

**ULTRASONIC INVESTIGATIONS OF 2-ETHYLHEXADIOLE-1.3. IN THE
REGION OF VISCOELASTIC RELAXATION****MAREK WACIŃSKI**Institute of Chemistry, Silesian University
(40-006 Katowice, ul. Szkolna 6)**RYSZARD PŁOWIEC**Institute of Fundamental Technological Research, Polish Academy of Sciences
(00-049 Warsaw, ul. Świętokrzyska 21)

This paper gives the results of measurements of mechanical shear impedance in 2-ethylhexadiol-1.3., at frequencies of 0.520, 29.9 and 500 MHz. Measurements carried out with transverse waves in the region of viscoelastic relaxation permitted the determination of viscoelastic relaxation times and the characteristic constant quantities such as the modulus of elasticity, mechanical compliance and dynamic viscosity.

1. Introduction

The interest in shear transverse waves results from the fact that they can be used to measure the dynamic properties of a fluid, and thus to investigate the nature and character of the processes of change in the molecular structure.

The developments in the phenomenological theory of viscoelasticity have been inspired by investigations of the properties of construction materials and problems of elastohydrodynamic lubrication. The classical investigations of TOBOLSKY *et al.* [1, 2] and a number of other authors have shown that the viscoelastic behaviour of an elastomer undergoing rapidly changing shear deformations is related to the chemical degradation of long molecular chains with covalent bonds. They have thus pointed out the "chemical" aspect of viscoelasticity which results from the relationship between a macroscopic

deformation and the molecular structure and molecular displacements in the medium being deformed.

The further developments in the theory of viscoelasticity were instigated by the interest in problems related to elasto-hydrodynamic lubrication, e.g. in the investigations of BARLOW, LAMB *et al.* [3, 4]. The non-Newtonian behaviour of fluids under such conditions is related to the translational and configurational molecular processes.

The chemical aspect of viscoelasticity of fluids was given attention by the investigations of LITOVITZ, HERZFELD, DAVIES *et al.* [5, 6].

In the present investigations, measurements of the mechanical impedance of shear waves were carried out over a large frequency and temperature range. The use of suitably high frequencies permitted not only the relaxation range in a given fluid but also its limiting shear elasticity to be determined.

2. Theoretical analysis

According to the theory of linear viscoelasticity, the following generally known relations occur [4, 5, 7],

$$G = G_{\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + iG_{\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2} = G' + iG''$$

$$= G_{\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + i\omega \frac{\eta}{1 + \omega^2 \tau^2} = G_{\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + i\omega \eta(\omega), \quad (1)$$

where G' is a dynamic modulus of elasticity, G'' is a dynamic modulus of viscosity, G_{∞} is the limiting modulus of shear elasticity, $\eta(\omega)$ is dynamic viscosity, τ is the relaxation time and ω is the angular frequency.

In view of the large attenuation of the transverse wave and the impossibility of measuring the attenuation and velocity over a given path, as in the case of the longitudinal wave, the complex mechanical shear impedance Z (i.e. the ratio of the strain (σ) to the displacement velocity ($\partial u / \partial t$)) must first be measured,

$$Z = - \frac{\sigma}{\left(\frac{\partial u}{\partial t} \right)} = R + iX, \quad (2)$$

where σ is the shear strain, R and X are mechanical resistance and shear reactance.

The relationship between G and Z can readily be found, since

$$Z = (\rho G)^{1/2}, \quad (3)$$

$$Z = (\rho / J)^{1/2}. \quad (4)$$

hence

$$G' = \frac{R^2 - X^2}{\rho}, \quad (5)$$

$$G'' = \frac{2RX}{\rho}, \quad (6)$$

$$J' = \frac{\rho(R^2 - X^2)}{(R^2 + X^2)^2}, \quad (7)$$

$$J'' = \frac{2\rho RX}{(R^2 + X^2)^2}. \quad (8)$$

It follows that the experimental determination of the two components of any of the complex functions given above (impedance Z , modulus G , compliance J) permits the calculation of the other two quantities, irrespective of the molecular base, i.e. of what molecular processes determine the macroscopic behaviour of the body. From the form of the relations of $G'(\omega)$, $G''(\omega)$ and $\eta(\omega) = G''(\omega)/\eta_s$, where η_s is stationary viscosity and $\tau = \eta_s/G_\infty$,

$$G' = G_\infty \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}, \quad (9)$$

$$G'' = G_\infty \frac{\omega \tau}{1 + \omega^2 \tau^2}, \quad (10)$$

$$\eta(\omega) = \frac{G_\infty \tau}{1 + \omega^2 \tau^2} = \frac{\eta_s}{1 + \omega^2 \tau^2}, \quad (11)$$

it follows that:

1. ω always occurs in the form of the product $\omega\tau$, and therefore it can be regarded as a function of the variable $x = \omega\tau$, provided it is normalised in the following way: G'/G_∞ , G''/G_∞ , $\eta(\omega)/\eta_s$;

2. when $\omega\tau \ll 0$, i.e. $\omega\tau \rightarrow 0$, the region is viscous, $\eta(\omega) = \eta_s$ and $G' = 0$;

3. when $\omega\tau \gg 0$, i.e. $\omega\tau \rightarrow \infty$, the region is elastic, $G' = G_\infty$;

4. when $\omega\tau = 1$, the region is viscoelastic, $G' = 0.5 G_\infty$, $G'' = 0.5 G_\infty$, i.e. $G' = G''$ and $\eta(\omega) = 0.5 \eta_s$;

5. $G'/G'' = \omega\tau$, since $\tan \delta = G''/G'$, $\tan \delta = 1/\omega\tau$;

6. G' , G'' and $\eta(\omega)$ are symmetrical with respect to the scale $\log \omega\tau$, τ has its time dimension and can therefore be regarded as the inverse of some frequency characteristic of the relaxation $\omega_{rel} = \tau^{-1}$. Hence, $\omega\tau = \omega/\omega_{rel}$ and the scale $\omega\tau = \omega/\omega_{rel}$ or $\log \omega\tau = \log \omega/\omega_{rel}$ can be regarded as the characteristic frequency scale of the relaxation (or simply the relaxation frequency ω_{rel}). At the same time, G' and G'' can also be normalized, by dividing these quantities

by G_∞ and $\eta(\omega)$ by η_s ,

$$\frac{\eta(\omega)}{\eta_s} = \frac{1}{1 + \omega^2\tau^2} \rightarrow 0 < \frac{\eta(\omega)}{\eta_s} \leq 1;$$

$$\frac{G'}{G_\infty} = \frac{\omega^2\tau^2}{1 + \omega^2\tau^2} \rightarrow 0 < \frac{G'}{G_\infty} \leq 1;$$

$$\frac{G''}{G_\infty} = \frac{\omega\tau}{1 + \omega^2\tau^2} \rightarrow 0 < \frac{G''}{G_\infty} \leq \frac{1}{2}.$$

The behaviour of the shear moduli in the relaxation region is usually represented in the form of such normalised diagrams (provided G_∞ and η_s can be measured), which has an enormous advantage: since $x = \omega\tau$, this parameter can be altered by changing the frequency (ω) or temperature ($\tau = \tau(t)$). This permits investigations of the relaxation region at different frequencies and temperatures. Instead of the shear moduli, the relaxation region can also be represented graphically using the directly measured shear resistances and shear reactances (R and X), most frequently in the form of normalised $R/(\rho G_\infty)^{1/2}$, $X/(\rho G_\infty)^{1/2}$. Solution of the previous equations, which relate the components of the modulus to the components of the impedance with respect to R and X , gives

$$R^2 = \rho \frac{G'}{2} \left\{ \left[1 + \left(\frac{G''}{G'} \right)^2 \right]^{1/2} + 1 \right\}; \quad (12)$$

$$\frac{R^2}{\rho G_\infty} = \frac{\omega^2\tau^2}{2(1 + \omega^2\tau^2)} \left[\left(1 + \frac{1}{\omega^2\tau^2} \right)^{1/2} + 1 \right]; \quad (13)$$

$$X^2 = \rho \frac{G''}{2} \left\{ \left[1 + \left(\frac{G''}{G'} \right)^2 \right]^{1/2} - 1 \right\}; \quad (14)$$

$$\frac{X^2}{\rho G_\infty} = \frac{\omega^2\tau^2}{2(1 + \omega^2\tau^2)} \left[\left(1 + \frac{1}{\omega^2\tau^2} \right)^{1/2} - 1 \right]. \quad (15)$$

Thus, the normalised resistances and reactances are only functions of $\omega\tau$ and give normalised curves on a half-logarithmic scale, on which points corresponding to the frequency and temperature of measurements arrange themselves.

Since a description of the behaviour of real fluids would, for a generalized Maxwell model, require an infinite number of elements, summation should be replaced by integration, giving a continuous spectrum of relaxation times,

$$G' = G_\infty \int_0^\infty \frac{g\left(\frac{\tau}{\tau_s}\right) \omega^2\tau^2}{1 + \omega^2\tau^2} \cdot d\left(\frac{\tau}{\tau_s}\right) = G_\infty \int_0^\infty \frac{g(x) \omega^2\tau_s'^2 x^2}{1 + \omega^2\tau_s'^2 x^2} dx; \quad (16)$$

$$G'' = G_\infty \int_0^\infty \frac{g\left(\frac{\tau}{\tau_s}\right) \omega \tau}{1 + \omega^2 \tau^2} \cdot d\left(\frac{\tau}{\tau_s}\right) = G_\infty \int_0^\infty \frac{g(x) \omega \tau_s' x}{1 + \omega^2 \tau_s'^2 x^2} dx, \tag{17}$$

