ARCHIVES OF ACOUSTICS
9, 3, 363-380 (1984)

DYNAMIC AND STATIC VISCOSITY AND ELASTICITY MODULI OF BINARY MIXTURES OF POLYHYDROXYALCOHOLS

MAREK WACIŃSKI, EDWARD ZORĘBSKI, KRZYSZTOF BEBEK

Institute of Chemistry, Silesian University
(40-006 Katowice, ul. Szkolna 9)

This paper presents the results of measurements of viscosity and mechanical shear impedance, for frequencies of 0.5, 500 and 600 MHz, of liquid mixtures of glycerol-2-methylpentanediol-2.4 and glycerol-butanediol-1.3. The components of mechanical shear impedance, dynamic viscosities, relaxation times and limiting shear moduli were calculated.

This permitted the determination of the reaction of the liquids under study to shear deformation over a wide frequency range, including viscous, viscoelastic and pure elastic reactions.

1. Introduction

A large number of interesting papers have been published recently on the viscoelasticity and structural relaxation of non-polymerised liquids, both associated and non-associated [1, 2, 3].

In the case of associated liquids both the bulk and shear viscosities relax over roughly the same frequency range, i.e. the respective relaxation times are very close [4, 5], in contrast to Knesser liquids, where thermal relaxation occurs. In addition the relaxation times show approximately the same temperature dependence. It can thus be expected that the molecular mechanisms of the two processes are similar.

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 one, i.e. the relaxation of tensions which occur as a result of bulk and stuctural deformations, but not to temperature functions (close to 277 K the water compression is practically isothermal), it can be assumed that also in other associated liquids the bulk viscosity is related to structural changes, where hydrogen bonds break and reproduce again in the acoustic field. Obviously, the viscous relaxation (where viscosity decreases as frequency increases), observed in shear impedance measurements, must be related to both the structure of the liquid and intermolecular reactions, where hydrogen bonds play the main role. Therefore the phenomena observed for bulk and structural deformations of the medium, effected by longitudinal or transverse acoustic waves, are strictly related to the structure of the liquid. Thus, any change in the thermodynamic parameters (e.g. pressure, or temperature), or change in the composition of the liquid, should be reflected not only in the viscosity, but also in the elasticity moduli and relaxation times, determined from acoustic wave propagation, and in the impedance of transverse waves.

In the present paper, the limiting shear elasticity moduli, dynamic and static viscosities, and relaxation times, were determined from shear impedance measurements in mixtures of polyhydroxyalcohols (glycerol-2-methylpentanediol-2.4 and glycerol-butanediol-1.3).

It is shown on the basis of the investigations carried out that the shear elasticity and dynamic viscosity of polyhydroxyalcohols are affected not only by intermolecular hydrogen bonds, but also by an additional factor, related to the spatial structure (the so-called steric factor).

This would suggest the usefulness of acoustical investigation methods, based on simple shear, for structural studies of liquids and liquid mixtures.

2. Measurement quantities

The investigations have shown that the viscosity of a liquid depends on the deformation frequency and is lower under the conditions of rapidly changing shear deformations than for very slow deformation. The decrease in the viscosity is accompanied by an increase in the shear elasticity of the liquid, and thus an increase in the shear modulus G. In the case of high-frequency shear strain the shear elasticity reaches a limiting value G_∞. G_∞ is a quantity related to the molecular structure of a given liquid. The reaction of the liquid to shear stress is determined acoustically by measuring the so-called characteristic shear impedance Z, which is the ratio of shear stress to acoustic velocity.

For a solid, it is a real quantity, and is

$$Z = \varrho c_T = (\varrho G)^{1/2}, \tag{1}$$

where ϱ – density of the medium, c_T – propagation velocity of transverse waves in the medium, G – shear elasticity modulus.

In the case of a viscoelastic liquid the characteristic shear impedance Z_c^* is a complex quantity, similarly to the shear elasticity modulus G^*:

$$Z_c^* = R_c + jX_c, \quad G^* = G' + jG'';$$

thus, it follows that

$$Z_c^* = (\varrho G^*)^{1/2}. \tag{2}$$

With sufficiently high measurement frequency the imaginary component of the impedance X_c is much lower than the real component R_c, and thus can be practically neglected over this range. Hence, the high-frequency shear elasticity modulus is

$$G_\infty = \frac{R_c^2}{\varrho}, \tag{3}$$

while its inverse is the shear compliance J_∞, defined as

$$J_\infty = \frac{1}{G_\infty} = \frac{\varrho}{R_c^2}. \tag{4}$$

The viscosity isotherms, calculated from the Arrhenius equation of ideal binary mixtures, can be represented in the following way:

$$\log\eta(x_2, T) = x_1\log\eta_1(T) + x_2\log\eta_2(T), \tag{5}$$

where $\eta_i(T)$ and x_i are respectively the viscosity and the mole fraction of a pure component.

In order to explain deviations from the additivity of viscosity as a function of composition, GRUNBERG and NISSAN's [6] modification of equation (5) was used in the form

$$\log\eta(x_2, T) = x_1\log\eta_1(T) + x_2\log\eta_2(T) + 2x_1x_2\Gamma, \tag{6}$$

where Γ is considered the measure of deviation from the ideal behaviour of binary liquid mixtures (for $\Gamma = 0$ – ideal mixture – equation (6) becomes (5)). For $\Gamma > 0$ (positive deviation from additivity) negative deviation from the Raoult law occurs, and for $\Gamma > 0$ (negative deviation from additivity) we have positive deviation from the Raoult law [7], which involves a linear dependence of the partial pressure and total pressure as a function of the mole fraction.

The value of the mean Maxwell relaxation time $\bar{\tau}_s$ is calculated in the following way:

$$\bar{\tau}_s = \frac{\eta_s}{G_\infty}, \tag{7}$$

where η_s – static viscosity (measured by the stationary method).

In turn, the dynamic viscosity is defined in the following way:

$$\eta_d = \frac{G''}{\omega}, \tag{8}$$

where ω – angular frequency ($\omega = 2\pi f$), f – frequency.

