

RHEOLOGICAL AND VOLUME EFFECTS IN LIQUID BINARY MIXTURES OF POLYHYDROXYALCOHOLS¹⁾

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The shear elasticity and viscosity of binary mixtures of glycerol, butanediol-1,3 and 2-methylpentanediol-2,4, determined as functions of temperature and composition, were analysed by applying the hydrogen-bond model of the shear compliance of Madigosky, McDuffie and Litovitz and the two-component hole diffusion model of Isakovitch and Chaban. It was shown that those models offer a physically acceptable molecular interpretation of the rheological properties of the hydroxyl liquid mixtures under test indicating the significance of the free volume or concentration of holes in determining their behaviour in shear. The conclusions were found to be compatible with the IR spectra of those mixtures.

РЕОЛОГИЧЕСКИЕ И ОБЪЕМНЫЕ ЭФФЕКТЫ В ЖИДКИХ БИНАРНЫХ СМЕСЯХ ПОЛИГИКОЛЕЙ

В работе приведен анализ упругости второго рода и вязкости бинарных смесей глицерина, бутилпентандиоля-1,3 и 2-метилпентандиоля-2,4 как функций температур и состава на основе применения модели водородной связи Мадигоски, Маклаффи и Литовича для деформации сдвига и двухкомпонентной дырочной модели диффузии Исаковича и Чабана. Показано, что эти модели предлагают физически приемлемую молекулярную интерпретацию реологических свойств испытываемых гидроксильных жидких смесей, указывающих на важность свободного объема и концентрации дырок в определении их поведения при сдвиге. Оказалось, что приведенные выводы не противоречат данным об инфракрасных спектрах этих смесей.

1. INTRODUCTION

The time anomalies of the stress-strain relation in supercooled liquids can be thought of as a combination of their viscous and elastic properties [1—3], the latter being determined by both the intermolecular interaction energy and the free

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volume effects. Consequently, the relationship between the rheological properties of those highly viscous liquids and their microscopic structure and the molecular processes accompanying a macroscopic deformation seems to be a particularly tempting problem in spite of its complexity. In the case of polyhydroxyalcohols, both the potential of intermolecular interactions and the microscopic structure of the liquid are determined primarily by specific hydrogen bond interactions.

In the paper presented the energy and volume effects on the behaviour of polyhydroxyalcohols in shear will be in the centre of attention. Hence, the shear elasticity and viscosity of binary mixtures of glycerol, butanediol-1,3 and 2-methylpentanediol-2,4 determined as functions of temperature and composition will be analysed within the hydrogen-bond model of the shear compliance suggested by Madigosky, McDuffie and Litovitz [4] and within the two component model of highly viscous liquids offered by Isakovitch and Chaban [5]. Binary mixtures of hydroxyl liquids seem to be specially suitable for such an analysis since the main parameters taken into account (hydrogen bond density and free volume or hole concentration) can vary continuously within certain limits.

II. EXPERIMENT

Chemical and liquid mixtures. Glycerol (GL), butanediol-1,3 (BD) and 2-methylpentanediol-2,4 (MPD) were dehydrated by allowing the water to boil off under reduced pressure at about 373 K. The liquid mixtures were prepared by mixing weighed portions of the above polyhydroxyalcohols.

Densities were measured pycnometrically within the temperature range 273 \div 303 K (± 0.05 K) and reduced to vacuum. The densities at lower temperatures were determined by linear extrapolation. The results and details of the measurements are given in [6].

Viscosities were measured with a Höppler viscometer within 263 \div 303 K (± 0.05 K) with an accuracy of about ± 2 per cent and extrapolated to lower temperatures using the equation of Meister et al. [7]. Results and details are given in [8].

Shear rigidities G_s of the liquids under test were determined from the high-frequency shear resistance ($G_s R_L^2/\rho$, where R_L is the shear resistance and ρ is the density of the liquid) measured with an accuracy of ± 10 per cent by the pulse reflection technique (measurements of the reflection coefficient of transverse shear waves at the plane interface between the delay line and liquid [9, 10]) at 500 and 650 MHz and within 218 \div 253 K (± 0.1 K). The limiting shear modulus $G_{s\infty}$ was extrapolated to higher temperatures assuming, according to [7, 11], a linear temperature dependence. Details and results can be found in [8].

