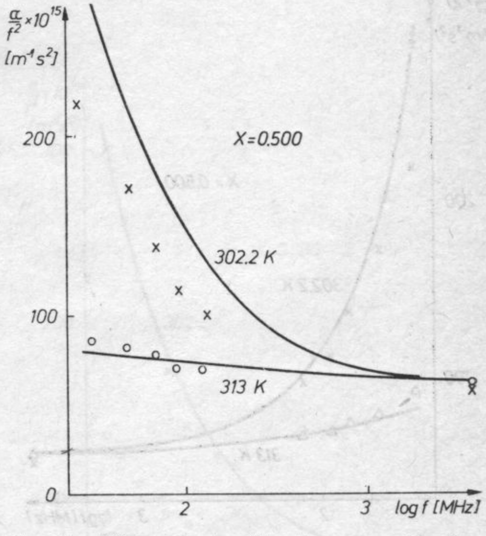

Fig 7. a/f^2 versus $\log f$ in the *n*-amylic alcohol-nitromethane mixture with concentration $x = 0.500$ (x — molar fraction of *n*-amylic alcohol) at two temperatures. Full lines obtained from formulae (5) and (6); ×, ○ — experimental points

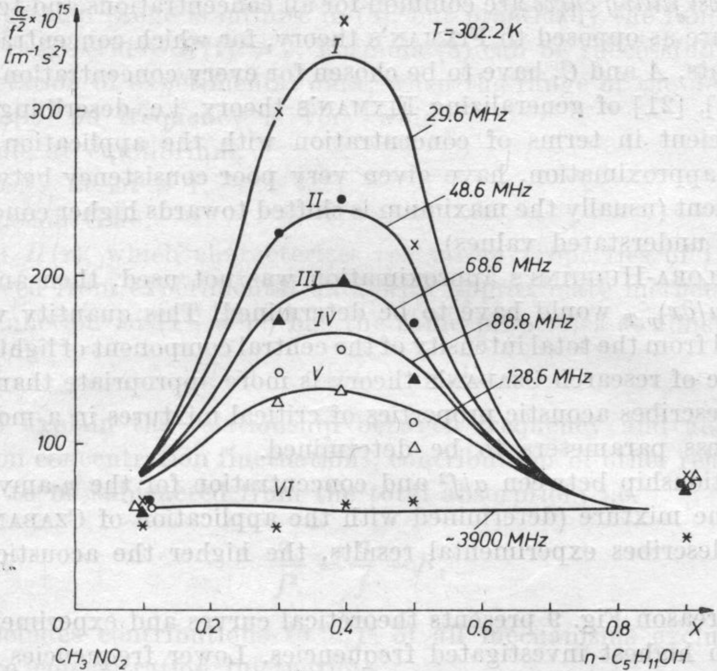

Fig. 8. α/f^2 versus concentration in the *n*-amylic alcohol-nitromethane mixture at temperature of 29.2°C for frequencies 29.6; 48.6; 68.6; 88.8; 128.6; ~ 3900 MHz (curves I-VI); concentration of components expressed in molecular fractions of *n*-amylic alcohol. Full lines obtained from formulae (5)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