3. Experimental part

The investigations used pure butanediol-1.3 (manufactured by Koch – Light Laboratories, U.K.), pure 2-methylpentanediol-2.4 (B.D.H. Ltd., U.K.) and glycerol, pure for analysis (P.O.Ch., Gliwice, Poland). The alcohols investigated were dehydrated by boiling under reduced pressure for about 8 hours. The water content, measured by the Fischer method, did not exceed 0.35 per cent of water by weight. The alcohol solutions were prepared by the weighing method.

3.1. Static viscosity measurement

Viscosity was measured as a function of temperature with error less than 2 per cent by using the Höppler BH 2 (GDR) viscosimeter over the temperature range 263–303 K, at temperature stability of 0.05 deg.

Since both alcohols and their mixtures, *AB*-1 to *AB*-7 and *AC*-1 to *AC*-5, satisfy the dependence proposed by Meister [8], $\log\eta = a + bT^{-3}$ (where a and b are constants determined by the least squares method), it was used to extrapolate viscosity over the whole measurement range. The results are listed in Table 1, which also shows the correlation coefficient r, defined as

$$r = \frac{\sum\limits_{i=1}^{n}(x_i-\overline{x})(y_i-\overline{y})}{\sqrt{\sum\limits_{i=1}^{n}(x_i-\overline{x})^2\sum\limits_{i=1}^{n}(y_i-\overline{y})^2}}, \tag{9}$$

where $x_i = T_i^{-3}$, $y_1 = \log\eta_i$; $\overline{x}$ and $\overline{y}$ are the corresponding mean values.

Table 1. The temperature dependence of viscosity (T expressed in K)

Liquid	a	$b\times10^{-7}$	Correlation coefficient
Glycerol *A*	−3.6995	9.6632	0.9998
Glycerol – Diol *B* (2-methylpentanediol-2.4)			
AB 1. $x_A = 0.185$	−4.4389	8.4821	0.9999
AB 2. $= 0.355$	−4.2686	8.7614	0.9999
AB 3. $= 0.552$	−4.1479	9.2125	0.9999
AB 4. $= 0.704$	−4.0477	9.4041	0.9998
AB 5. $= 0.828$	−3.9490	9.3014	0.9999
AB 6. $= 0.912$	−3.9034	9.5047	0.9999
AB 7. $= 0.968$	−3.8433	9.1510	0.9999
Glycerol – Diol *C* (Butanediol-1.3)			
AC 1. $x_A = 0.295$	−3.8489	7.9549	0.9998
AC 2. $= 0.495$	−3.8162	8.2019	1.0000
AC 3. $= 0.695$	−3.8205	8.5026	0.9999
AC 4. $= 0.796$	−3.8822	8.8223	1.0000
AC 5. $= 0.898$	−3.7935	9.5152	0.9998
Diol *B*	−3.9021	7.0763	0.9989
Diol *C*	−3.9602	7.3287	0.9995

3.2. Mechanical shear impedance measurements

The measurements of mechanical shear impedance were carried out:

a) at a frequency of 0.520 MHz using the devices UWE-1 and UWE-2 (built at the Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw, Poland), over the temperature range 245–293 K. The measurement principles were described in many papers [9], the measurement error, given by the producer, is ±5 per cent. The measured dynamic viscosity, as calculated from formula (8), was given in Table 2. This table also shows the ratio of the dynamic to the static viscosity.

b) at frequencies of 500 and 650 MHz using a prototype measurement device UWE-700, built at the Department of Physical Acoustics, Institute of Fundamental Technological Research, Polish Academy of Sciences, by means of the coefficient of shear wave reflection (k) at the liquid-solid interface. The measurement error did not exceed 10 per cent.

The measurements were carried out over the temperature range 218–253 K, determined with accuracy up to 0.1 deg. The results were calculated from the relation

$$R_c = Z_q \frac{1-k}{1+k}, \tag{10}$$

where Z_q – shear impedance of a $LiNbO_3$ crystal.

After calculating the value of R_c, the limiting moduli G_∞ were determined from relation (3) and the behaviour of its change defined as a function of temperature. The results are shown in Figs. 1 and 2.

Since the temperature dependence of G_∞ was found to be linear over the elastic range, a $G_\infty = m + nT$ type equation, where m and n are constants determined by the least squares method, was used for interpolation. The results and the correlation coefficient r are listed in Table 3.

The results are also shown graphically in the form of the dependence of G_∞ on the mole fraction of glycerol (Figs. 3 and 4). Figures also show dependencies of the relaxation times τ_s on the mole fraction of glycerol for three temperatures of 233, 253 and 273 K. The mean Maxwell relaxation time was calculated from formula (7), while its values are listed in Table 2 and shown in Figs. 7 and 8.

4. Discussion of results and conclusions

The measurements carried out on the high-frequency shear moduli and viscosity permit the following conclusions to be drawn:

1. The limiting shear modulus G_∞ of glycerol is over the whole temperature range higher than that of the mixtures of 2-methylpentanediol-2.4 and butanediol-1.3 with glycerol, despite the longer and more branched (particularly

