

VISCOELASTIC PROPERTIES OF BINARY LIQUID HYDROXYL MIXTURES IN THE LIGHT OF LOCAL MOLECULAR ORDER¹⁾

ZOŘEBSKI, E.,²⁾ ERNST, S.,²⁾ Kalowice

The viscoelastic behaviour of glycerol-butanediol mixtures was studied throughout the whole concentration range using shear ultrasonic waves. The results were interpreted in the light of the local molecular order theory of Quenec and coworkers that has been shown to be capable of explaining the origin of the broad spectrum of viscoelastic relaxation times on the basis of the dynamics of molecular motions.

1. INTRODUCTION

Dielectric, ultrasonic and hypersonic experiments indicate serious deviations of the relaxational behaviour of highly associating liquids, like polyhydroxyalcohols, from a single-time dispersion function $\sigma = (1 + i\omega\tau)^{-1}$ (where ω is the angular frequency and τ is the relaxation time). It is worthwhile noting that similar deviations from a single-time autocorrelation in the time domain are observed in light scattering and photon correlation spectroscopy experiments [1, 2]. In order to represent the behaviour of those liquids a distribution of relaxation times, i.e. a spectrum of times instead of a single one, has to be assumed. Different time distributions based on physical intuition have been proposed and applied by authors dealing with the problem. Although the proposed models are capable of reproducing the shear relaxation curves, they do not convey any insight into the molecular processes occurring in the liquid, and thereby they do not offer any molecular picture of a strained liquid. In other words, no molecular mechanism is implied by a particular time distribution function. The origin of the distribution of shear relaxation times was the subject on which we focused our attention in the present study.

Relaxation phenomena of highly viscous polyhydroxyalcohols indicate that, beside the flexibility of the alkane chain, the main factor determining molecular

motions is the dynamics of hydrogen bonds, and thereby the dynamics of the local molecular order related to those specific intermolecular interactions. It was therefore particular tempting to discuss the results of the viscoelastic measurements in the light of the local molecular order theory of Quenec and coworkers [3—5].

The liquids tested in our experiments were two polyhydric alcohols, butanediol-1.3 (BD) and glycerol (GL), and their mixtures. Those liquids seem to be particularly suitable for the study of the effect of hydrogen bonding on viscous and viscoelectric properties since the hydrogen bonds "concentration" can be varied continuously within rather wide limits by simply varying the composition of the mixtures.

II. EXPERIMENTAL

Pure butanediol-1.3 (Koch-Light Laboratories, U.K.) and glycerol of analytical grade (POCH Gliwice, Poland) were distilled under reduced pressure in order to remove water and mixtures of known concentration were prepared by weighing.

Densities and viscosities were determined within the temperature range 263—303 K using pycnometers and a Höppler BH2 (GDR) viscometer.

The shear mechanical impedance and the shear resistances were determined at frequencies of 0.5, 500 and 650 MHz by measuring the attenuation and phase delay of pulses of torsional vibrations travelling along an acoustical waveguide [6], and by measuring the coefficient of reflection of ultrasonic waves from a crystal-liquid interface with an equipment based on the idea worked out by Clark and Litovitz [7]. The systematic error is ± 5 per cent and achieves ± 20 per cent in the limit of high temperature, i.e. in the viscous limit that has a negligible effect on the shape of the relaxation curves. The scattering of the measurement points around the smooth model curves is usually characterized by the total mean root square deviations [5] which for the liquids under test range from 6.3×10^{-3} to 1.6×10^{-2} .

III. RESULTS AND PROCESSING OF DATA

The concentration dependence of the limiting shear modulus $G_\infty(x)_T$ was determined from values obtained as linear functions of temperature at constant mixtures compositions. Some typical shear resistances normalized with those G_∞ values are shown as functions of the reduced frequency $\omega\eta/G_\infty$ in Fig. 1.

In the analysis of the shear relaxation of the liquids in question, two well-known phenomenological models have been used:

i. The Barlow—Erginsav—Lamb model (BEL) [8, 9] consisting in a parallel

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²⁾ Silesian University, Institute of Chemistry, ul. Szkolna 9, KATOWICE 400 06 Poland.

combination of the shear impedance of an elastic solid, Z_s , with that of a Newtonian fluid, Z_N . $Z = Z_s + Z_N$, with two adjustable parameters, K and β . This model leads to the following equation for the shear resistance reduced by that of a corresponding solid $(\rho G_x)^{1/2}$:

$$\frac{R_T}{\sqrt{\rho G_x}} = \frac{1}{\sqrt{2}} \left[1 + \frac{Y^\beta + 2K \cos(\pi\beta/2)}{\{Y^\beta + 2K \cos(\pi\beta/2)\}^2 + [Y^{\beta-1} + 2K \sin(\pi\beta/2)]^2} \right]^{1/2} \quad (1)$$

where R_T is shear resistance, ρ and η — density and viscosity of the liquid, respectively, $Y = \omega\eta/G_x = \omega/\bar{\omega}$ — reduced frequency, ω — angular frequency, $\bar{\omega} = G_x/\eta$ — average relaxation frequency.