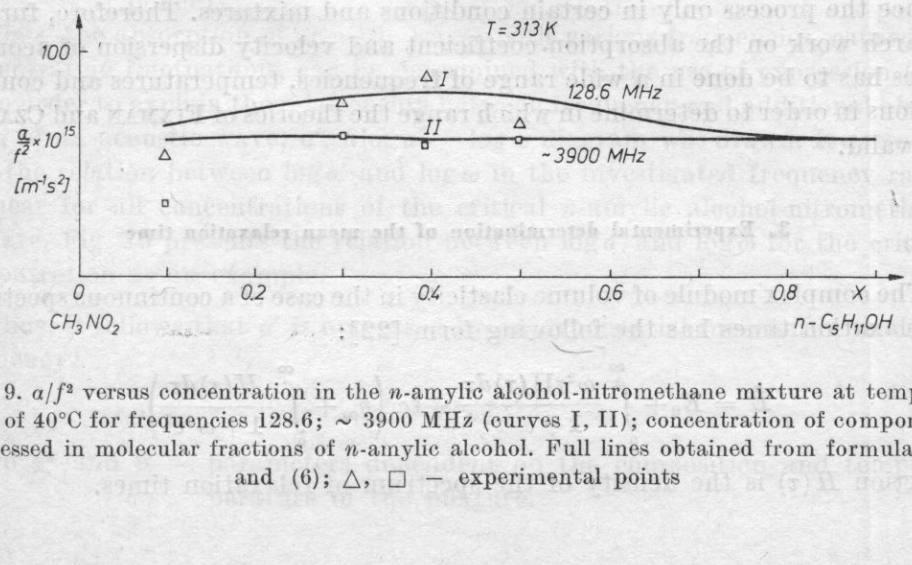

Fig. 9. α/f^2 versus concentration in the *n*-amylic alcohol-nitromethane mixture at temperature of 40°C for frequencies 128.6; ~ 3900 MHz (curves I, II); concentration of components expressed in molecular fractions of *n*-amylic alcohol. Full lines obtained from formulae (5) and (6); △, □ — experimental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

$$\tilde{E} = E_0 + \int_0^\infty \frac{\omega^2\tau \mathrm{H}(\tau)\,d\tau}{1+\omega^2\tau^2} + i\omega\left(\eta_\infty + \int_0^\infty \frac{H(\tau)\,d\tau}{1+\omega^2\tau^2}\right). \tag{8}$$

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.

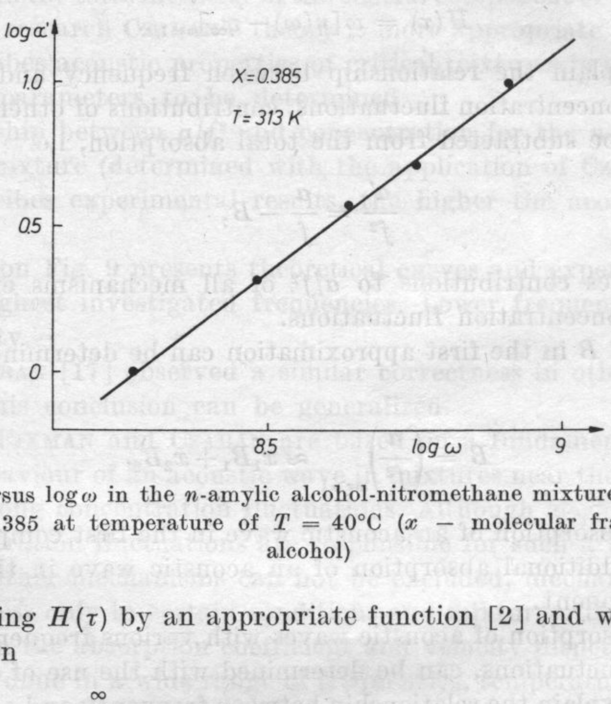

Fig. 10. $\log\alpha'$ versus $\log\omega$ in the n-amylic alcohol-nitromethane mixture with critical concentration $x = 0.385$ at temperature of $T = 40°\mathrm{C}$ (x − molecular fraction of n-amylic alcohol)

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	$1.34\cdot 10^{-9}$

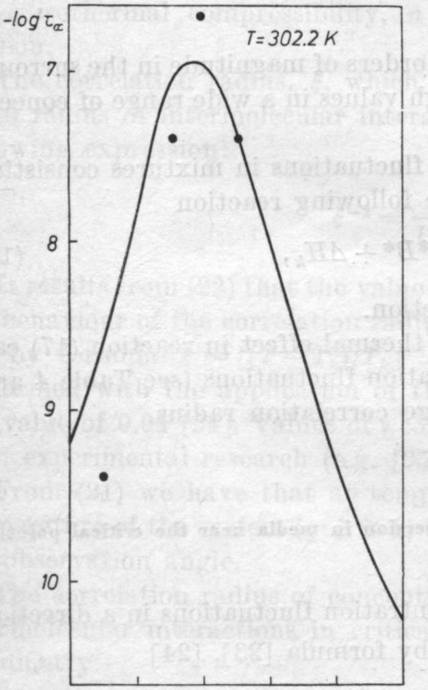

Fig. 11. $\log \tau_a$ versus concentration in the n-amylic alcohol-nitromethane mixture at temperature of $T = 29.2$°C. Full line obtained from formula (16); ● — experimental points