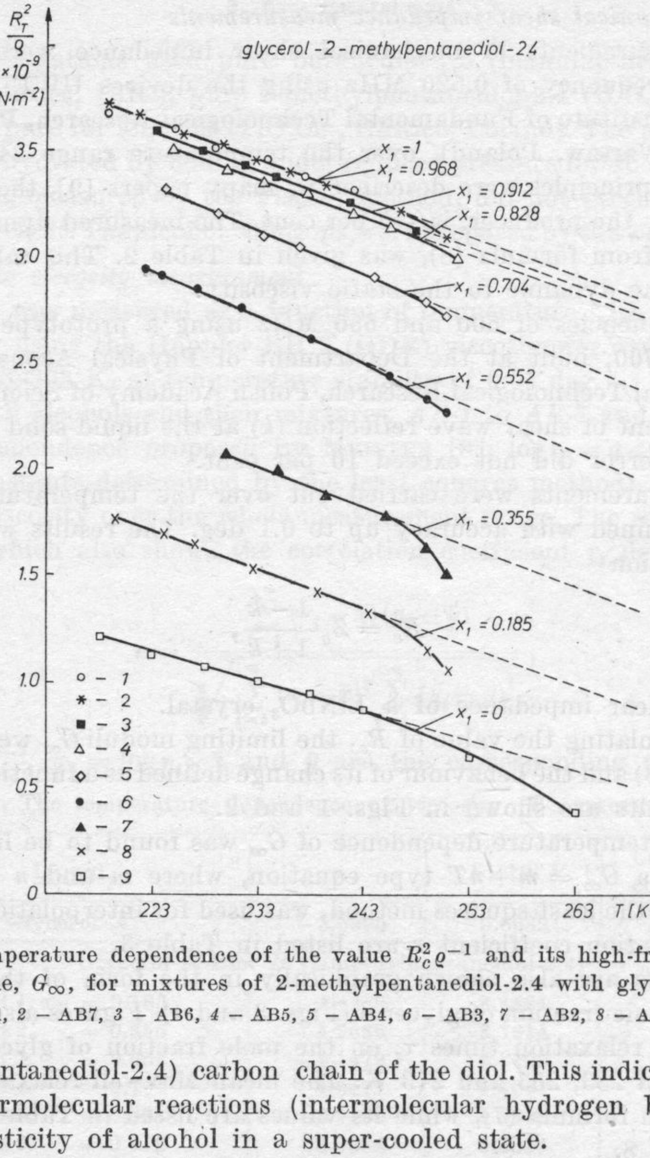

Fig. 1. The temperature dependence of the value $R_C^2 \varrho^{-1}$ and its high-frequency limiting value, G_∞, for mixtures of 2-methylpentanediol-2.4 with glycerol

1 – glycerol, 2 – AB7, 3 – AB6, 4 – AB5, 5 – AB4, 6 – AB3, 7 – AB2, 8 – AB1, 9 – diol

in 2-methylpentanediol-2.4) carbon chain of the diol. This indicates a decisive effect of intermolecular reactions (intermolecular hydrogen bonds) on the structural elasticity of alcohol in a super-cooled state.

The limiting shear modulus of the mixtures varies within the limits of the measurement error monotonously, depending on the composition of the mixture, but these changes are not a linear function of the mole fraction of the component (Figs. 3 and 4).

Over the range of low diol concentration (up to $x_{\mathrm{diol}} = 0.2$ for 2-methylpentanediol-2.4 and up to $x_{\mathrm{diol}} = 0.1$ for butanediol-1.3), its presence hardly affects the limiting shear modulus. The smooth, although not linear, behaviour of G_∞ as a function of the mole fraction of glycerol indicates that the elastic reaction to shear stress decreases as the cross-linking increases (i.e. with increasing density of hydroxyl groups forming hydrogen bonds).

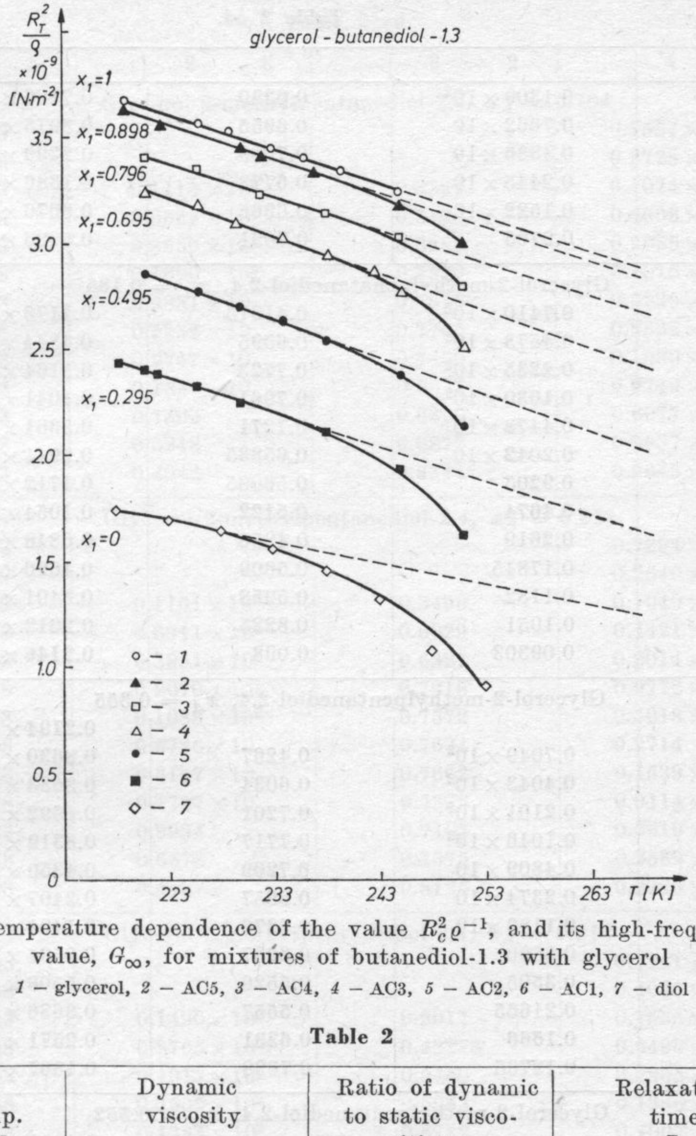

Fig. 2. The temperature dependence of the value $R_c^2 \varrho^{-1}$, and its high-frequency limiting value, G_∞, for mixtures of butanediol-1.3 with glycerol

1 — glycerol, *2* — AC5, *3* — AC4, *4* — AC3, *5* — AC2, *6* — AC1, *7* — diol

Table 2

Temp. [K]	Dynamic viscosity η_d [Nsm^{-2}]	Ratio of dynamic to static viscosities η_d/η_s	Relaxation time $\bar{\tau}_s$ [s^{-1}]
1	2	3	4
	Glycerol		
233			0.2441×10^{-5}
238			0.8476×10^{-6}
243	0.2083×10^{3}	0.1978	0.3213×10^{-6}
248	0.1244×10^{3}	0.2954	0.1318×10^{-6}
253	0.7341×10^{2}	0.4063	0.5811×10^{-7}
258	0.4128×10^{2}	0.4991	0.2734×10^{-7}
263	0.2359×10^{2}	0.58805	0.1364×10^{-7}

Table 2 cd.

