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SHEAR ULTRASONIC INVESTIGATIONS OF POLYHYDRIC ALCOHOLS

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The influence of the hydrogen bonds and the steric factor on the steady flow viscosity (η_0) and the limited shear elasticity (G_∞) of polyhydric alcohols have been investigated by ultrasonic methods.

1. Introduction

Hitherto investigations showed, that the viscosity of liquids depends on the frequency of shearing and decreases when the latter increases, i.e. a liquid behaves as a non-newtonian one. When the frequency of shearing is sufficiently high, the reaction of a liquid to the shearing stress may be viscoelastic or even elastic. To determine the reaction of a liquid on shear stress, the ultrasonic methods are irreplacable by other methods since they allow to generate the shear stress within a broad frequency range (from 10^4 Hz to 10^9 Hz). It is possible to extend this range up to 10^{12} Hz when the frequency-temperature superposition method is applied. [1, 2]. For most of the liquids it is possible to determine the full relaxation curve, i.e. to find the range of the viscous, viscoelastic and pure elastic reactions on shearing stresses.

2. Theory

In shear ultrasonic measurements the shear mechanical impedance is measured. This value is determined as a reaction of a liquid on the shearing stress. The shear impedance (Z_T) is the quotient of the shearing stress to the velocity of the particle. For a solid this value is real and equal to

$$Z_T = \rho C_T = \sqrt{\rho C_\infty}, \tag{1}$$

where C_T is the shear wave velocity, G_∞ – the shear elastic modulus and ρ is the density of solid.

The mechanical shear impedance of a liquid is complex and frequency dependent:

$$Z_T^*(\omega) = \sqrt{\rho G^*} = (1+j)\sqrt{\pi f \rho \eta} = R_T(\omega) + jX_T(\omega) \tag{2}$$

$$\text{as } G^x(j\omega) = G'(\omega) + jG''(\omega)$$

$$Z_T^*(\omega) = \rho G^* = \rho G'(\omega) + jG''(\omega)) \tag{3}$$

where ω is the angular frequency and ρ the density of the liquid. There is a simple relationship between the shear mechanical impedance, which is measured by ultrasonic methods, and the components of the shear elastic modulus:

$$G'(\omega) = \frac{R_T^2 - X_T^2}{\rho} \qquad G''(\omega) = \frac{2R_T X_T}{\rho} \tag{4}$$

$$\lim_{\omega\to 0} G'(\omega) = G_0 = 0 \qquad \lim_{\omega\to 0} G''(\omega) = \frac{2RT^2}{\rho} = \frac{2X_T^2}{\rho} = \omega\eta_0 \tag{5}$$

For a non-newtonian liquid, the real component (R_T) is higher than the imaginary one and when the frequency increases also the shear elasticity of the liquid does so. For very high frequencies of shearing the shear elasticity $G'_{(\omega)}$ reaches limited value, G_∞ while the viscosity decreases to zero:

$$\lim_{\omega\to 0} G'(\omega) = G_\infty = \frac{1}{I_\infty} = \frac{R_T^2}{\rho}; \qquad \lim_{\omega\to 0} G''(\omega) = 0, \tag{6}$$

where J_∞ is the shear compliance of the liquid.

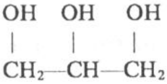
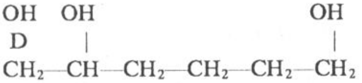
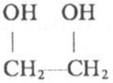
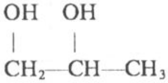
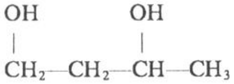
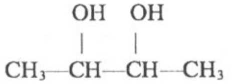
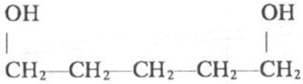
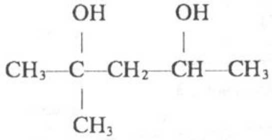
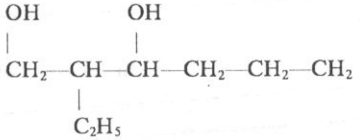
The G_∞ values are different for various liquids and characterize the molecular structure of the liquid. This investigation is aimed at the determination of the relation between G_∞ and the molecular structure of alcohols which have two or three hydroxyl groups in the molecule. The formulas of investigated alcohols are given in Table 1.