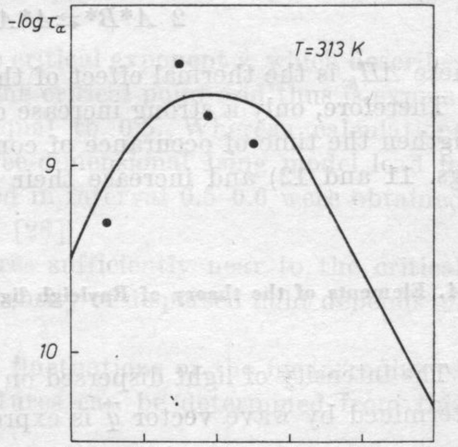

Fig. 12. $\log \tau_a$ versus concentration in the n-amylic alcohol-nitromethane mixture at temperature of $T = 40$°C. Full line obtained from formula (16); ● — experimental points

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
$\overline{x}_k = 0.385$ 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]

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

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.

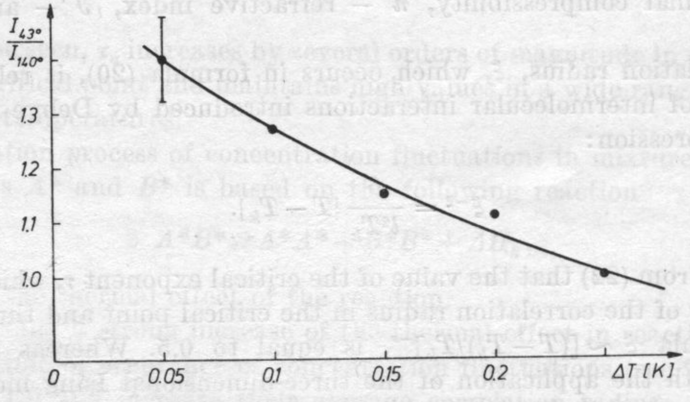

Fig. 13. Coefficient of light dispersion asymmetry versus temperature difference ($\Delta T = T - T_k$) in the *n*-amylic alcohol-nitromethane mixture with critical concentration $x = 0.385$

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].

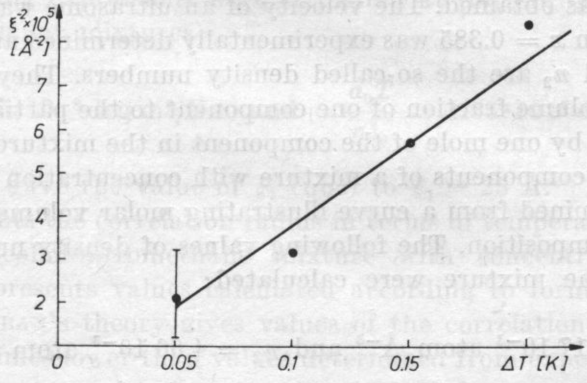

Fig. 14. ξ^{-2} versus ΔT for the n-amylic alcohol-nitromethane mixture with critical concentration $x = 0.385$. Slope of the straight line equals 0.0004 Å^{-2} deg^{-1}

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

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

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

$$M = \frac{1.44 \cdot k_B \varrho c_0 \tau_1}{4 \cdot \pi^2 \xi_1^2} \left(-\frac{\partial T_k}{\partial p} + \frac{T \alpha_0}{\varrho c_p} \right)^2$$

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)

$$\frac{\partial T_k}{\partial p} = 5\cdot 10^{-8}\,\mathrm{deg\,m^2/N}\quad \text{and}\quad \frac{\alpha_0 T}{\varrho c_p} = 1.55\cdot 10^{-7}\,\mathrm{deg\,m^2/N}.$$