1	2	3	4
268	0.1309×10^{2}	0.6380	0.7186×10^{-8}
273	0.7662×10	0.6955	0.3975×10^{-8}
278	0.4386×10	0.7099	0.2299×10^{-8}
283	0.2445×10	0.6778	0.1386×10^{-8}
288	0.1522×10	0.6965	0.8676×10^{-9}
293	0.9705	0.7091	0.5623×10^{-9}
Glycerol-2-methylpenatanediol-2.4, $x_A = 0.185$			
233	0.7410×10^{2}	0.41315	0.1176×10^{-6}
238	0.4573×10^{2}	0.6595	0.4844×10^{-7}
243	0.2235×10^{2}	0.7723	0.2164×10^{-7}
248	0.1030×10^{2}	0.7961	0.1041×10^{-7}
253	0.4478×10	0.7271	0.5361×10^{-8}
258	0.2042×10	0.65835	0.2941×10^{-8}
263	0.9205	0.56005	0.1712×10^{-8}
268	0.4674	0.5122	0.1054×10^{-8}
273	0.2619	0.4956	0.6848×10^{-9}
278	0.17845	0.5609	0.4696×10^{-9}
283	0.1182	0.5958	0.3401×10^{-9}
288	0.1051	0.8225	0.2612×10^{-9}
293	0.09303	0.098	0.2146×10^{-9}
Glycerol-2-methylpentanediol-2.4, $x_A = 0.355$			
233			0.2194×10^{-6}
238	0.7049×10^{2}	0.4267	0.8630×10^{-7}
243	0.4043×10^{2}	0.6034	0.3683×10^{-7}
248	0.2101×10^{2}	0.7201	0.1692×10^{-7}
253	0.1046×10^{2}	0.7717	0.8319×10^{-8}
258	0.4809×10	0.7209	0.4350×10^{-8}
263	0.2374×10	0.6657	0.2407×10^{-8}
268	0.1183×10	0.6276	0.1401×10^{-8}
273	0.6690	0.6237	0.8594×10^{-9}
278	0.3505	0.5520	0.5508×10^{-9}
283	0.21665	0.5557	0.3686×10^{-9}
288	0.1566	0.6331	0.2571×10^{-9}
293	0.12785	0.7898	0.1867×10^{-9}
Glycerol-2-methylpentanediol-2.4, $x_A = 0.552$			
233			0.4858×10^{-6}
238	0.1352×10^{3}	0.2872	0.1802×10^{-6}
243	0.8392×10^{2}	0.4606	0.7276×10^{-7}
248	0.4748×10^{2}	0.6246	0.3172×10^{-7}
253	0.2536×10^{2}	0.7472	0.1483×10^{-7}
258	0.1294×10^{2}	0.8030	0.7387×10^{-8}
263	0.6648×10	0.8224	0.3900×10^{-8}
268	0.3435×10	0.8051	0.2171×10^{-8}
273	0.3435×10	0.71715	0.1269×10^{-8}
278	0.1691×10	0.6470	0.7764×10^{-9}
283	0.8790	0.6843	0.4954×10^{-9}
288	0.5565	0.6756	0.3287×10^{-9}
293	0.3407	0.8766	0.2264×10^{-9}

Table 2 cd.

1	2	3	4
Glycerol-2-methylpentanediol-2.4, $x_A = 0.704$			
233			0.7557×10^{-6}
238			0.2728×10^{-6}
243	0.1113×10^{3}	0.3567	0.1074×10^{-6}
248	0.6528×10^{2}	0.5108	0.4568×10^{-7}
253	0.3639×10^{2}	0.6485	0.2085×10^{-7}
258	0.1920×10^{2}	0.7322	0.1015×10^{-7}
263	0.9831×10	0.7618	0.5239×10^{-8}
268	0.5232×10	0.7745	0.2852×10^{-8}
273	0.2747×10	0.7450	0.1630×10^{-8}
278	0.1394×10	0.6635	0.9749×10^{-9}
283	0.7863	0.6320	0.6077×10^{-9}
288	0.5248	0.6872	0.3937×10^{-9}
293	0.4042	0.8344	0.2643×10^{-9}
Glycerol-2-methylpentanediol-2.4, $x_A = 0.828$			
233			0.7294×10^{-6}
238			0.2640×10^{-6}
243	0.1161×10^{3}	0.3496	0.1040×10^{-6}
248	0.6911×10^{2}	0.5029	0.4421×10^{-7}
253	0.3851×10^{2}	0.6327	0.2014×10^{-7}
258	0.2070×10^{2}	0.7216	0.9772×10^{-8}
263	0.1083×10^{2}	0.7572	0.5018×10^{-8}
268	0.5726×10	0.7634	0.2714×10^{-8}
273	0.3157×10	0.7662	0.1539×10^{-8}
278	0.1747×10	0.7396	0.9114×10^{-9}
283	0.9994	0.7103	0.5616×10^{-9}
288	0.6578	0.7575	0.3589×10^{-9}
293	0.44975	0.8125	0.2373×10^{-9}
Glycerol-2-methylpentanediol-2.4, $x_A = 0.912$			
233			0.1141×10^{-5}
238			0.4035×10^{-6}
243	0.1490×10^{3}	0.2917	0.1556×10^{-6}
248	0.8765×10^{2}	0.42275	0.6490×10^{-7}
253	0.4917×10^{2}	0.5450	0.2905×10^{-7}
258	0.2503×10^{2}	0.5983	0.1386×10^{-7}
263	0.1384×10^{2}	0.6742	0.7007×10^{-8}
268	0.7551×10	0.7111	0.3736×10^{-8}
273	0.4231×10	0.7346	0.2091×10^{-8}
278	0.2451×10	0.7518	0.1223×10^{-9}
283	0.1405×10	0.7315	0.7449×10^{-9}
288	0.8753	0.7462	0.4710×10^{-9}
293	0.6012	0.8120	0.3082×10^{-9}
Glycerol-2-methylpentanediol-2.4, $x_A = 0.968$			
233			0.6996×10^{-6}
238			0.2576×10^{-6}
243	0.1247×10^{3}	0.3746	0.1031×10^{-6}
248	0.7422×10^{2}	0.5312	0.4447×10^{-7}
253	0.4254×10^{2}	0.6782	0.2053×10^{-7}

Table 2 cd.