The value $^{n}OH/n_c$ in Table 1 is the number of - OH groups corresponding to a carbon atom, and may be considered to be the concentration of H bonds. The last column informs about the number of alkyl groups $^{n}CH_3$,$^{n}CH_5$ $^{n}C_2H_7$, present in a molecule of the investigated alcohols.

3. Measurements

- The density of alcohols was measured by a pycnometer within the temperature range 273 – 303 K. The temperature was stabilized better than ± 0.05 deg. and the density was measured with an accuracy of ± 0.02%,

Table 1.

Alcohol investigated	Structural formula	$^{n}OH : n_c$	No. of alkyl groups
Glycerol	 $\overset{OH}{CH_2}-\overset{OH}{CH}-\overset{OH}{CH_2}$	3:3 (1:1)	0
Hexanetriol-1,2,6	 $\overset{OH}{CH_2}-\overset{OH}{CH}-CH_2-CH_2-CH_2-\overset{OH}{CH_2}$	2:6 (1:3)	0
Ethanediol-1,2 (Ethylene glycol)	 $\overset{OH}{CH_2}-\overset{OH}{CH_2}$	2:2 (1:1)	0
Propanediol	 $\overset{OH}{CH_2}-\overset{OH}{CH}-CH_3$	2:3 (1:1,5)	1 (-CH_3)
Butanediol-1,3	 $\overset{OH}{CH_2}-CH_2-\overset{OH}{CH}-CH_3$	2:4 (1:2)	1 (-CH_3)
Butanediol-1,3	 $CH_3-\overset{OH}{CH}-\overset{OH}{CH}-CH_3$	2:4 (1:2)	2 (-CH_3)
Pentanediol-1,5	 $\overset{OH}{CH_2}-CH_2-CH_2-CH_2-\overset{OH}{CH_2}$	2:5 (1:2,5)	0
2-Methyl- pentanediol-2, 4	 $CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{OH}{CH}-CH_3$	2:6 (1:3)	3 (-CH_3)
2-Ethyl- hexanediol-1, 3	 $\overset{OH}{CH_2}-\underset{C_2H_5}{CH}-\overset{OH}{CH}-CH_2-CH_2-CH_2$	2:8 (1:4)	2 (-C_2H_5) (-C_3H_7)

- A Hoeppler and an ultrasonic viscometer UNIPAN 304A were used for viscosity measurements in temperature range 263 – 303 K. The stabilisation of temperature was better than ± 0.05 deg. and the values of the measured viscosity was determined with an accuracy of 2%,
- The ultrasonic shear resistance (R_T) in the high frequency range, (350 – 1300 MHz) was measured by means of a Matec instrument at the IFTR Warsaw [1, 2]. These measurements were performed in temperature range 218 – 243 K ± 0.1 deg. The shear mechanical resistance was determined with an accuracy of ± 10%.

4. Results

4.1. Density

The densities of the alcohols under test confirm a linear dependence on temperature according to the formula:

$$\rho = a + bT. \tag{7}$$

This relation is shown in Fig. 1 and the values of the coefficients a and b are listed in Table 2. The linear relationship between density and temperature allows to extrapolate the density out of the measurement range. As shown in Table 2, the values of coefficients a and b of the alcohols tested do not differ much from each other, while the values of density increase in the following sequence:

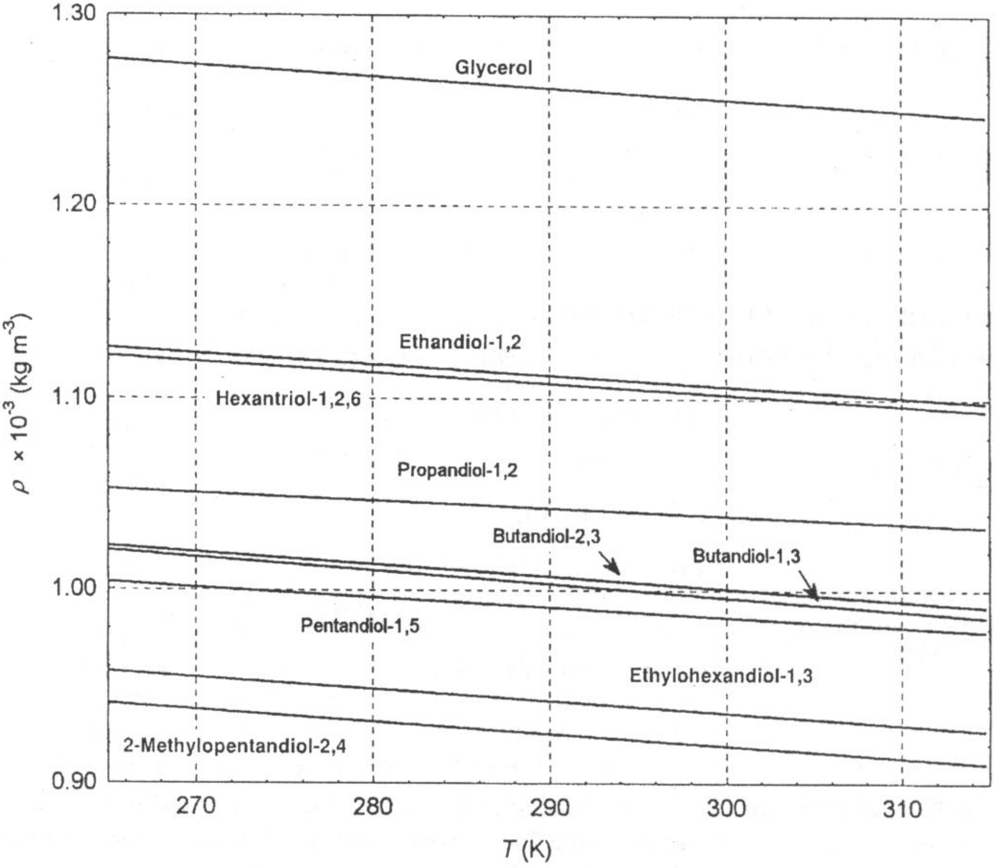


Fig. 1. The density of investigated alcohols as a function of temperature.

Table 2. The coefficients *a* and *b* (Eq. 7) and *c* and *d* (Eq. 9) of investigated alcohols

AICOHOL INVESTIGATED	**DENSITY (kg/m^3)** $[\rho = a\text{-}bT]$			**VISCOSITY (Pa·s)** $[\lg\eta = c + dT^{-3}]$		
	a	b	r	c	d	r
1. GLYCEROL	$1.4360\ 10^3$	-0.6012 T	-0.9995	-3.6345	$0.93908\ 10^8\ T^{-3}$	0.0998
2. HEXANETROIL-1,2,6*	$1.2724\ 10^3$	-0.5671 T	-0.9997	-3.5278	$1.00231\ 10^8\ T^{-3}$	0.9998
3. ETHYLENE GLYCOL	$1.1218\ 10^3$	-0.5710 T	-0.9998	-3.6924	$0.49085\ 10^8\ T^{-3}$	0.9995
4. PROPANEDIOL-1,2	$1.0487\ 10^3$	-0.3750 T	-0.9994	-3.2237	$0.48346\ 10^8\ T^{-3}$	0.9972
5. BUTANEDIOL-1, 3	$1.0155\ 10^3$	-0.7090 T	-0.9997	-3.9602	$0.73287\ 10^8\ T^{-3}$	0.9995
6. BUTANEDIOL-2, 3	$1.0176\ 10^3$	-0.6290 T	-0.9999	-3.4451	$0.64036\ 10^8\ T^{-3}$	0.9996
7. PENTANEDIOL-1,5	$1.1382\ 10^3$	-0.5074 T	-0.9995	-3.1607	$0.57197\ 10^8\ T^{-3}$	0.9994
8. 2-METHYLOPENTANEDIOL-2,4	$1.1051\ 10^3$	-0.6197 T	-0.9996	-3.9021	$0.70763\ 10^8\ T^{-3}$	0.9999
9. 2-ETHYLOHEXANEDIOL-1,3	$1.1206\ 10^3$	-0.6150 T	-0.9992	-4.7946	$1.0532\ 10^8\ T^{-3}$	0.9989

* Densities and static viscosities were measured at the Institute of Chemistry, University of Wroclaw (3, 4).

Table 3. The coefficients *m, n* and *r* (reliablity) of Eq. (11) and values of activation energy *E** for different temperatures.