Absorption spectra of the binary glycerol-diol mixtures were recorded within

the frequency range 2800 \div 3800 cm^{-1} with a UV 5240 Beckman spectrophotometer and the integral intensities were determined.

III. THE EFFECT OF HYDROGEN BONDING AND FREE VOLUME ON THE SHEAR ELASTICITY AND VISCOSITY OF POLYHYDROXYALCOHOLS

Experimental data proved a linear temperature dependence of the high-frequency shear modulus of polyhydric alcohols [7, 11], their mixtures [8] and solutions of electrolytes in polyhydroxyalcohols [10, 12, 13]. In order to explain this type of the dependence of G_s on temperature, Madigosky, McDuffie and Litovitz [4] assumed that, according to Zwanzig's and Mountain's suggestion [14], the elastic constants of hydrogen-bonded liquids were directly related to the internal configurational energy and thereby to the hydrogen bond density, i.e. to the equilibrium number of hydrogen bonds per unit volume $\rho_H = N/V$ (where N is the equilibrium number of hydrogen bonds in volume V).

Madigosky et al. [4] assumed a simple relationship between the shear compliance J_s and ρ_H :

$$J_s = A + B\rho_H^{-1} \quad (1)$$

where A and B are constants.

If a) J_0 is the minimum compliance corresponding to $\rho_{H,0} = N_0/V_0$ where N_0 is the maximum possible number of bonds and V_0 the corresponding volume, i.e. the volume with no broken bonds and b) the equilibrium between the broken bonds ($N_0 - N$) and the unbroken ones is given by $(N_0 - N)/N = \exp(-\Delta G/RT) = \exp(-\Delta H/RT + \Delta S/R)$ (where ΔG , ΔH and ΔS are the free enthalpy, enthalpy and entropy necessary to break one mole of hydrogen bonds, resp.), Eq. (1) may be rewritten as follows

$$J_s = J_0 + \frac{B}{n_H N_A} V \left[\exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) + \frac{V - V_0}{V} \right] \quad (2)$$

where the volume V and V_0 refer to one mole of the liquid, n_H is the number of hydroxyl groups per molecule and N_A is the Avogadro number ($N_H N_A = N_0$).

Eq. (2) is of particular interest from the viewpoint of the microscopic structure of the liquid and the intermolecular interactions since it relates the compliance to a fundamental molecular structure parameter, i.e. to the number of hydroxyl groups of a molecule determining both the molecular interactions and the free volume $V^F = V - V_0$.

Madigosky et al. applied Eq. (2) to glycerol, butanediol-1,3 and propanol-1 using V_0 values either estimated by fitting the Macedo-Litovitz hybrid theory [15] to the shear viscosity data ($5.95 \times 10^{-5} \text{ m}^3 \text{ mole}^{-1}$ for glycerol) or from the

temperature and the pressure dependence of the dielectric relaxation time ($7.2 \pm 0.2 \times 10^{-5} \text{ m}^3 \text{ mole}^{-1}$ for butanediol-1,3). They also proved that the constants B and ΔH , as determined for glycerol, are applicable to other alcohols. Assuming $J_0 \approx 0$, as suggested by Madigovsky et al., we have rewritten Eq. (2) as follows:

$$\left[\frac{J_\infty n_H}{(B/N_A)V} - 1 \right] e^{\frac{\Delta H}{RT}} = e^{-\frac{\Delta S}{R}} - V_0 \frac{e^{\frac{\Delta H}{RT}}}{V} \quad (3)$$

The above linear equation allows to determine ΔS and V_0 if the B and ΔH values are known and the compliance, $J_\infty = G_\infty^{-1}$, and molar volume, V , are determined experimentally as functions of temperature. The B and ΔH values found by Madigovsky et al. and the mean numbers of hydrogen bonds per molecule, $n_H = n_{H,1} + (n_{H,2} - n_{H,1})x_2$ (where the indices 1 and 2 refer to the components and x is mole fraction), have been used to check the linearity of Eq. (3) (Fig. 1). From Fig. 1 one learns that deviations from linearity appear only for MPD and some GL-MPD mixtures at higher temperatures. The finding that the linearity of Eq. (3) is maintained within a relatively broad temperature range is of considerable interest since it confirms the assumption that the value of the enthalpy