1	2	3	4
258	0.2174×10^{2}	0.7265	0.1009×10^{-7}
263	0.1209×10^{2}	0.8015	0.5239×10^{-8}
268	0.6495×10	0.8125	0.2864×10^{-8}
273	0.3558×10	0.8024	0.1641×10^{-8}
278	0.2066×10	0.8054	0.9808×10^{-9}
283	0.1205×10	0.7823	0.6097×10^{-9}
288	0.7817	0.8157	0.3929×10^{-9}
293	0.5231	0.8501	0.2617×10^{-9}
2-methylpentanediol-2.4			
233	0.3359×10^{2}	0.6996	0.4794×10^{-7}
238	0.1770×10^{2}	0.8146	0.2323×10^{-7}
243	0.6731×10	0.6423	0.1206×10^{-7}
248	0.2845×10	0.5313	0.6673×10^{-8}
253	0.1306×10	0.4529	0.3916×10^{-8}
258	0.5069	0.3117	0.2428×10^{-8}
263	0.1937	0.2023	0.1587×10^{-8}
268	0.09713	0.1657	0.1091×10^{-8}
273	0.06843	0.1841	0.7894×10^{-9}
278			0.6017×10^{-9}
283			0.4817×10^{-9}
Butanediol-1.3			
233	0.3781×10^{2}	0.5692	0.4130×10^{-7}
238	0.2434×10^{2}	0.8328	0.1870×10^{-7}
243	0.1271×10^{2}	0.9253	0.9052×10^{-8}
248	0.6996×10	1.020	0.4656×10^{-8}
253	0.3700×10	1.030	0.2529×10^{-8}
258	0.2199×10	1.100	0.1444×10^{-8}
263	0.1478×10	1.290	0.8629×10^{-9}
268	0.9387	1.350	0.5373×10^{-9}
273	0.5544	1.280	0.3474×10^{-9}
278	0.2999	1.070	0.2326×10^{-9}
283	0.1745	0.9410	0.1608×10^{-9}
288			0.1144×10^{-9}
293			0.8368×10^{-10}
Glycerol-butanediol-1.3, $x_A = 0.295$			
233	0.9736×10^{2}	0.3636	0.1215×10^{-6}
238	0.5761×10^{2}	0.5246	0.5181×10^{-7}
243	0.3193×10^{2}	0.6599	0.2378×10^{-7}
248	0.1702×10^{2}	0.7484	0.1166×10^{-7}
253	0.9108×10	0.8033	0.6073×10^{-8}
258	0.4935×10	0.8283	0.3342×10^{-8}
263	0.2722×10	0.8286	0.1934×10^{-8}
268	0.1704×10	0.9011	0.1172×10^{-8}
273	0.9157	0.8079	0.7408×10^{-9}
278	0.4916	0.6981	0.4870×10^{-9}
283	0.3033	0.6708	0.3320×10^{-9}

Table 2 cd.

1	2	3	4
Glycerol-butadienol-1.3, x_A = 0,495			
288	0.2156	0.7205	0.2342×10^{-9}
293	0.1717	0.8433	0.1700×10^{-9}
233	0.1458×10^{3}	0.3423	0.1717×10^{-6}
238	0.9154×10^{2}	0.5075	0.7104×10^{-7}
243	0.5078×10^{2}	0.6552	0.3170×10^{-7}
248	0.2704×10^{2}	0.7598	0.1514×10^{-7}
253	0.1388×10^{2}	0.7998	0.7695×10^{-8}
258	0.7321×10	0.8188	0.4137×10^{-8}
263	0.3972×10	0.8209	0.2342×10^{-8}
268	0.2242×10	0.8184	0.1398×10^{-8}
273	0.1260×10	0.7799	0.8605×10^{-9}
278	0.7315	0.7398	0.5547×10^{-9}
283	0.4710	0.7521	0.3710×10^{-9}
288	0.2881	0.7040	0.2568×10^{-9}
293	0.2276	0.8273	0.1835×10^{-9}
Glycerol-butanediol-1.3, x_A = 0.695			
233			0.2350×10^{-6}
238	0.1255×10^{3}	0.4207	0.1008×10^{-6}
243	0.7218×10^{2}	0.5811	0.4338×10^{-7}
248	0.4186×10^{2}	0.7551	0.2003×10^{-7}
253	0.2347×10^{2}	0.8912	0.9861×10^{-8}
258	0.1193×10^{2}	0.9011	0.5143×10^{-8}
263	0.6258×10	0.8932	0.2827×10^{-8}
268	0.3217×10	0.8283	0.1631×10^{-8}
273	0.1734×10	0.7719	0.9831×10^{-9}
278	0.1034×10	0.7659	0.6171×10^{-9}
283	0.6931	0.8239	0.4020×10^{-9}
288	0.4199	0.7760	0.2711×10^{-9}
293	0.2982	0.8317	0.1887×10^{-9}
Glycerol-butanediol-1.3, x_A = 0.796			
233			0.3697×10^{-6}
238	0.1558×10^{3}	0.3486	0.1411×10^{-6}
243	0.9163×10^{2}	0.5095	0.5836×10^{-7}
248	0.5127×10^{2}	0.6585	0.2595×10^{-7}
253	0.2831×10^{2}	0.7870	0.1232×10^{-7}
258	0.1497×10^{2}	0.8496	0.6209×10^{-8}
263	0.7766×10	0.8530	0.3302×10^{-8}
268	0.4000×10	0.8104	0.1845×10^{-8}
273	0.2165×10	0.7759	0.1078×10^{-8}
278	0.1335×10	0.8903	0.5663×10^{-9}
283	0.8179	0.8103	0.4149×10^{-9}
288	0.5047	0.7856	0.2715×10^{-9}
293	0.3800	0.9119	0.1835×10^{-9}
Glycerol-butanediol-1.3, x_A = 0.898			
233			0.1525×10^{-5}
238			0.5383×10^{-6}
243	0.1790×10^{3}	0.2674	0.2072×10^{-6}

Table 2 cd.