Alcohol investigated	Limiting shear modulus G_∞[N m^{-2}]			273 [K]					
	m	10^{-9}	$^{n}10^{-7}$ r	η [Pa s]	E^H [kJ mol^{-1}]	G_∞ [N m^{-2}]	T_g [K]	T_o [K]	U [J] 10^{21}
1. Glycerol	.3831	-1.6883T	-0.9833	9.40	69.9	2.77	182	473	6.04
2. Hexanetriol-1, 2, 6	5.8840	-1.4250T	-0.9899	24.2	74,5	1.95	186	410	5.67
3. Ethanediol-1, 2	2.9199	-0.8910T	-0.9869	0.0519	36.5	0.487	146	328	4.53
4. Propanediol-1, 3	3.1224	-0.9211T	-0.9902	0.141	36.0	0.611	147	339	4.68
5. Butanediol-1, 3	4.3250	-1.1800T	-0.9963	0.432	54.6	1.10	166	366	5.06
6. Butanediol-1, 5	4.2293	-1.1122T	-0.9956	0.498	47.7	1.19	162	380	5.25
7. Pentanediol-1,5	2.6990	-0.9006T	-0.9872	0.442	42.6	0.239	156	300	4.13
8. 2-Methylopentanediol-2, 4	4.0951	-1.3269T	-0.9992	0.372	52.4	0.473	165	309	4.26
9. 2-Ethylohexanediol-1, 3	5.1380	-1.3786T	-0.9589	2.36	78.4	1.37	184	373	5.14

glycerin > glycol et. > hexanetriol -1.2.6 > propanediol -1.2 > butanediols -2.3 and -1.3 > 2-ethylheksanediol -1.3 > 2-methylpentanediol -2.4.

The numbers of -OH groups corresponding to one carbon atom in the molecule and thereby the densities of hydrogen bonds are ordered in the same sequence. This sequence of the densities may suggest an increasing compactness of the molecules. It is also of interest that the lowest values of density have been found for 2-ethyloheksanediol -2.4, and 2-methylopentanediol -2.4, i.e. for the diols with relatively large molecules but with a low density of hydrogen bonds. In this case the low densities may be caused by an additional steric hindrance. This steric effect seems to be likely because the molecules of both the diols contain the sizable rigid groups -CH_3 and -C_2H_5 which may cause a lower compactness of the molecules.

4. 2. Viscosity

To present the relationship between viscosity and temperature, the Arrhenius-Guzman formula is usually used:

$$\eta = A\exp\left(\frac{E^*}{RT}\right), \tag{8}$$

where η is the viscosity, E^* – the activation energy of viscous flow, R – gas constant, T – temperature and A – a constant for a given liquid. However, the viscosities of the liquids studied do not follow the Arrenius-Guzman formula, and the viscosity temperature relation may by described by the logarithmic formula [5], [6]:

$$\ln\eta = c + dT^{-3}, \tag{9}$$

The viscosity-temperature relation is shown on Fig. 2.

The activation energy of viscous flow can be calculated with the formula:

$$E^{*} = R\left[\frac{\delta(\ln\eta)}{\delta(T^{-1})}\right] \tag{10}$$

where $\frac{\delta(\ln\eta)}{\delta(T^{-1})}$ is the tangential coefficient of the function (9) which may be related approxymately Arrenius-Guzman equation (8). The values of the activation energy E^* calculated for different temperatures are listed in Table 3. Both the density and steady flow viscosity measurements were performed at the Institute of Chemistry of the University of Wrocław [3, 4].

4.3. Shear mechanical resistance

The shear mechanical resistance was measured within the frequency range 350 – 1300 MHz. The results at low temperatures allow to determine the values of G_∞ and the elastic region of the tasted liquids. A linear dependence of G_∞ on temperature was found according to the formula:

$$G_\infty = m - nT.$$

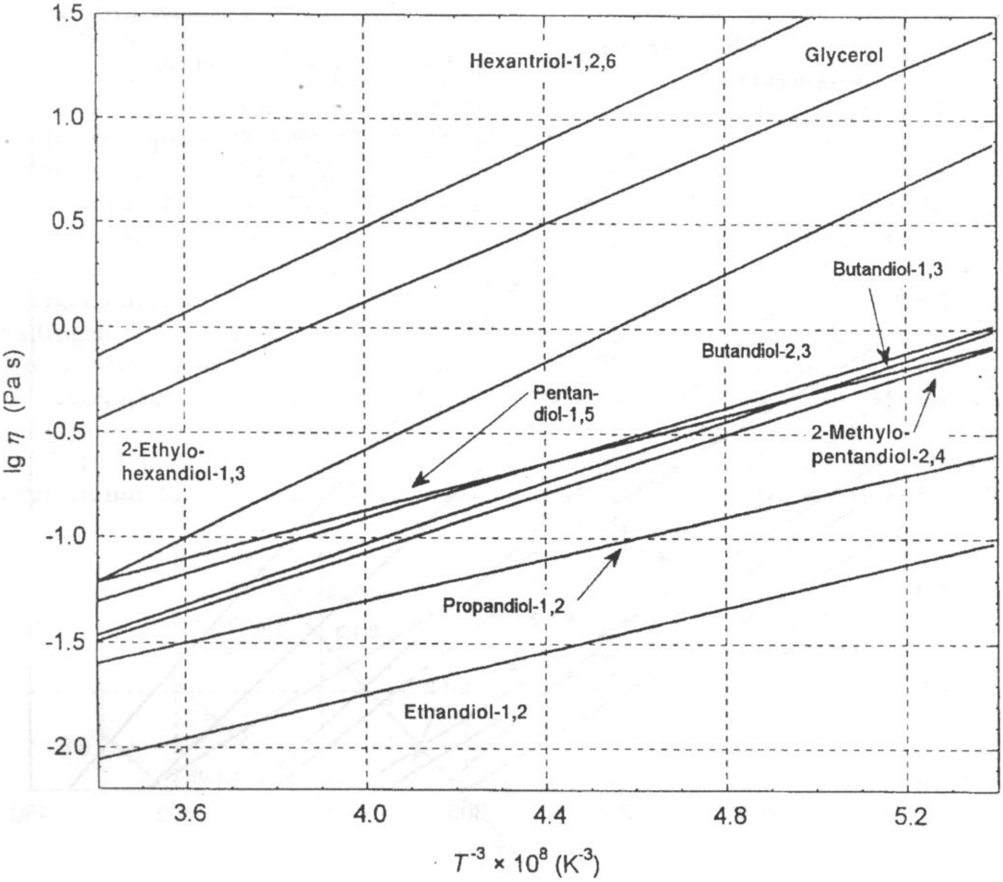


Fig. 2. Viscosity of investigated alcohols as a function of temperature.

The coefficients *m* and *n* of this equation are given in Table 3.

The extrapolation of G_∞ to the lower temperatures makes the determination of the glass transition temperature, T_g, possible. At that temperature the viscosity of a liquid is equal to 10^{12} Pa · s [8]. It is usually assumed that all relaxation processes in a liquid are locked up at the temperature T_g and the latter behaves as a solid. The values of T_g for investigated alcohols are given in Table 3. The linear dependence of G_∞ on temperature is shown in Fig. 3.

Issakovitch's and Caban's hole theory of very viscous liquids assumes the existence of two phases in a liquid with different arrangements of the molecules. The first phase consists of molecules in a pseudo-crystalline arrangement and the second one, a disordered phase, is made of free molecules. This mixture of two phases is in equilibrium at a given temperature and pressure. The ultrasonic wave, propagating in the liquid, disturbs the equilibrium between this two phases. A new equilibrium is reached by a diffusion processes after some time.