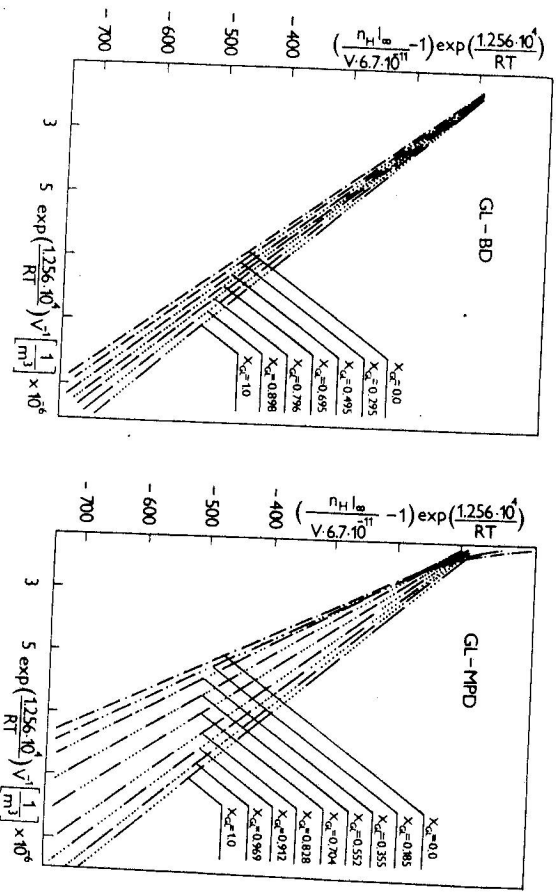


Fig. 1. Plot of $\left[\frac{J_\infty n_H}{(B/N_A)V} - 1 \right] \exp(\Delta H/RT)$ (left-hand side of Eq. (3)) vs $\exp(\Delta H/RT)V^{-1}$, B and ΔH values taken from Ref. [4]; compliance and volume data obtained from measurements.

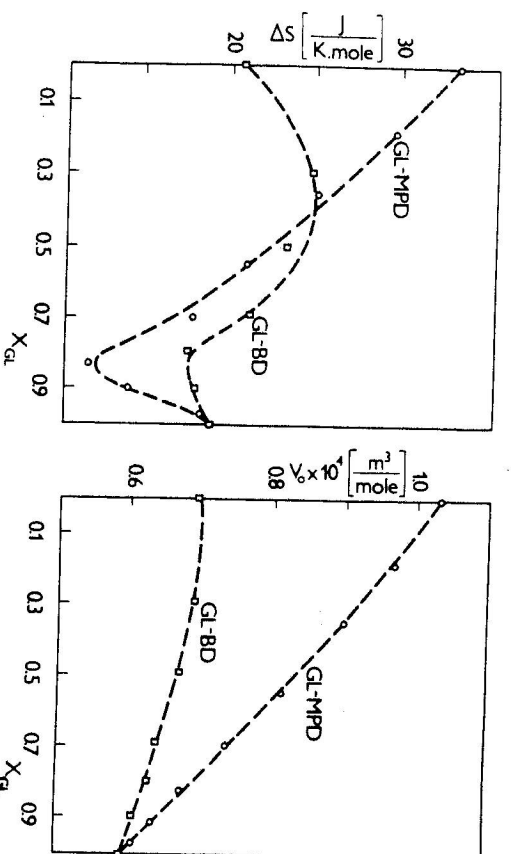


Fig. 2. Plots of the molar volume with no broken hydrogen bonds, V_0 , and the entropy change accompanying the rupture of the mole of hydrogen bonds, ΔS , vs mole fraction of glycerol, X_{GL} .

necessary to rupture one mole of hydrogen bonds ($\Delta H = 1.256 \times 10^4 \text{ J mole}^{-1}$) is justifiable for the three polyhydric alcohols and their mixtures investigated.

Using the above ΔH value and the experimental data from the temperature range within which the linearity of Eq. (3) is maintained (188 + 258 K), the ΔS and V_0 values were determined and plotted as functions of composition in Fig. 2. It is worthwhile noting that the V_0 values of glycerol and butanediol-1,3 determined from Eq. (3) (59.1×10^{-6} and $69.5 \times 10^{-6} \text{ m}^3 \text{ mole}^{-1}$, respectively) are in an excellent agreement with those used by Madigovsky et al. [4] and obtained from quite independent experiments.