1	2	3	4
248	0.1096×10^{3}	0.4040	0.8623×10^{-7}
253	0.6400×10^{2}	0.5391	0.3851×10^{-7}
258	0.3724×10^{2}	0.6817	0.1834×10^{-7}
263	0.1998×10^{2}	0.7453	0.9255×10^{-8}
268	0.1102×10^{2}	0.7954	0.4925×10^{-8}
273	0.6034×10	0.8039	0.2750×10^{-8}
278	0.3427×10	0.8070	0.1605×10^{-8}
283	0.2066×10	0.8263	0.9759×10^{-9}
288	0.1237×10	0.8104	0.6157×10^{-9}
293	0.7663	0.7959	0.4019×10^{-9}

Table 3. The temperature dependence of the limiting shear elasticity modulus $G_\infty = m+nT$ [Nm^{-2}]. Temperature in K

Liquid	$m\times10^{-9}$	$n\times10^{-7}$	Correlation coefficient
1	2	3	4
Glycerol *A*	7.3831	−1.6883	−0.9833
Glycerol-Diol *B* (2-methylpentanediol-2.4)			
AB 1. x_A = 0.185	5.9202	−1.8848	−0.9986
AB 2. x_A = 0.355	6.4504	−1.9046	−0.9975
AB 3. = 0.552	7.7481	−2.1565	−0.9991
AB 4. = 0.704	8.1202	−2.1449	−0.9991
AB 5. = 0.828	7.3807	−1.7218	−0.9987
AB 6. = 0.912	7.5626	−1.7603	−0.9965
AB 7. = 0.968	7.5043	−1.7578	−0.9980
Glycerol-Diol *C* (Butanediol-1.3)			
AC 1. x_A = 0.295	6.1291	−1.6837	−0.9989
AC 2. x_A = 0.495	7.0447	−1.8918	−0.9972
AC 3. = 0.695	7.5498	−1.9274	−0.9867
AC 4. = 0.796	7.0216	−1.6209	−0.9746
AC 5. = 0.898	7.2868	−1.6686	−0.9988
Diol *B*	4.0951	−1.3269	−0.9992
Diol *C*	3.7300	−0.9100	−1.000

The deviations of G_∞ from additivity with respect to the mole fraction vary for the two mixtures, depending on the temperature.

For 2-methylpentanediol-2.4 the deviation is positive over the whole concentration range with temperatures below 273 K. It reaches its maximum value for diol concentration $x_{\text{diol}} = 0.25$, i.e. for the mole ratio glycerol: diol = 3:1, suggesting particularly strong cross-linking of the mixture close to this concentration. In the case of butanediol-1.3 mixtures the deviation becomes positive over the whole concentration only at a temperature of 223 K. At higher temperatures the sign of deviation from additivity changes.

2. Figs. 5 and 6 show the dependence of log η on the mole fraction of glycerol for three temperatures of 253, 273 and 283 K. The dashed line represents the behaviour of the dependence of viscosity isotherms for ideal binary mixtures.

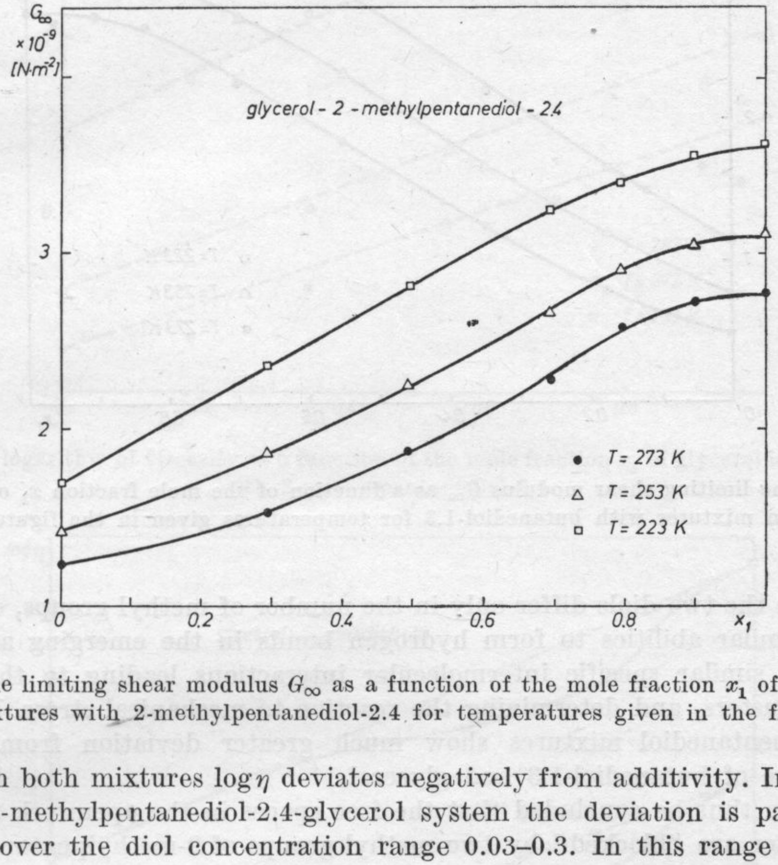

Fig. 3. The limiting shear modulus G_∞ as a function of the mole fraction x_1 of glycerol in mixtures with 2-methylpentanediol-2.4 for temperatures given in the figure

With both mixtures log η deviates negatively from additivity. In the case of the 2-methylpentanediol-2.4-glycerol system the deviation is particularly distinct over the diol concentration range 0.03–0.3. In this range there are also large irregularities, possibly indicating some structural peculiarities.