where $g(\tau/\tau_s)$ is a function of the distribution of normalised relaxation times (i.e. referred to τ_s' , which is the main time of a given distribution), whereas $g(\tau/\tau_s) d(\tau/\tau_s)$ is the share in the limiting modulus G_∞ of those moduli whose relaxation time lies in the interval $\tau + d\tau$ and which are normalised over the interval $(\tau/\tau_s) + d(\tau/\tau_s)$. Similarly, the components of the impedance are represented in the normalised form:

$$\frac{R}{(\rho G_\infty)^{1/2}} \tag{18}$$

$$= \sqrt{\frac{1}{2} \int_0^\infty \frac{g(x) \omega^2 \tau_0^2 x^2}{1 + \omega^2 \tau_0^2 x^2} dx \left\{ 1 + \left[1 + \frac{\left(\int_0^\infty (g(x) x / (1 + \omega^2 \tau_0^2 x^2)) dx \right)^2}{\int_0^\infty \frac{g(x) \omega^2 \tau_0^2 x^2}{1 + \omega^2 \tau_0^2 x^2} dx} \right]^{1/2} \right\}^{1/2}};$$

$$\frac{X}{(\rho G_\infty)^{1/2}} \tag{19}$$

$$= \sqrt{\frac{1}{2} \int_0^\infty \frac{g(x) \omega^2 \tau_0^2 x^2}{1 + \omega^2 \tau_0^2 x^2} dx \left\{ \left[1 + \frac{\int_0^\infty (g(x) x / (1 + \omega^2 \tau_0^2 x^2)) dx}{\int_0^\infty (g(x) \omega^2 \tau_0^2 x^2 / (1 + \omega^2 \tau_0^2 x^2)) dx} \right]^{1/2} \right\}^{1/2}},$$

where $x = \tau_s/\tau_{s,0}$, $g(x) = (b/\eta^{1/2} x) \exp - [b \ln x]^2$, $0 < \tau_s < \infty$, b is a parameter which defines the width of the distribution of the relaxation times.

The viscoelastic properties of 2-ethylhexadiole are described by both the Maxwell model and by the *B-E-L* one [4]. In the Maxwell model with a Gaussian distribution of the relaxation times, the matching of the curve calculated from equation (18) to the experimental points requires that the theoretical coefficient $\exp - (-1/4b^2)$ should be replaced by an experimental one which relates the main time of the Gaussian distribution $\tau_{s,0}$ with the Maxwell relaxation time $\tau_s = \eta_s/G_\infty$, according to the equation $\tau_{s,0} = (\eta_s/G_\infty) a$ (a being some displacement with respect to the frequency axis). It can thus be seen that the Maxwell relaxation time is different from the mean time of the Gaussian distribution, in opposition to the theory (with the difference between these two times being about 10 per cent).

In order to make the interpretation of results independent from the arbitrarily assumed function of the distribution of the relaxation times and to achieve a more correct representation of the viscoelastic relaxation, the *B-E-L*

(BARLOW, ERGINSAY, LAMB) model of supercooled fluids was used to describe the relaxation curves.

The *B-E-L* model [4] is constructed of the parallel-linked acoustic impedances for a solid (Z_s) and a Newtonian fluid (Z_n),

$$\frac{1}{Z} = \frac{1}{Z_n} + \frac{1}{Z_s} \tag{20}$$

Transformation of this equation gives a formula for the shear compliance of the fluid, J , depending on the characteristic constants of the medium under study,

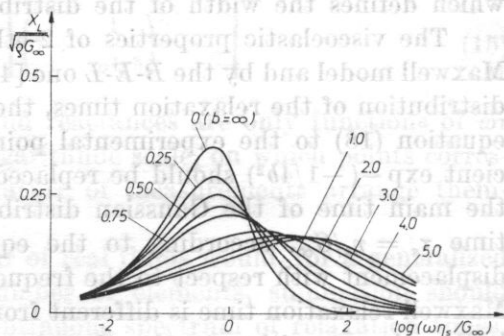
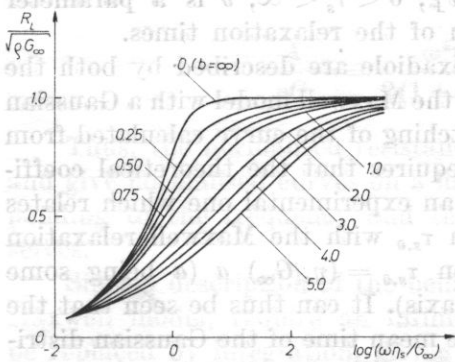
$$\frac{J}{G_\infty} = \frac{1}{G_\infty} + \frac{1}{j\omega\eta} + 2k \left(\frac{1}{j\omega G_\infty} \right)^\beta \tag{21}$$