IV. APPLICATION OF THE ISAKOVITCH-CHABAN TWO-COMPONENT MODEL OF HIGHLY VISCOUS MEDIA TO POLYHYDRIC LIQUIDS

Since the application of Eq. (2) to the hydrogen-bonded liquids studied have brought out the significance of free volume for the behaviour of strongly viscous hydroxyl liquids in shear, it was of interest to apply to the latter the hole model of Isakovitch and Chaban [5] according to which the structure of highly viscous liquids can be thought of as a microinhomogeneous medium consisting of inclusions of one component with an ordered molecular arrangement in a disordered one. The thermodynamic state of the ordered component is described (besides pressure and entropy) by a structural parameter, i.e. by the structure-dependent concentration of holes.

A compressional wave, as well as a shear one, changes the molecular order in the ordered phase and thereby the equilibrium concentration of holes. The equilibrium is restored by the diffusion of holes between the two components. The phase shift between the diffusive process and the incident wave, leading to a frequency-dependent shear modulus, is determined by the time of equilibrating the hole concentration within the ordered regions $\tau = a^2/2D$, where a is the radius of the ordered

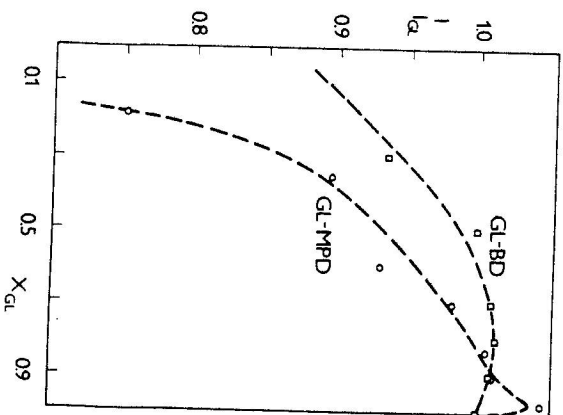


Fig. 3. Integral intensities of the OH stretching band reduced against that of glycerol as functions of the mole fraction of glycerol.

inclusions and D the diffusion coefficient of the holes, which may be identified with that of the molecules. In the case of shear deformations it is assumed that also a usual Maxwellian relaxation of shear stresses by energy exchange between different degrees of freedom takes place. According to the formalism of Isakovitch and Chaban, the relaxational compressional modulus, $K_r = K_\infty - K_0$, as well as the limiting shear modulus, G_∞ , are approximately proportional to the volume fraction of the ordered component $\varphi = V_1/(V_1 + V_2)$, and therefore disappear simultaneously at a temperature T_0 with $\varphi = 0$, i.e. at the temperature at which the ordered component disappears. Consequently, at $T \geq T_0$ all positions of the molecules become equally probable and $kT_0 = U$ is the depth of the potential well of the selfconsistent field of intermolecular interactions. From the linear equations $G_\infty = aT + b$ with parameters determined by the Gauss method, the temperature T_0 and the corresponding depths of the potential wells were calculated (Table 1). The potential well depths per mole, $\bar{u} = UN_A$, were plotted as functions of the mole fraction of glycerol in Fig. 4.

Table 1
Parameters of the linear equation $G_\infty = aT + b$, their standard errors S_a and S_b , T_0 and the depth of the potential well $\bar{u}(x_{GL})$ —mole fraction of glycerol).

Liquid	$10^7 a$ $\text{Nm}^{-2} \text{K}^{-1}$	b 10^6Nm^{-2}	S_a $10^5 \text{nm}^{-2} \text{K}^{-1}$	S_b 10^6Nm^{-2}	T_0 K	\bar{u} 10^3Jmol^{-1}
GL	1.688	7.383	13.946	3.206	437.3	3.636
MPD	1.327	4.095	2.632	0.608	308.6	2.566
BD	0.910	3.730	0.577	0.129	409.9	3.408
GL-MPD						
$x_{GL} = 0.185$	1.885	5.920	4.942	1.143	314.1	2.612
$x_{GL} = 0.355$	1.905	6.451	9.521	2.262	2.816	
$x_{GL} = 0.552$	2.157	7.748	4.703	1.090	3.593	2.987
$x_{GL} = 0.704$	2.145	8.120	4.565	2.080	3.786	3.148
$x_{GL} = 0.828$	1.722	7.381	4.389	1.038	4.287	3.564
$x_{GL} = 0.912$	1.760	7.563	6.007	1.396	4.296	3.572
$x_{GL} = 0.968$	1.758	7.504	4.964	1.167	4.269	3.550
GL-BD						
$x_{GL} = 0.295$	1.684	6.129	5.359	1.211	364.0	3.027
$x_{GL} = 0.495$	1.892	7.045	8.160	1.868	372.4	3.096
$x_{GL} = 0.695$	1.927	7.550	18.307	4.211	391.7	3.257
$x_{GL} = 0.796$	1.621	7.022	18.604	4.234	3.603	
$x_{GL} = 0.898$	1.669	7.287	4.037	0.925	436.7	3.631