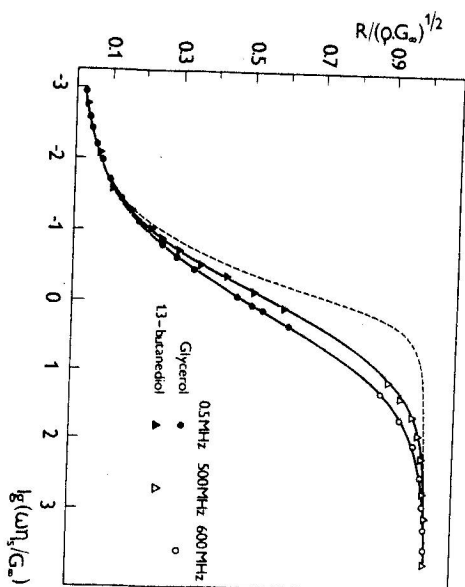


Fig. 1. Reduced resistances of glycerol and 1,3-butanediol as functions of the reduced frequency. The solid lines were calculated from the BEL model according to Eq. 1. The broken line corresponds to the single-time Maxwell model.

ii. The Maxwell model with a Gaussian distribution of relaxation times [10] resulting from a summation of the Maxwell elements, each consisting of a Hookean element (spring) and a Newtonian element (damper) connected in series. If the number of the Maxwell elements increases infinitely, the reduced shear resistance, R_T , may be written as follows:

$$\frac{R_T}{\sqrt{\rho G_x}} = \frac{1}{\sqrt{2}} \left\{ \left(\int_0^\infty \frac{g(x) \varepsilon^2 Y'^2 x^2}{1 + \varepsilon^2 Y'^2 x^2} dx \right)^2 + \left(\int_0^\infty \frac{g(x) \varepsilon Y' x}{1 + \varepsilon^2 Y'^2 x^2} dx \right)^2 \right\}^{1/2} + \int_0^\infty \frac{g(x) \varepsilon^2 Y'^2 x^2}{1 + \varepsilon^2 Y'^2 x^2} dx \quad (2)$$

where $x = \tau/\tau_0$ is the shear relaxation time normalized with regard to the main time, τ_0 , of the assumed Gaussian distribution of times

$$g(x) = \frac{b}{x\sqrt{\pi}} \exp[-(b \ln x)^2] \quad (3)$$

and $\varepsilon = \frac{\tau_0}{\tau} \exp(1/4b^2)$ is an empirical coefficient that corrects the theoretical relationship between the average time, $\bar{\tau}$, and the main time of the distribution, τ_0 , $Y' = Y \exp\left(-\frac{1}{4b^2}\right)$.

Both models described above are equally capable of reproducing the experimental relaxation curves of the studied liquids (examples are given in Fig. 1).

IV. DISCUSSION AND CONCLUSIONS

Two points resulting from the analysis based upon the phenomenological models are worthy of notice:

- The relaxation regions of the liquids under test are, as usually in the case of hydroxyl liquids, considerably broader than the region corresponding to the single-time Maxwell relaxation model and, for the pure components, they increase with the increasing number of hydroxyl groups in the molecule.
- If the other hydroxyl component is added to glycerol or to diol, the spectrum of relaxation times (as defined by the Maxwell model and characterized by the b -parameter of Eq. 3) or the relaxation region (as defined by the BEL model and characterized by the K -parameter of Eq. 1) are narrowing. This is clearly indicated by the concentration dependence of b and K in Fig. 2 (b is increasing and K is decreasing with the narrowing relaxation region).

The increase in the width of the relaxation time spectrum of glycerol, compared with that of butanediol, is consistent with the suggestion of Kono et al. [11], who relate the broadening width of the relaxation time spectrum to the increase in the lattice energy. The latter is expected to be larger in glycerol because of the higher concentration of the OH groups capable of forming intermolecular hydrogen bonds. However, such a correlation between the hydroxyl group concentration and the relaxation spectrum width is not revealed by the binary mixtures.