The components of the acoustic shear impedance of the fluid, R and X , are, from formula (21),

$$\frac{R}{(\rho G_\infty)^{1/2}} = \frac{(\omega\eta/2G_\infty)^{1/2} [1 + (2\omega\eta/G_\infty)^{1/2}]}{[1 + (\omega\eta/2G_\infty)^{1/2}]^2 + \omega\eta/2G_\infty}; \tag{22}$$

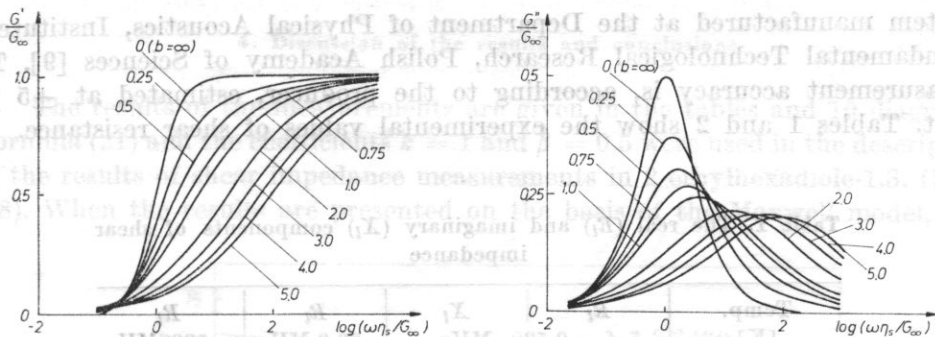
$$\frac{X}{(\rho G_\infty)^{1/2}} = \frac{(\omega\eta/2G_\infty)^{1/2}}{[1 + (\omega\eta/2G_\infty)^{1/2}]^2 + \omega\eta/2G_\infty} \tag{23}$$

In the case of simple fluids the measured results satisfy equation (21) for $k = 1$ and $\beta = 0.5$. In the case of complex fluids or their mixtures the formula is modified by the coefficients k and β . Figs. 1-4 give theoretical behaviours of the normalised shear moduli and impedance calculated for $\beta = 0.5$.



Figs. 1, 2. Theoretical behaviour of the normalised shear impedances $\frac{R}{(\rho G_\infty)^{1/2}}$ and

$\frac{X}{(\rho G_\infty)^{1/2}}$ as a function of $\log \omega\tau$



Figs. 3, 4. Theoretical behaviour of the normalised moduli G'/G_∞ , G''/G_∞ as a function of $\log \omega\tau$

3. Experimental part

2-ethylhexadiole-1.3. (B.D.H., Ltd.) which was dehydrated by distillation under lowered pressure was used in the investigations. The water content in the diole was determined by the Fischer method at 0.12 per cent by weight.

The density was determined pycnometrically over the temperature range 253-303 K, with an accuracy of up to 0.05 K. For lower temperatures the density (ρ) was extrapolated from the linear equation $\rho = A + BT$, where A and B are constant quantities and T is temperature. There is the following temperature dependence of density,

$$\rho = 1.1206 \times 10^3 - 6.1500 \times 10^{-1} T \text{ [kg/m}^3\text{]}.$$

The static viscosity (η_s) was determined by a Höppler viscosimeter and capillary viscometers over the temperature range 253-303 K. The accuracy of viscosity measurements varied, depending on the measurement method, from 0.5 to 2 per cent. For lower temperatures the values of viscosity were extrapolated by the equation $\log \eta = C + D/T^3$, proposed by MEISTER [7], where C and D are constants. There is the following temperature dependence of viscosity,

$$\log \eta = -4.7946 + 1.0532 \times 10^8 T^{-3} \text{ [Nsm}^{-2}\text{]}.$$

The shear impedance measurements were carried out at a frequency of 0.520 MHz, using UWE-1 and UWE-2 systems manufactured at the Institute of Fundamental Technological Research, Polish Academy of Sciences in Warsaw, over the temperature range 223-303 K. The principles of the measurements were described in many papers [8], whereas the measurement error, as defined by the producer, was ± 5 per cent.

The shear impedance measurements at frequencies of 29.9 and 500 MHz were carried out over the temperature range 218-303 K, using a measurement

system manufactured at the Department of Physical Acoustics, Institute of Fundamental Technological Research, Polish Academy of Sciences [9]. The measurement accuracy is, according to the producer, estimated at ± 5 per cent. Tables 1 and 2 show the experimental values of shear resistance.