V. IR SPECTRA

The integral intensities of the OH stretching vibration band ($2800 \div 3800 \text{ cm}^{-1}$) of the liquids under test normalized against that of glycerol are given in Fig. 3 as functions of composition. The maxima of the normalized intensities ($x_{GL} \approx 0.8$ and $x_{GL} \approx 0.9$ for the GL-BD and GL-MPD mixtures, respectively) may be considered to correspond approximately to the most stable compositions, i.e. to compositions of most pronounced hydrogen-bond interactions (although such an interpretation is strictly applicable only if autocomplexation does not occur in the pure components [16, 17]).

VI. ACTIVATION ENERGIES OF MOLECULAR FLOW

Within limited temperature intervals, the temperature dependence of the mean relaxation time of the studied liquids defined as $\tau = \eta/G_\infty$ may be described approximately by the following exponential equation $\tau = \tau_0 \exp(\epsilon_r/kT)$, where ϵ_r is the apparent activation free energy of molecular flow, i.e. the potential barrier a molecule must overcome in order to jump from one lattice site to another of

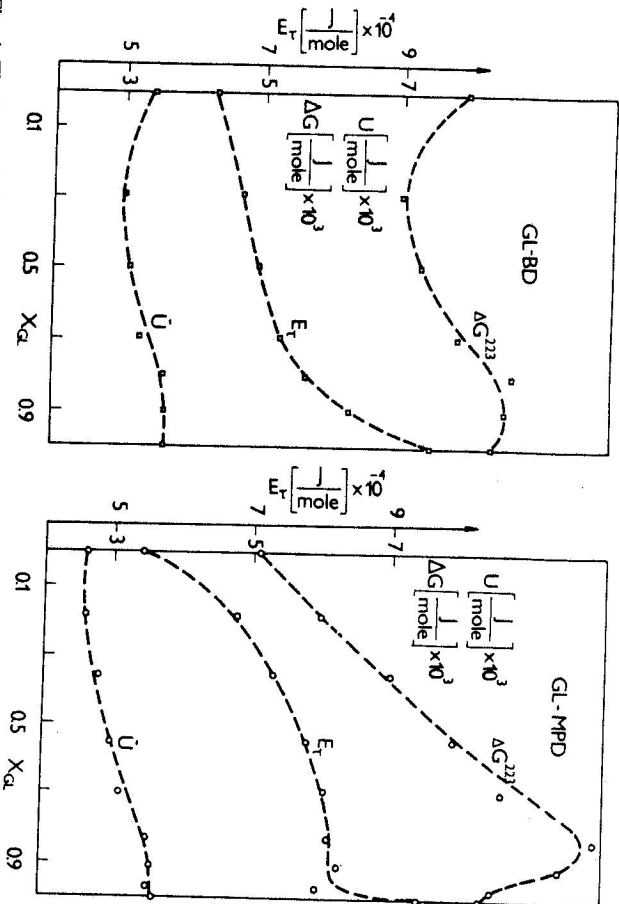


Fig. 4. The free enthalpy of rupture of one mole of hydrogen bonds at 223 K, ΔG , the depth of the potential well per mole, u , and the potential barriers restraining molecular translation per mole, E_r , vs mole fraction of glycerol.

lower free energy and τ_0 is the period of oscillations of the molecule in the potential well. The activation free energies per mole, $E_r = N_A \epsilon$, calculated from the plots of $\ln \tau$ against $1/T$ are shown in Fig. 4 as functions of the mole fraction of glycerol.