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

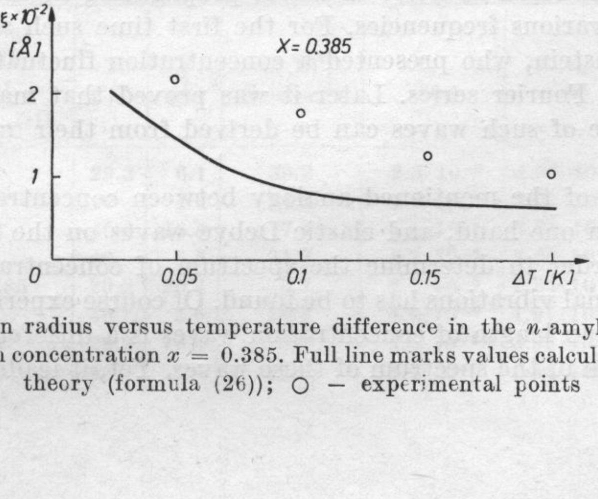

Fig. 15. Correlation radius versus temperature difference in the n-amylic alcohol-nitromethane mixture with concentration $x = 0.385$. Full line marks values calculated from CZABAN'S theory (formula (26)); ○ – experimental points

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 ($\Delta T = 0.05°C$). 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).

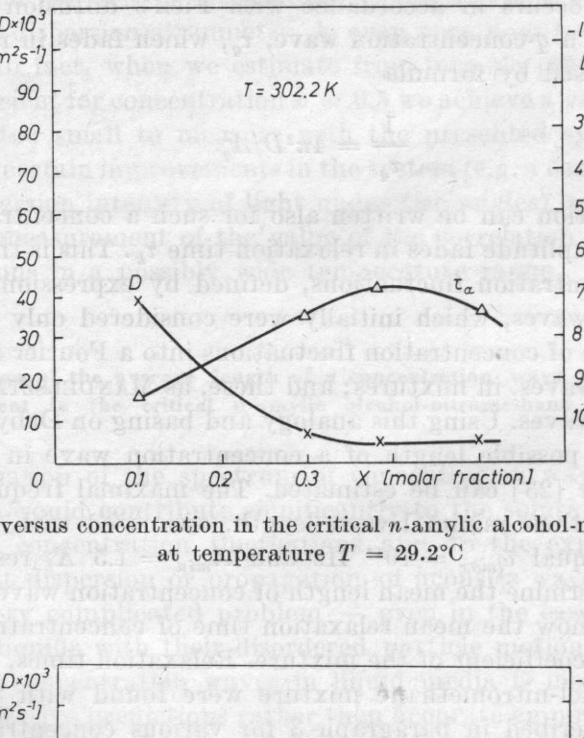

Fig. 16. D and τ_α versus concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 29.2$°C

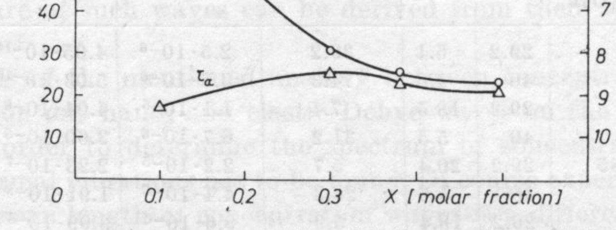

Fig. 17. D and τ_α versus concentration in the critical n-amylic alcohol-nitromethane mixture at temperature $T = 40$°C

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.