As shown by Quentrec et al. [3, 4] and by Eldin et al. [5], the local molecular order may affect the shear impedance if the wave period $T = \frac{2\pi}{\omega}$ is close to the correlation time of the local molecular order, τ , while both must

obviously exceed the time τ_2 necessary to define a local thermodynamic equilibrium. Thus, if $\tau_1 \geq \frac{2\pi}{\omega} > \tau_2$, the transverses ultrasonic data can be successfully interpreted by dynamic quantities which result from a constitutive equation that relates the traceless part of the stress tensor σ to the velocity gradient and to the traceless parts of three independent tensorial quantities \mathbf{G} , \mathbf{I} , and \mathbf{J} . The first and the second, \mathbf{G} and \mathbf{I} , are related to the local order of the centres of gravity and to the orientational order of the molecules, respectively. The third tensor,

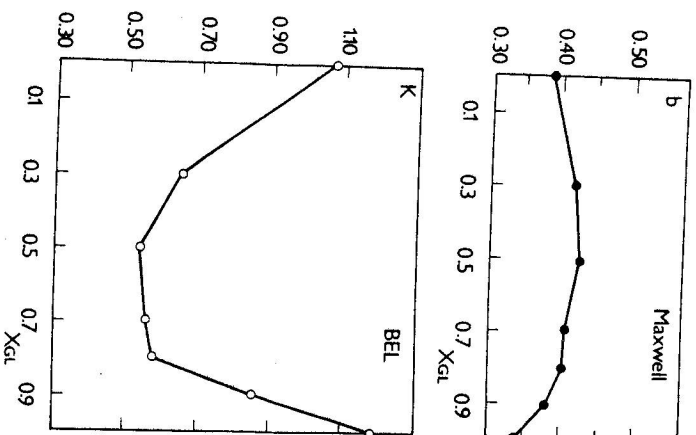


Fig. 2. Dependence of the width of the relaxation region characterized by the parameters b (Maxwell model) and K (BEL model) on the mole fraction of glycerol.

\mathbf{J} , describes the correlation between those orders and is expected to be of particular importance in highly viscous liquids of non-spherical molecules since it can be thought of as a gearing effect between entangled molecules. It is also interesting to note that the hydrodynamic equation derived by Eldin et al. [5] is capable of describing the viscoelastic behaviour of liquids obeying the simple BEL 1969 model [12], (a simple combination of the shear impedances of a elastic solid and a Newtonian liquid without any adjustable parameters) as well as very broad relaxation regions [13].

If the relaxation of the positional (translational) and the orientational (rotational) orders, as well as the gearing effect are assumed to be independent, the Eldin constitutive equations lead to the following expressions for the reduced shear resistance and reactance [13]:

$$\frac{R_T}{\sqrt{\rho G_\infty}} = \left(\frac{AY^2 \varphi}{2} \left\{ \left[1 + \left(\frac{\Psi}{AY\varphi} \right)^2 \right]^{1/2} + 1 \right\} \right)^{1/2} \quad (4)$$

$$\frac{X_T}{\sqrt{\rho G_\infty}} = \left(\frac{Y\Psi}{2} \left\{ \left[1 + \left(\frac{\Psi}{AY\varphi} \right)^2 \right]^{1/2} - 1 \right\} \right)^{1/2} \quad (5)$$

where

$$\begin{aligned} \varphi &= \frac{R_{12}\epsilon_2}{\epsilon_2^2 + A^2 Y^2} + \frac{R_{13}\epsilon_3}{\epsilon_3^2 + A^2 Y^2} + \frac{R_{14}}{1 + A^2 Y^2} \\ \Psi &= \frac{\epsilon_2^2 + (1 - R_{12})A^2 Y^2}{\epsilon_2^2 + A^2 Y^2} - \frac{R_{13}A^2 Y^2}{\epsilon_3^2 + A^2 Y^2} - \frac{R_{14}A^2 Y^2}{1 + A^2 Y^2} \\ \epsilon_2 &= \tau_4/\tau_2, \quad \epsilon_3 = \tau_4/\tau_3, \quad A = \frac{G_\infty}{\eta} \tau_4 \end{aligned}$$

R_{ij} are the coupling factors between the traceless tensors σ_i and \mathbf{G}_s , \mathbf{I}_s and \mathbf{J}_s , and τ_2 , τ_3 , τ_4 are the relaxation times related to the tensors \mathbf{G} , \mathbf{I} and \mathbf{J} , respectively and thereby to the corresponding molecular orders.