VII. DISCUSSION AND CONCLUSIONS

For the three polyhydroxylalcohols in question, the ΔS values increase in the sequence $GL < BD < MPD$ as could be expected, since the rupture of one hydrogen bond in BD produces a larger increase in the number of possible configurations than it does in GL where the two other bonds still reduce the molecular configurations available. The increase in ΔS of about 100% between BD and MPD is doubtlessly due to the additional $-\text{CH}_2$ group of the latter, which leads to a considerable increase in the number of possible configurations when the hydrogen bonds are broken off. Thus the ratio of broken to unbroken bonds $\exp(-\Delta G/RT) = \exp(-1.256 \times 10^4/RT + \Delta S/R)$ is entropy controlled and is increasing with the decreasing number of hydroxyl groups per molecule and with the increasing variety of conformations of the alcohol molecule. However, in the

binary liquids studied, ΔS and thereby the stability of the hydrogen bonded structures do not change monotonically with the mean number of hydroxyl groups per molecule (Fig. 2). The most stable hydrogen-bonded structures appear within the concentration range of glycerol $x_{GL} \approx 0.8 \div 0.9$ that roughly corresponds to the concentration range of maximum positive deviations of the shear rigidity from additivity (Fig. 5). The GL-BD system shows a maximum ΔS at $x_{GL} \approx 0.3$ that however is not reflected in the concentration dependence of the compliance.

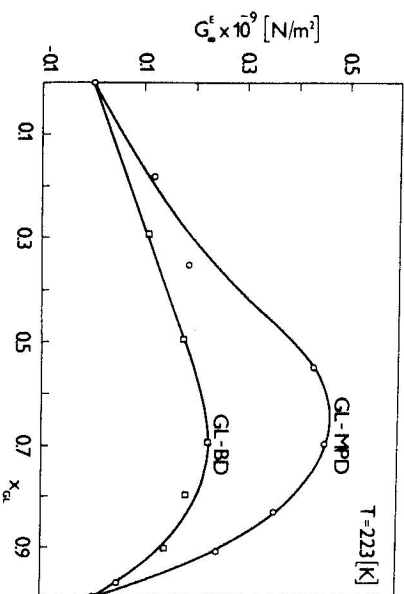


Fig. 5. "Excessive" rigidity defined as deviation of the limiting modulus from additivity, $G_e^E = G_e - (G_{e,1}x_1 + G_{e,2}x_2)$ vs mole fraction of glycerol.

The above thermodynamic conclusions are rather compatible with the normalized integral intensities calculated from the IR spectra (Fig. 3): the concentrations of maximum intensity ($x_{GL} \approx 0.8$ and $x_{GL} \approx 0.9$ for the GL-BD and GL-MPD systems, respectively) correspond rather well with the ΔS minima in Fig. 2 and, furthermore, the slower trop of the intensity curve of the GL-BD system indicates a strengthening of hydrogen bonding at higher diol concentrations in the GL-BD system in comparison with the GL-MPD one. This remains in rather good qualitative agreement with the ΔS curves (Fig. 2): for mole fractions of glycerol smaller than 0.5, the entropies of rupture of one mole of hydrogen bonds in the GL-BD system are smaller than those in the GL-MPD one.

The free volume defined as $V_f = V - V_0$ is plotted against mole fraction of glycerol in Fig. 6, which shows that within the limits $x_{GL} = 1.0 \div 0.5$ the free volumes in both systems are very close to each other and remain almost constant, i.e. the presence of the diols has a negligible effect on the intermolecular distances. At higher diol concentrations, the spacing of the molecules becomes more similar to that in pure diols, while surprisingly, the free volume in MPD and in the

GL-MPD mixtures are larger than in BD and in the GL-BD mixtures although one could expect the additional methyl group of MPD to act as a space filling factor. However, according to EQ. (2), the limiting compliance is determined not by the free volume but by the ratio V_F/V as well as by the energy term $\exp(-\Delta G/RT)$. With decreasing temperature, the latter term, i.e. the fractional number of broken hydrogen bonds, decreases much faster than the fractional free volume (as

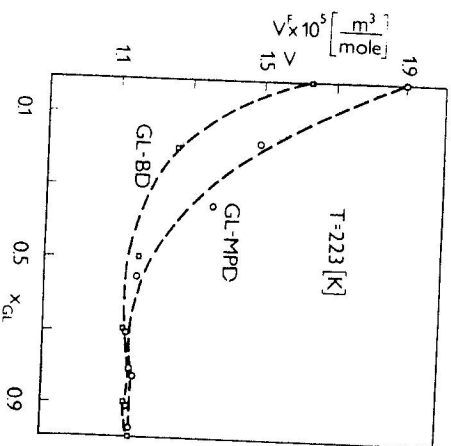


Fig. 6. Plot of molar free volume, $V^F = V - V_{\infty}$, vs mole fraction of glycerol.

illustrated in Fig. 7). Consequently, the shear compliance at lower temperatures is controlled mainly by the free volume since the fraction of broken bonds is negligible. The only exceptions are MPD and GL-MPD mixtures of $x_{Gl} < 0.2$, since in those liquids the V_F/V and $\exp(-G/RT)$ terms remain comparable up to 263 K because of the relatively high ΔS values.