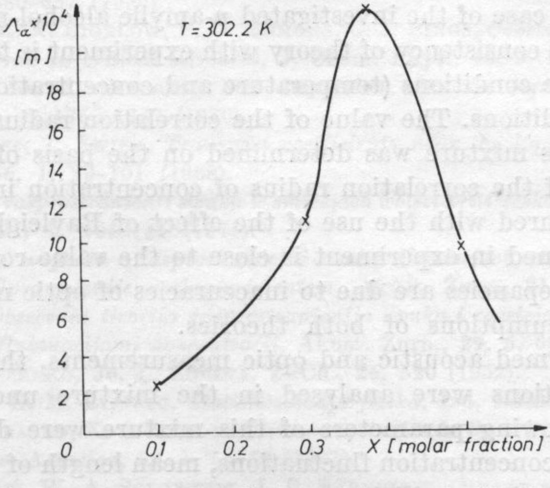

Fig. 18. Mean length of concentration waves in terms of concentration in the critical n-amylic alcohol-nitromethane mixture at temperature of $T = 29.2°C$

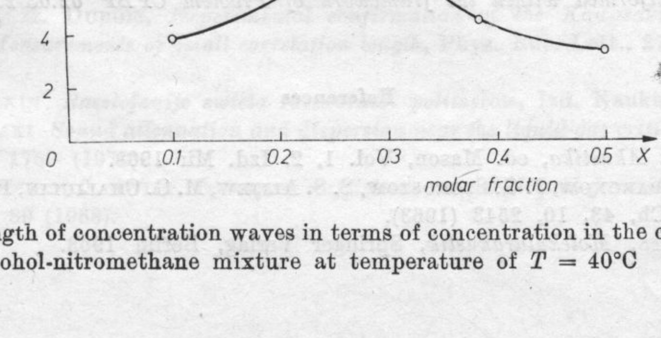

Fig. 19. Mean length of concentration waves in terms of concentration in the critical n-amylic alcohol-nitromethane mixture at temperature of $T = 40°C$

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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CHRONICLE

3-rd SPRING SCHOOL ON ACOUSTO-OPTICS AND APPLICATIONS

Gdańsk — Wieżyca, May 29-31, 1986

The 3-rd School on Acousto-optics and Applications like the two previous ones (in 1980 — Arch. Acoust. 6 (1981) 85–86 and in 1983 — Arch. Acoust. 9 (1984) 382–382) took place at Wieżyca near Gdańsk in the recreation centre of the Gdynia Shipyard. The School was organized by the Institute of Experimental Physics, University of Gdańsk in cooperation with the Section of Quantum and Molecular Acoustics of the Polish Acoustical Society and with support by the Institute of Fundamental Technological Research, Polish Academy of Sciences.

The Scientific Committee of the School included Prof. Dr. I. Malecki — the Member of the Polish Academy of Sciences; Prof. Dr. A. Opilski Silesian Technical University Gliwice; Prof. Dr. K. Patorski Technical University, Warszawa; Prof. Dr. J. Ranachowski, Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw.

The Organizing Committee included Prof. Dr. A. Śliwiński, Chairman; Dr. A. Markiewicz, Secretary; Dr. I. Wojciechowska, Deputy Secretary; and Drs M. Borysewicz, M. Kosmol, P. Kwiek, B. Linde as members.

In the working international meeting specialists of few domains covering physical, technical and technological aspects of acousto-optics took part. There were 55 participants among them 10 from abroad. 8 invited lectures and 19 original papers were red. Also, 2 round table discussion were organized. The meeting was valuable and the programme was rich, although it was a bit reduced comparing to the planed one (34 presentations) because 7 guests from abroad recalled their participation at the last moment.

The realized programme of the School was following:

Invited lectures:

1. W. G. Mayer T. H. Neighbors (Georgetown University, USA), *Acousto-optic interactions produced by pulsed ultrasound.*
2. P. Kwiek (University of Gdańsk, Poland), *Light diffraction on two spatially separated ultrasonic waves.*
3. D. A. Hutchins, K. Londgren (Queen's University, Kingston, Canada), *Optical penetration and detection of ultrasonic pulses in solids.*
4. W. H. Jones (Technical University of Nova Scotia, Halifax, Canada), *Reconstruction of phase and amplitude tomograms in media with significant acoustic refraction.*
5. R. Reibold (Physikalisch — Technische Bundesanstalt, Braunschweig, FRG), *Light diffraction tomography, a powerful tool for ultrasonic field investigations.*
6. J. Sapriel (Centre National d'Etudes de Telecommunications, France), *Acoustic and acousto-optic properties of layered media and superlattice.*
7. A. Śliwiński (University of Gdańsk, Gdańsk, Poland), *Light and ultrasonic interaction in optically and acoustically active media.*
8. J. Motylewski, J. Ranachowski (Institute of Fundamental Technological Research

of Polish Academy of Sciences), M. Rzeszotarska (Technical University of Warsaw), Warsaw, Poland, *Photoacoustic cells for gases liquids investigations.*