The other symbols have their previous meaning. It can be shown that the mean (experimental) relaxation time $\bar{\tau} = \eta/G_\infty$ is related to the times τ_2 , τ_3 and τ_4 as follows:

$$\bar{\tau} = \left(\sum_{j=2}^4 R_{ij}/\tau_j \right)^{-1} = \frac{\tau_2 \tau_3 \tau_4}{R_{12} \tau_3 \tau_4 + R_{13} \tau_2 \tau_4 + R_{14} \tau_2 \tau_3} \quad (6)$$

i.e. the mean relaxational frequency $\bar{\omega}_r = 1/\bar{\tau}$ is a linear combination of the corresponding relaxational frequencies $\omega_{r,j} = 1/\tau_j$:

$$\bar{\omega}_r = \sum_{j=2}^4 R_{ij} \omega_{r,j} \quad (7)$$

In order to determine the parameters in the equations (4) and (5), the curves calculated from them have been fitted to the phenomenological 2-parameter BEL curve (Eq. 1) for the liquids under test using the computer procedure described in [13]. The values of the parameters obtained in this way are given in the Table. The quality of the fit is indicated by the total mean root square deviations F .

Table
Parameters of the local-molecular-order model for glycerol (GL), 1,3-butanediol (BD) and their mixtures (X_{GL} — mole fraction of glycerol).

	R_{12}	R_{13}	$R_{14} \times 10$	$\epsilon_1 \times 10$	$\epsilon_2 \times 10^2$	$F \times 10^2$
GL	0.72	0.26	0.20	0.85	0.27	1.9
$X_{GL} = 0.898$	0.66	0.32	0.21	0.92	0.44	1.6
$X_{GL} = 0.796$	0.53	0.44	0.32	1.25	0.69	1.2
$X_{GL} = 0.695$	0.56	0.42	0.20	0.96	0.73	1.3
$X_{GL} = 0.495$	0.54	0.44	0.23	1.1	0.75	1.2
$X_{GL} = 0.295$	0.58	0.40	0.24	1.0	0.64	1.3
BD	0.71	0.27	0.19	0.85	0.32	1.9

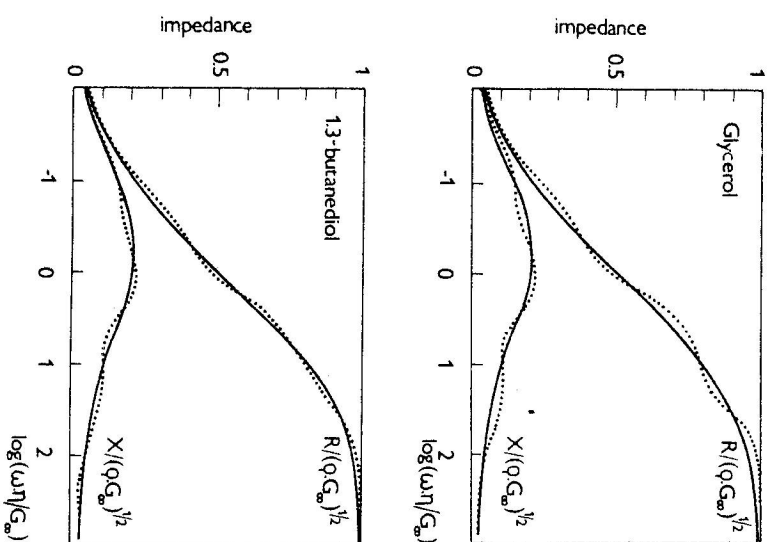


Fig. 3. The reduced impedances of glycerol and 1,3-butanediol as functions of the reduced frequency. The solid lines were calculated from the BEL model. The broken lines were calculated from the local-molecular-order model (Eqs. 4 and 5).

From the figures in the Table, as well as from inspection of Fig. 3, we are led to conclude that the fitting is rather satisfactory.

The "waving" of the theoretical curves along the "experimental" ones is not surprising since, according to the local molecular order theory, the broad relaxation regions result from an overlap of three discrete relaxation processes governed by three well separated time constants. However, despite this discrepancy, the analysis based on the local molecular order theory conveys, in spite of the phenomenological models, a significant and interesting insight into the molecular origin of the distribution of relaxation times.

It can be concluded that the experimental viscoelastic relaxation time cannot be attributed to the translational motions of the molecules only, since both the positional and the orientational correlations, as well as the gearing effect, contribute to it according to Eq. 6.