In contrast to 2-methylpentanediol-2.4-glycerol mixtures, in the glycerol-butanediol-1.3 system the deviation from additivity shows smooth (monotonous) behaviour, occurring over the diol concentration range 0.1–0.7, and when little more diol is added, no sharp viscosity drop results. Thus, there emerges a distinct effect of the density of OH^- groups, participating in the specific intermolecular interactions.

3. Similar deviations from additivity are characteristic of the mean relaxation time; where it is interesting to note a sharp drop in relaxation time, caused by a small addition of 2-methylpentanediol-2.4 to glycerol. This effect is not observed for mixtures of butanediol-1.3 and glycerol (Figs. 7 and 8).

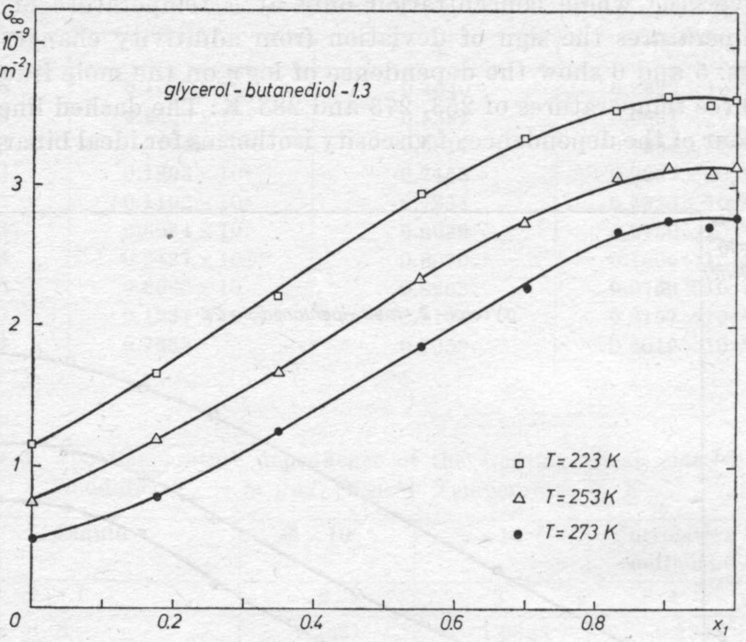

Fig. 4. The limiting shear modulus G_∞ as a function of the mole fraction x_1 of glycerol in mixtures with butanediol-1.3 for temperatures given in the figure

Since the two diols differ only in the number of methyl groups, one could expect similar abilities to form hydrogen bonds in the emerging associates, and thus similar specific intermolecular interactions leading to the formation of clusters, and determining the reaction to mechanical stress. However, 2-methylpentanediol mixtures show much greater deviation from ideality than those of butanediol-1.3 and glycerol.

It can thus be concluded that the free spaces in the openwork structure of a cluster are "blocked" by two methyl groups of 2-methylpentanediol-2.4, and that, in addition to cross-linking by hydrogen bonds, another steric factor occurs.

The results obtained indicate that peculiarities in the structure of the solutions under study are reflected in their behaviour under dynamic load. This seems to suggest the usefulness of rheological investigations based on pure stress (and thus not related to density and temperature changes) for studying the structure of liquid solutions, although it is so far impossible, in view of the necessary measurement frequency range of the order of 10^{12}–10^{13} Hz and in view of the impossibility of super-cooling over a sufficiently wide temperature range, to extend the studies to the most interesting range of aqueous solutions.

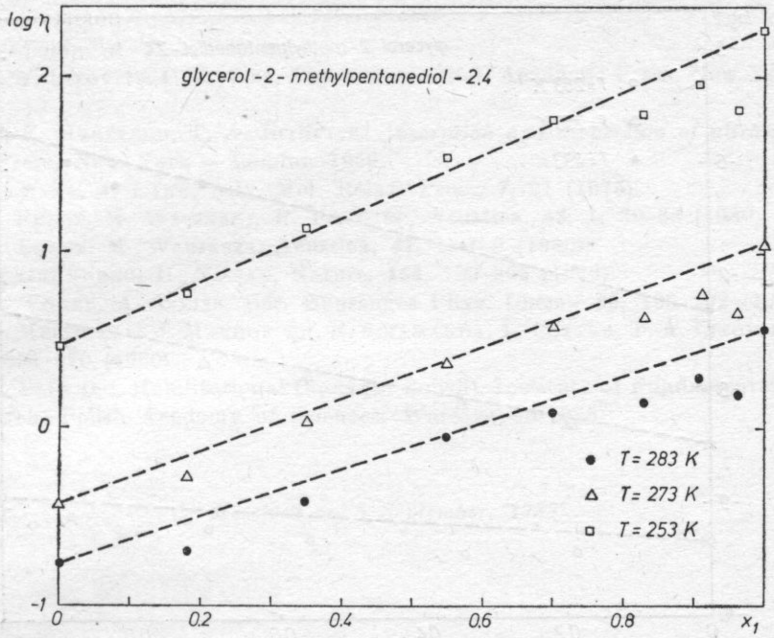

Fig. 5. The logarithm of viscosity as a function of the mole fraction x_1 of glycerol in mixtures with 2-methylpentanediol-2.4