Oral papers and communications:

1. L. Jakab, P. Richter (Technical University of Budapest, Hungary), *Spectrum analyzer with acousto-optic Bragg cell.*
2. A. Markiewicz (University of Gdańsk, Gdańsk, Poland), *Some numerical results for light-diffraction on ultrasonic pulses.*
3. J. Kozłowski (Technical University of Warsaw, Poland), *Experimental investigations of TeO_2 acousto-optic filter at $0.6-0.9$ μm spectral range.*
4. B. Hałaciński, A. Latuszek (Technical University of Warsaw, Poland), *Acousto-optical method of velocity measurements by means of convergent SAWs on arbitrary surfaces of solids in reflected light.*
5. J. Kozłowski, A. Latuszek (Technical University of Warsaw, Poland), *Investigation of the bulk waves produced by means of the interdigital transducer immersed in liquid.*
6. M. Baszun, A. Milewski, J. Samuła (Technical University of Warsaw, Poland) *Photoacoustically controlled variable SAW phase shifter.*
7. R. Bukowski (Silesian Technical University, Gliwice, Poland), *Non-stationary stimulated acousto-optical interaction in solid dielectrics.*
8. Z. Chojnacki, E. Kotlicka, A. Domański (Technical University of Warsaw, Poland), *Three-positional acoustooptic switch on SAW in $LiNbO_3$.*
9. Z. Niechoda (Technical University of Warsaw, Poland), *Thermal phenomena in acousto-optic devices.*
10. J. Zieniuk (Institute of Fundamental Technological Research of Polish Academy of Sciences, Warsaw, Poland), *An acoustical optics of the ultrasonic microscope.*
11. J. Litniewski (Institute of Fundamental Technological Research of Polish Academy of Sciences, Warsaw, Poland), *The quality of images and measurements obtained with acoustic microscope.*
12. H. J. Hein, F. Tischka, R. Millner (Martin Luther University, Halle, NRD), *Remarks on the receive operating characteristics of medical diagnostic system — some results of B-scan visual system.*
13. E. Soczkiewicz (Silesian Technical University, Gliwice, Poland), *Calculation of ultrasonic waves scattering in the region of the critical mixing point of binary liquids.*

Poster form papers:

1. I. B. Esipov (Institute of Radiophysics and Radioelectronics A.N. USSR, Moskwa), *Effects of acousto-optics interaction on a rough surface.*
2. A. Opilski, Z. Opilski, R. Rogoziński (Silesian Technical University, Gliwice, Poland), *Technology of producing gradient lenses for acousto-optics.*
3. J. Berdowski (Silesian Technical University, Gliwice, Poland), *The influence of geometry interaction on the light diffraction by SAW in the crystals ADP type.*
4. J. Szurkowski (Technical University of Poznań, Poland) and A. Tessier, R. M. Leblanc (Université de Québec, Troisvivier, Canada) *Mirage effect.*
5. M. Sowiński, T. Jabłoński (Institute of Fundamental Technological Research of Polish Academy of Sciences, Warsaw, Poland), *Propagation analysis of doublecore optical fibers.*
6. J. Jabłoński (Institute of Fundamental Technological Research of Polish Academy of Sciences, Warsaw, Poland), *Computation of fundamental modes in fibers with cross sectional shape.*

Round table discussions:

1. *Light and ultrasonic pulses interaction.*
2. *Possibilities of acousto-optics in material examination.*

The sessions involved numerous debates, in addition the two programmatic round table discussions above mentioned.