It may be concluded that the simple relationship between the shear compliance and hydrogen-bond density postulated by Madigosky et al. constitutes strong evidence for the importance of the free volume in determining the shear elasticity of supercooled hydrogen-bonded liquids. As already stressed by Madigosky et al., Eq. (2) is capable of giving a satisfactory explanation of the approximately linear variation of the shear rigidity with temperature since, within the temperature limits available for measurements, the shear rigidity is nearly proportional to the reciprocal of free volume which is varying slowly with temperature.

There is a satisfactory correlation between the concentration dependence of the depth of the potential well, U , and that of the entropy change ΔS accompanying the rupture of one mole of hydrogen bonds (or the corresponding free enthalpy ΔG): a) the ΔS minima (or the ΔG maxima) correspond to the highest U values at

low diol concentrations, b) for the GL-BD system, the maximum of ΔS at $x_{Gl} \approx 0.3$, indicating a less stable structure of this composition, corresponds to the U minimum, c) in the case of GL-MPD mixtures of higher diol concentrations, the monotonic increase in ΔS is consistent with the corresponding U decrease. The high stability of diluted diol solutions in glycerol is confirmed by the maxima of the normalized integral intensities of the OH stretching band (Fig. 3).

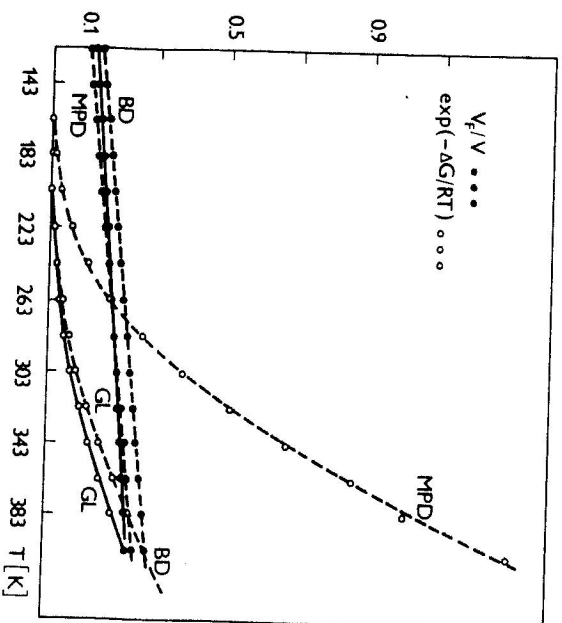


Fig. 7. The fractional free volume, V^F/V , and the ratio of broken to unbroken bonds, $\exp(-\Delta G/RT)$, as a function of temperature for glycerol, butanediol-1,3 and 2-methylpentanediol-2,4.

The depths of the potential well per mole, $\bar{u} = UN_A$, and the mean molar free energies, ΔG , are of the same order of magnitude although they arise from quite different and independent molecular pictures of the liquids (Fig. 4).

The free energy barriers, E , are one order of magnitude higher than the well depth potentials, \bar{u} , and free enthalpies ΔG , and vary more smoothly with composition than the latter (Fig. 4). This indicates that the shear viscosity, $\eta_s = G_{\infty} \tau = G_{\infty} \tau_0 \exp(-E_s/RT)$ (where G_{∞} varies slowly with temperature and τ_0 may be assumed to be independent of temperature), is not seriously affected by molecular interactions of the hydrogen bonding type but rather by the probability that a molecule having sufficient translational energy will find in its neighbourhood a free space to jump, i.e. in terms of the hole model, by the concentration of holes. The results of the above analysis of the rheological properties of the hydroxyl liquids in the light of the concept of hydrogen-bond determined shear compliance

and of the hole diffusion model constitute strong evidence that those models are capable of giving a physically acceptable interpretation of the behaviour of hydroxyl liquids in shear despite of the simplicity of the assumed molecular pictures of those liquids.

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