Table 1. The real (R_l) and imaginary (X_l) components of shear impedance

Temp. [K]	R_l	X_l	R_l	R_l
	$f = 0.520$ MHz		29.9 MHz	500 MHz
	[Nsm ⁻³] $\times 10^{-5}$			
228.15			13.9	13.9
233.15			13.4	13.8
238.15	8.54	1.38	12.8	13.5
243.15	6.09	1.38	11.9	13.1
248.15	4.33	1.77	10.5	12.4
253.15	3.06	1.61		11.9
263.15	1.31	0.953		
268.15	0.886	0.690		
273.15	0.629	0.511		
278.15	0.477	0.378		
283.15	0.364	0.289		
288.15	0.288	0.233		
293.15	0.231	0.182		
298.15	0.192	0.163		
303.15	0.144	0.144		

Table 2. The shear moduli G' and G'' , the dynamic viscosity η_d and the relaxation time $\tau_s = \tau_s/G_{\infty}$

Temp. [K]	G'	G''	η_d	τ_s
	$f = 0.520$ MHz		[Nm ⁻²]	[s]
	[Nm ⁻²] $\times 10^{-9}$			
238.15	0.728	0.242	1.01×10^3	5.30×10^{-7}
243.15	0.363	0.172	3.40×10^2	1.82×10^{-7}
248.15	0.162	0.158	1.25×10^2	6.81×10^{-8}
253.15	0.0702	0.102	4.975×10	2.76×10^{-8}
258.15	0.0232	0.0543	2.12×10	1.20×10^{-8}
263.15	0.00834	0.0260	9.65	5.58×10^{-9}
268.15	0.00323	0.0128	4.65	2.74×10^{-9}
273.15	0.00138	0.00672	2.36	1.42×10^{-9}
278.15			1.26	7.75×10^{-10}
283.15			0.699	4.40×10^{-10}

4. Discussion of the results and conclusions

The results of the measurements are given in the tables and 10 diagrams. Formula (21) and the coefficients $k = 1$ and $\beta = 0.5$ were used in the description of the results of shear impedance measurements in 2-ethylhexadiol-1.3. (Figs. 5-8). When the results are presented on the basis of the Maxwell model, this

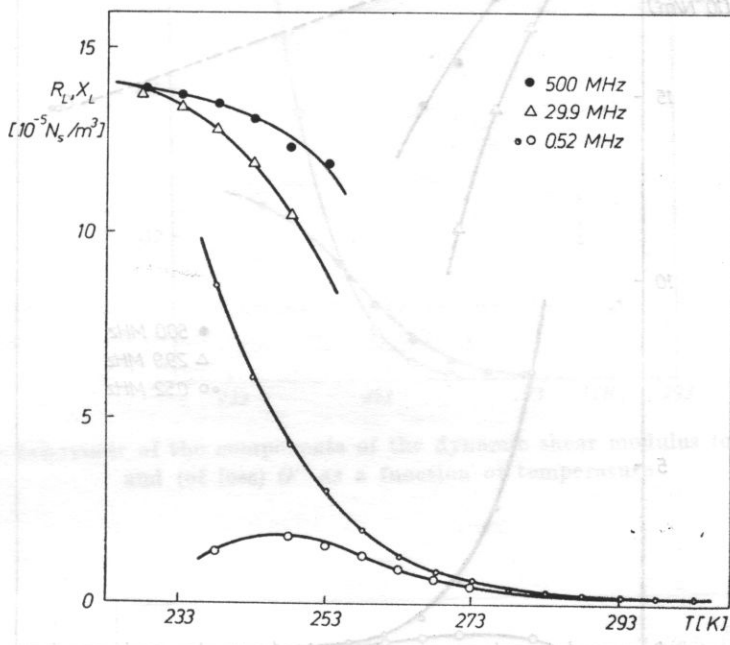


Fig. 5. The results of the measurements of the impedance components R_L and X_L as a function of temperature

corresponds to the parameter of the distribution width $b = 0.35$. A relaxation region was found to exist and was defined as one of viscoelastic relaxation.

The non-Newtonian behaviour of the fluid under these conditions is related to the translational molecular processes and configurational changes.

It can be seen that the range of viscoelastic relaxation of the diol investigated covers 4 decades of frequency (the dependence of the impedance components on frequency in Fig. 8) and that the behaviour of the normalised curve is much different from the behaviour of the relaxation curve in a simple Maxwell model.