The discussion on light and ultrasonic pulses interaction indicated that the subject has come at the top not only in acousto-optics but in many other domains of physics and technology where the diffraction problems in a case of non-stationary processes are not common ones. Mutual relations between the Fourier spectrum (in the frequency domain) and trancients, mainly in the near field of ultrasonic transducers, the analysis of pulses in the time domain, the distribution of amplitudes and phases of non-stationary processes those are only some of the problems brought up in the discussion. The moderator of the discussion was Professor W. G. Mayer (Georgetown University, USA) and following persons participated: D. A. Hutchins (Queen's University, Canada), L. Jakab (Technical University of Budapest, Hungary), T. Jabłoński (Institute of Fundamental Technological Research Polish Academy of Sciences, Warsaw), E. Kozaczka (Navy High School, Gdynia), H. Lasota (Technical University, Gdańsk), A. Markiewicz (University of Gdańsk), R. Reibold (Phys. Techn. Bundesanstalt, Braunschweig, Germany), A. Śliwiński (University of Gdańsk), P. Voss (University of Kopenhagen, Denmark).

The discussion on the possibilities of applying acousto-optics in material examination was moderated by Professor H. G. Jones (Technical University, Halifax, Canada). In the discussion participated: R. Bukowski (Silesian Technical University, Gliwice), A. Gierus and A. Sokolovskij (Institute of Radiophysics and Radioelectronics of USSR Academy of Sciences Moskva), L. Jakab (Technical University of Budapest, Hungary), E. Kotlicka and A. Latuszek (Technical University of Warsaw), J. Kozłowski (Technical University of Warsaw), A. Markiewicz (University of Gdańsk), W. G. Mayer (Georgetown University, USA), J. Motylewski (Inst. of Fundamental Technological Research PAN, Warsaw), Z. Niechoda (Technical University, Warsaw), J. Sapriel (CNET, Paris France), A. Śliwiński and I. Wojciechowska (University of Gdańsk). Deliberations took place on what the acousto-optics does present itself and what it should be; what is its scientifical future as a separate domain and which are will be its applications.

The matters of using acousto-optical methods for velocity and attenuation of ultra- and hipersound waves measurements, determination of elastic constants (in linear as well as in nonlinear cases) of light transparent media were widely discussed. Acoustooptical properties of crystals and ceramic materials are important for their application in integrated optical systems, in fibreoptics and optoelectronics. The acousto-optical interaction of elastic waves of all types are utilized, particularly the surface waves.

It was stated, that the 3-rd School, similarly as the previous ones included photoacoustic topics into the programme. Although it involves problems of inverse phenomena towards acousto-optic ones, so, however there takes place interaction between the same kinds of waves. Particularly, in material examinations the methods based on photoacoustic phenomena are very useful and they fastly develope. Attention was paid for applying optical holography for detection and measuring of vibrations and ultrasonic fields as processes in real time and averaged ones. Perspectives of construction of acousto-optical deflectors, modulators and filters were discussed, too.

In opinion of the participants the meeting was useful and fruitful.

The organizers provided opportunity for the excursion to visit Three-town, particularly monuments in Gdańsk.

The Proceedings of the 3-rd School will be published in a compact form at the end of 1986.

The next 4-th Spring School on Acousto-optics and Applications was proposed to be organized in May 1989.

A. Śliwiński

ANNOUNCEMENT

Istituto di Acustica ,,O. M. Corbino", 50th anniversary celebration, Rome, Italy, 28–30 april 1987.

The "Istituto di Acustica O. M. Corbino" of the Italian National Research Council will celebrate its Fiftieth Anniversary of activity with a 3 days meeting (28–30 april 1987) in Rome, Italy. Several invited speakers will review the state of the art and future trends of different topics in Acoustics. A tentative list of subjects includes Ultrasonics, Quantum Acoustics, Noise, Architectural Acoustics, Acoustic Signal Processing Speech and Transduction. A Symposium on the work of O. M. Corbino founder of the Institute, will be organized on the first day jointly with the Department of Physics of the University of Roma. For further information please contact Dr. P. E. Giua, Director, Istituto di Acustica Via Cassia 1216 00189 Roma, Italy; tel. +6 – 3765757 –

P. E. Giua