From the figures given in the Table, and Eq. 6 it results that the experimental relaxation frequency ($\bar{\omega}_r = R_{12}\omega_{r,2} + R_{13}\omega_{r,3} + R_{14}\omega_{r,4}$) where $\omega_{r,i} = 1/\tau_i$ is determined predominantly by the dynamics of orientational molecular motions and by the gearing effect since $R_{13}\omega_{r,3} \approx R_{14}\omega_{r,4} \approx \frac{1}{2}\bar{\omega}_r$, while $R_{12}\omega_{r,2}$ is by one order of magnitude less than $\bar{\omega}_r$. The significance of the gearing effect in the case of highly viscous liquids of non-spherical molecules was suggested by Quenec and Bossis [4].

It is obvious that the width of the relaxation region is determined by the separation of the relaxation times, τ_i . Thus the dependence of the ratio $\tau_2/\tau_4 = 1/\epsilon_2$ on the mixture composition (Fig. 4) resembles of the K —parameter of the BEL 1973 model. Since both times, τ_2 and τ_4 , increase with increasing glycerol concentration (Fig. 5) and thereby with the increasing number of hydrogen bonds, Figs. 2 and 4 indicate that τ_4 increases more rapidly than τ_2 does on passing from butanediol to glycerol and that in the binary mixtures the gearing effect is of more importance than in the pure components. Because of the difference in the molecular shapes and sizes, the intermolecular spaces existing in the pure polyhydric alcohols, because of the coordination of the molecules by hydrogen bonds, are likely to be penetrated by the relatively long chains of butanediol and by the relatively small and compact glycerol molecules. Therefore it may be concluded that in the binary mixtures the spacefilling factor becomes important in determining the viscoelastic behaviour.

Because of the intermolecular hydrogen bondings, polyhydroxyalcohols resemble to some extent water. As results from computer simulation experiments reported by Geiger et al. [14], water can be thought of as a space-filling gel-like transient network of hydrogen bonds containing small regions (patches) of increased connectivity and decreased local density. Assuming that similar

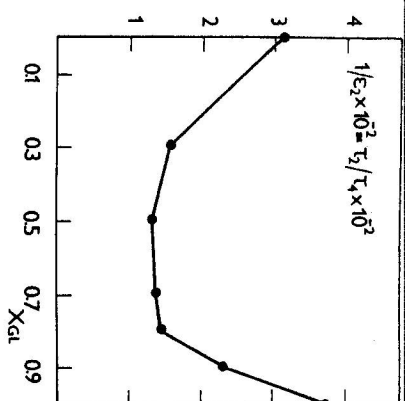


Fig. 4. The ratio of the relaxation times τ_2 and τ_1 (Table). This ratio is proportional to the width of the relaxation region.

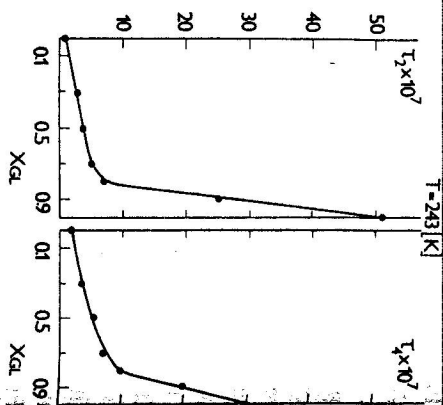


Fig. 5. The relaxation times τ_2 and τ_1 at 243 K as functions of the mole fraction of glycerol.

local structures (patches or clusters) exist in liquid polyhydric alcohols, although the network of hydrogen bonds is expected to be less perfect, the local molecular order is likely to be the main factor determining their viscoelastic behaviour. We believe that this study really proves that the viscoelastic properties of highly associated hydroxyl liquids are explicable within the framework of the local molecular order theory proposed by Quentrec and coworkers that offer an interesting molecular picture of the dynamics and the structure of the liquids.

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УПРУГОВЯЗКИЕ СВОЙСТВА БИНАРНЫХ ЖИДКИХ ГИДРОКСИЛЬНЫХ СМЕСЕЙ

В работе исследуется упруговязкое поведение бинарных гидросильных смесей во всем диапазоне концентрации. Результаты измерений интерпретируются в свете теории локального молекулярного упорядочения, выдвинутой Квентреком и соавторами. Эта теория дает возможность объяснить природу широкого спектра упруговязких релаксационных времён на основе динамики молекулярного движения.