The results of the measurements indicate that the behaviour of this diol and other polyhydroxide alcohols investigated by the present authors [10, 11, 12] can be explained within the relaxation theory, under the assumption of a continuous spectrum of the relaxation times with a given distribution. Although the problem of associated fluids still seems to be far from solved, the presence

in alcohols of multimers which form as a result of intermolecular hydrogen bonds has indisputably been confirmed by X-ray, spectroscopic and ultrasonic investigations. The diffraction of X-rays and neutrons indicates the presence,

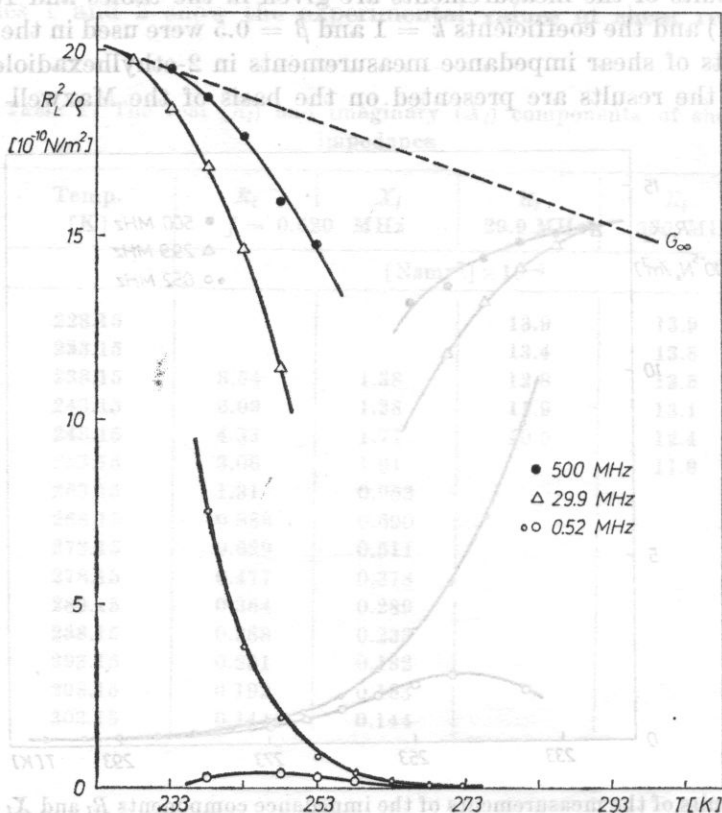


Fig. 6. The behaviour of the high-frequency modulus of shear elasticity as a function of temperature. The dashed line represents the extrapolated limiting shear modulus G_∞

both in a glaucous and a fluid state, of disturbed pieces of the crystalline structure undivided by the limits of discontinuity. Structures of this type should play a particularly important role in a supercooled state, where unlike a glaucous state, structural pieces both undergo translation and disintegrate and reform continually [16].

According to McDUFFIE and LITOVITZ [13], the structural rearrangements which occur in fluids as a result of external (electric or mechanical) forces have a cooperative character, since they cover a whole group of molecules (cluster) under the short-range molecular order. They constitute a relaxation process related to the structural relaxation time. The cooperative nature of such rearrangements is reflected in the viscosity of the non-Arrhenius fluid, i.e. a fluid whose viscosity is not proportional to $\exp(-E/RT)$, where E is the activation

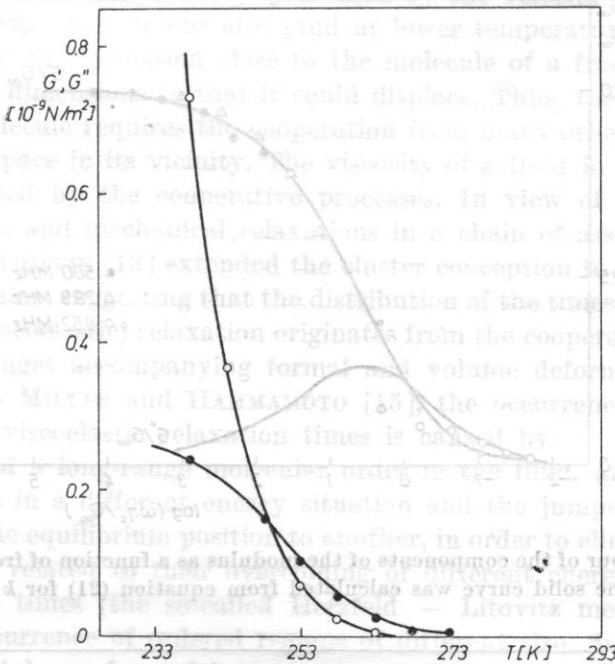


Fig. 7. The behaviour of the components of the dynamic shear modulus (of elasticity) G' and (of loss) G'' as a function of temperature