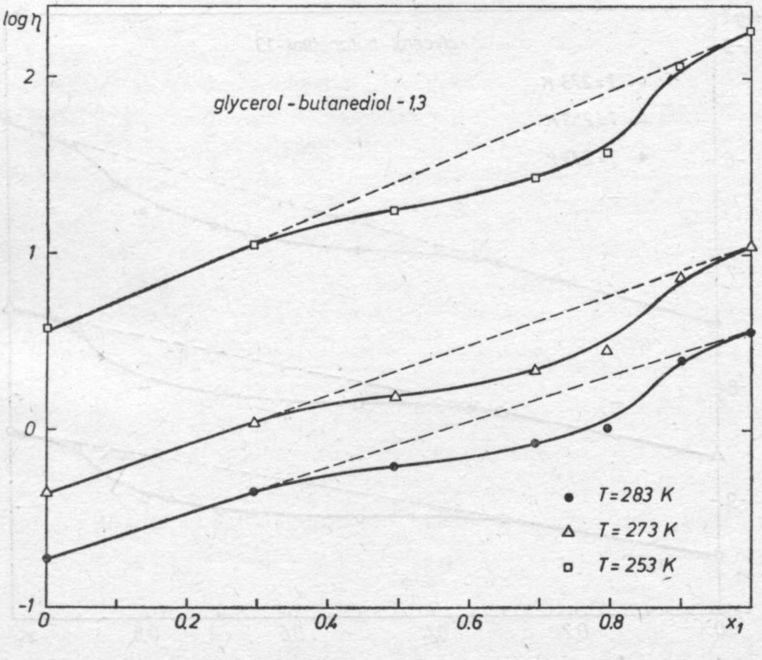

Fig. 6. The logarithm of viscosity as a function of the mole fraction x_1 of glycerol in mixtures with butanediol-1.3

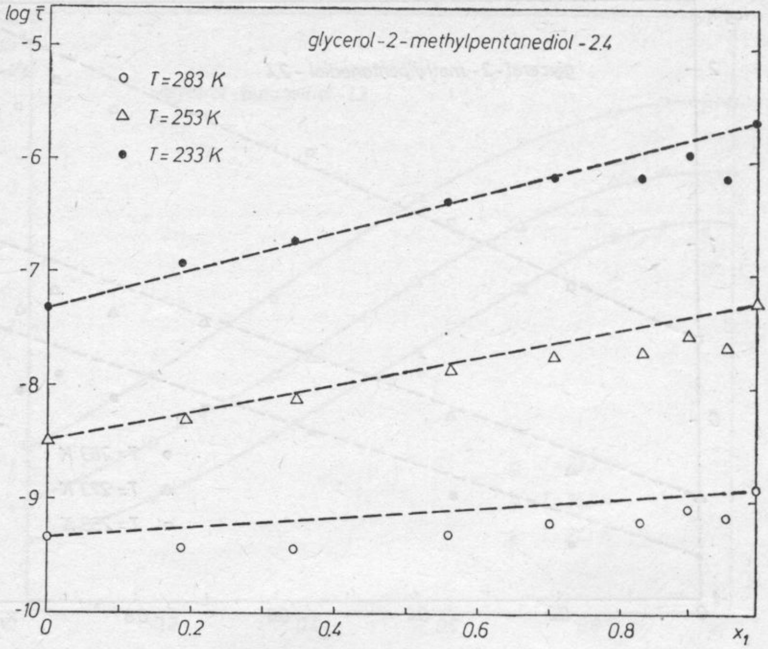

Fig. 7. The logarithm of the mean relaxation time as a function of the mole fraction x_1 of glycerol in mixtures with 2-methylpentanediol-2.4

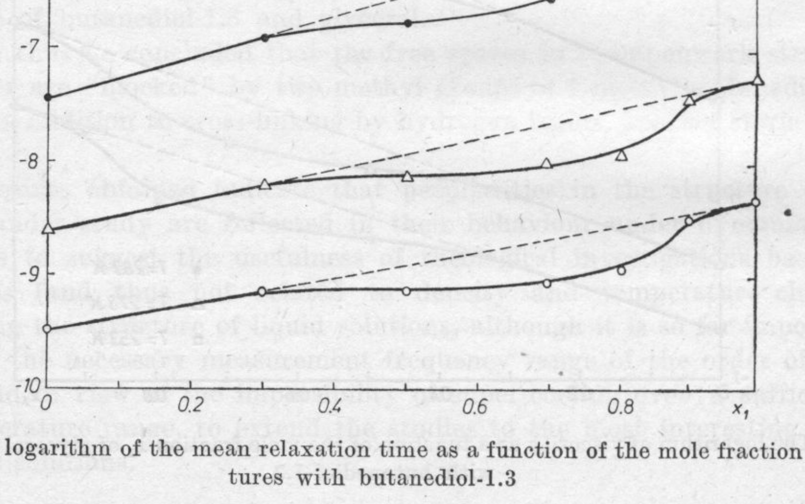

Fig. 8. The logarithm of the mean relaxation time as a function of the mole fraction in mixtures with butanediol-1.3

References

[1] T. A. LITOVITZ, C. DAVIES, *Physical acoustics*, Academic Press, New York – London 1965.

[2] K. F. HERZFELD, T. A. LITOVITZ, *Absorption and dispersion of ultrasonic waves*, Academic Press, New York – London 1959.

[3] R. ZANA, J. LANG, Adv. Mol. Relax. Proc., 7, 21 (1975).

[4] S. ERNST, M. WACIŃSKI, R. PŁOWIEC, Acustica, **45**, 1, 30–38 (1980).

[5] S. ERNST, M. WACIŃSKI, Acustica, **47**, 1, 1–9 (1980).

[6] L. GRUNBERG, H. NISSAN, Nature, **164**, 799–805 (1949).

[7] H. VOGEL, A. WEISS, Ber. Bunsenges Phys. Chem., **86**, 193–202 (1982).

[8] R. MEISTER, C. J. MARHOFFER, R. SCIAMANDA, L. COTTER, T. A. LITOVITZ, J. Appl. Phys., 31, 854–870 (1960).

[9] R. PŁOWIEC, Habilitational thesis (in Polish), Institute of Fundamental Technological Research, Polish Academy of Sciences, Warsaw, 60/1975.

Received on 5 September, 1983