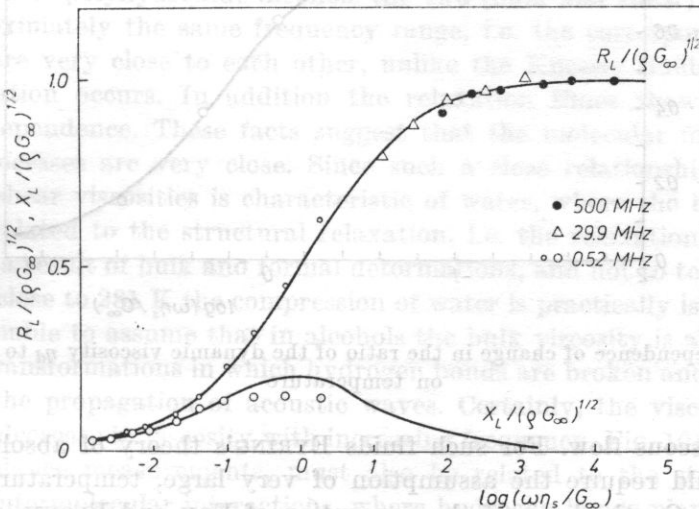


Fig. 8. The behaviour of the components of mechanical shear impedance as a function of frequency, in a normalised system. The solid curve represents the theoretical curve calculated from equation (22) for $k = 1$ and $\beta = 0.5$

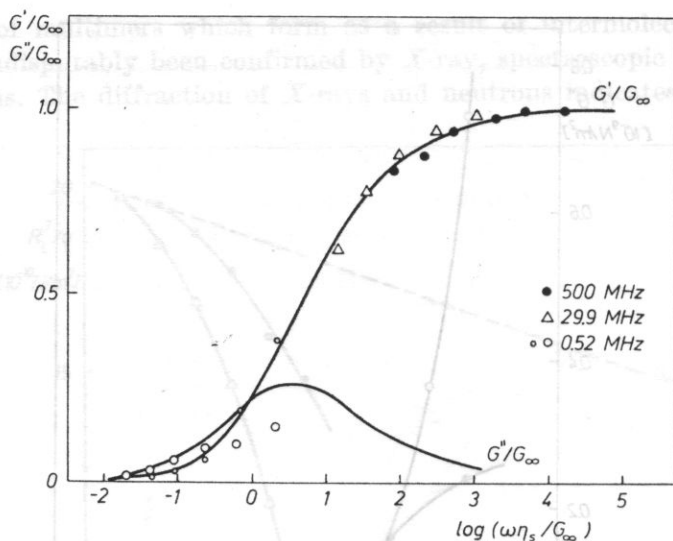


Fig. 9. The behaviour of the components of the modulus as a function of frequency, in a normalised system. The solid curve was calculated from equation (21) for $k = 1$ and $\beta = 0.5$

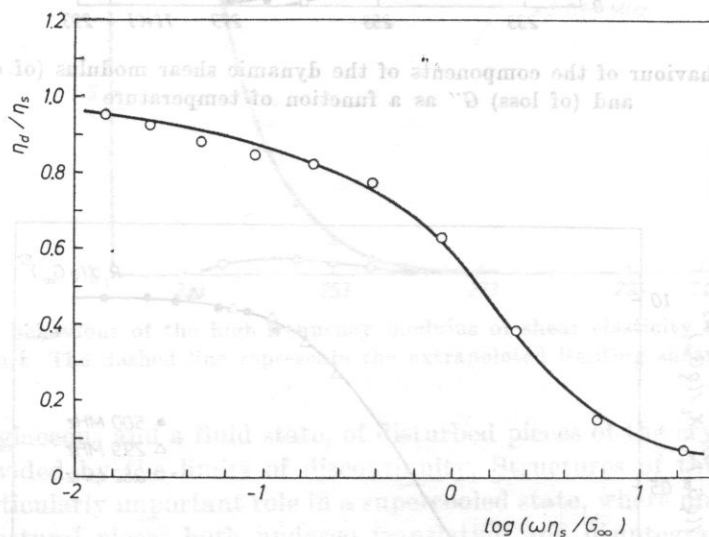


Fig. 10. The dependence of change in the ratio of the dynamic viscosity η_d to the static one on temperature

energy of viscous flow. For such fluids EYRING'S theory of absolute reaction velocity would require the assumption of very large, temperature-dependent values of E_a . On the basis of the conception of FOX and FLORY, according to which the translation of molecules of a supercooled fluid is mainly determined by the volume of the free fluid, MACEDO and LITOVITZ [14] assumed that the

mobility of fluid molecules is not only defined by the velocity at which they overcome the energy barrier but also (and at lower temperatures mainly) by the probability of the formation close to the molecule of a free volume with sufficiently large dimensions so that it could displace. Thus, the translation of an individual molecule requires the cooperation from many others which must form an empty space in its vicinity. The viscosity of a fluid in a supercooled state is determined by the cooperative processes. In view of the similarity between dielectric and mechanical relaxations in a chain of associated fluids, LITOVITZ and McDUFFIE [13] extended the cluster conception to the relaxation of mechanical strains, suggesting that the distribution of the times of mechanical (structural and viscoelastic) relaxation originates from the cooperative character of structural changes accompanying formal and volume deformations [16].

According to MILLES and HAMMAMOTO [15], the occurrence of the wide spectrum of the viscoelastic relaxation times is caused by:

a) the lack of a long-range molecular order in the fluid, and as a result every molecule is in a different energy situation and the jumps of particular molecules from one equilibrium position to another, in order to eliminate mechanical strains, are related to their overcoming of different energy barrier and thus to different times (the so-called Herzfeld — Litovitz mechanism [6]);

b) the co-occurrence of ordered regions of different size. Since the decay time of such crystal pseudo-nuclei, under shear forces, should increase as their spatial range expands, the factors changing the molecular order (e.g. temperature change) should affect the spectrum of the times of viscoelastic relaxation.

The results of the measurements carried out seem to confirm the molecular mechanisms given above.

In the case of polyhydroxide alcohols the two (bulk and shear) viscosities relax in approximately the same frequency range, i.e. the corresponding relaxation times are very close to each other, unlike the Knesser fluids in which thermal relaxation occurs. In addition the relaxation times show a similar temperature dependence. These facts suggest that the molecular mechanisms of the two processes are very close. Since such a close relationship between the bulk and shear viscosities is characteristic of water, where the bulk viscosity must be related to the structural relaxation, i.e. the relaxation of strains which arise as a result of bulk and formal deformations, and not to temperature functions (for close to 281 K the compression of water is practically isothermal), it seems reasonable to assume that in alcohols the bulk viscosity is also related to structural transformations in which hydrogen bonds are broken and reformed again during the propagation of acoustic waves. Certainly, the viscosity relaxation (i.e. an decrease in viscosity with increasing frequency, Fig. 10), observed in shear impedance measurements, must also be related to the structure of the fluid and intermolecular interactions, where hydrogen bonds play the main role. Thus, the phenomena observed in volume and formal deformations of the medium using acoustic waves are closely related to the cybotactic structure

of the fluid, which in the case of associated diols is an intermediate stage between a weak dispersive structure with thixotropic properties and a condenser structure.

This was confirmed by the present investigations, since the change in the structure of the fluid caused by a temperature change was reflected by a change not only in viscosity, but also in moduli of elasticity and relaxation times.

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References

- [1] R. D. ANDREWS, A. V. TOBOLSKY, E. E. HANSON, *J. Appl. Phys.*, **17**, 352, 280-292 (1946).
- [2] A. V. TOBOLSKY, A. MERCURIO, *J. Polym. Sci.*, **36**, 467-475 (1959).
- [3] J. BARLOW, *Molecular and nonlinear acoustics, ultrasonic investigations of the viscoelastic properties of fluid* (in Polish), Zakład Naukowy im. Ossolińskich, Warsaw - Cracow 1965.
- [4] A. J. BARLOW, A. J. ERGINSAY, J. LAMB, *Viscoelastic relaxation of supercooled liquids*, *Proc. Roy. Soc., A* **298**, 481-494 (1967).
- [5] T. A. LITOVITZ, C. DAVIES, *Physical acoustics*, Academic Press, New York - London 1965.
- [6] K. F. HERZFELD, T. A. LITOVITZ, *Absorption and dispersion of ultrasonic waves*, Academic Press, New York - London 1959.
- [7] R. MEISTER, C. J. MARHOFFER, R. SCIAMANDA, L. COTTER, T. A. LITOVITZ, *J. Appl. Phys.*, **31**, 854-870 (1960).
- [8] R. PŁOWIEC, *Investigations of the rheological properties of oils in the region of viscoelastic relaxation using ultra - and hypersonic shear deformations* (in Polish), Institute of Fundamental Technological Research, 60/1975. Habilitational diss.
- [9] R. PŁOWIEC, *Measurement of the viscoelastic shear properties of fluids at frequencies of the order of 1000 MHz* (in Polish), *Archiwum Akustyki*, **3**, 5, 411-419 (1970).
- [10] S. ERNST, M. WACIŃSKI, R. PŁOWIEC, J. GLIŃSKI, *Acustica*, **47**, 4, 292-303 (1981).
- [11] S. ERNST, M. WACIŃSKI, R. PŁOWIEC, *Acustica*, **45**, 1, 30-38 (1980).
- [12] R. PŁOWIEC, S. ERNST, M. WACIŃSKI (in Polish), XXVIII Open Seminar on Acoustics, Gliwice 1981.
- [13] T. A. LITOVITZ, G. E. MC DUFFIE JR., *J. Chem. Phys.* **39**, 729-734 (1963).
- [14] P. MACEDE, T. A. LITOVITZ, *J. Chem. Phys.* **42**, 245-257 (1965).
- [15] D. O. MILLES, D. S. HAMMAMOTO, *Nature*, **193**, 644-646 (1962).
- [16] S. ERNST, *Some physico-chemical aspects of viscoelasticity* (in Polish), *Zeszyty Naukowe Uniwersytetu Śląskiego* (in press).

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