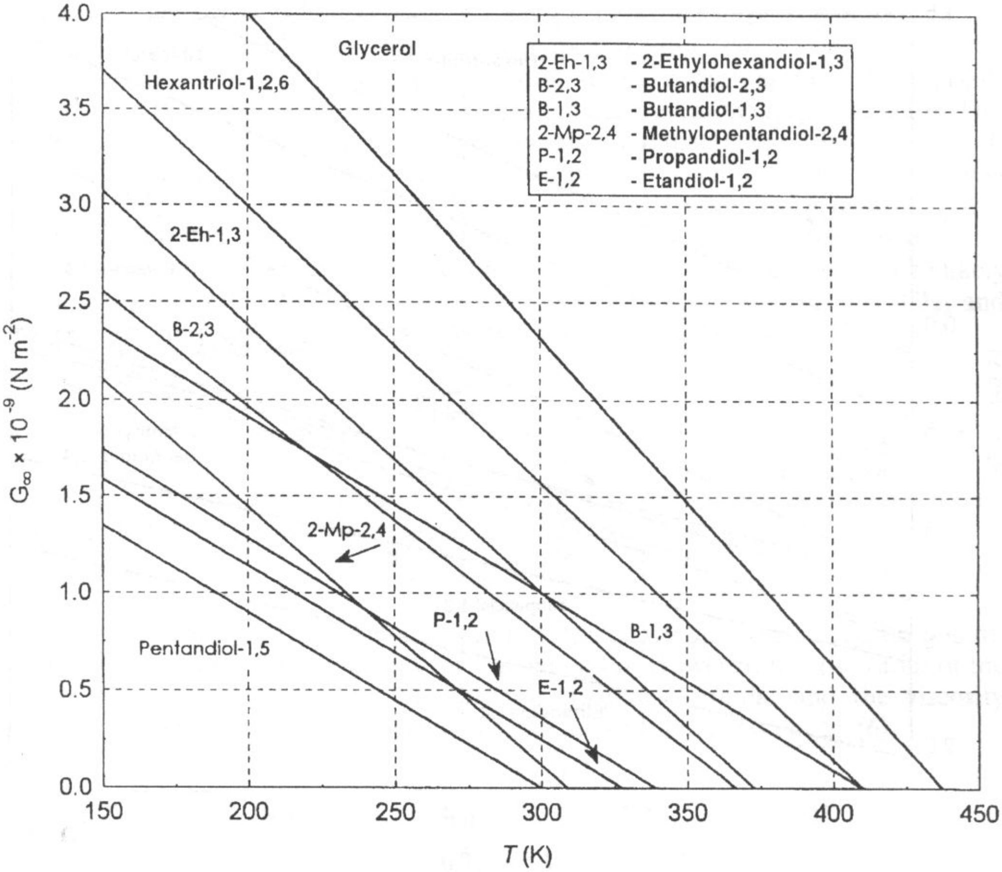


Fig. 3. G_∞ value of investigated alcohols as a function of temperature.

For a very high frequency the diffusion of holes is delayed in comparison with the stress variations. This causes a velocity dispersion and an additional absorption in the liquid. At the temperature T_0 the ordered phase diminishes and the longitudinal modulus K_0 and shear modulus G_∞ are equal to K_∞ and 0, respectively. At the temperature higher than T_0 all the molecules are free of any limitations due to the potential barrier, and the probability of any locations of a molecule is equal. From the linear dependence of G_∞ on temperature the values of the temperature T_0 and the interlocking potential barrier $U = KT_0$ (k is Boltzman constant) may be calculated.

All this values are given in Table 3.

5. Summary

To show the correlation between the chemical structure and space arrangements of molecules in the tested alcohols, the results may be divided into three groups

a) glycerol, hexanetriol -1.2.6 and 2 ethylheksanediol -1.3 show the highest viscosity, (9.40, 24, 2, 2, 36, Pa·s), the highest activation energy of viscous flow (69.9, 74.5, 78.4 kJ/mol), the highest values of the shear elasticity modulus G_∞ (2.77, 1.95, 1.37 N/m^2 × 10^9), and the lowest potential barrier.

In this group of alcohols large differences in the density of -OH groups (hydrogen bonds) and in the spatial arrangements exist. For example glycol and hexanetriol have any spatial arrangement of the alkyl groups, on the contrary, 2-ethylheksanetriol has big -C_2H_5 and C_3H_7 groups in a molecule, which are spatially arranged,

b) butanediol -1.3, pentanediol -2.3, 2 methylpentanediol -2.4, i.e. diols with hydrogen bonds density: 1/1, 1/2, 1/3 and an increasing amount of H bonds from 1 to 3. Also pentanediol -1.5 with H density bonds 1/2.5 and without alkyl groups. In the temperature 273 K the values of viscosity (0.432. 0.498, 0.372, 0.442 Pa·s), activation energy (54.6, 47.7, 52.4, 42.6 kJ/mol), and shear elasticity modulus G_∞ (1.10, 1.19, 0.473, 0.239 N/m^2 × 10^9), show moderate values. The glass transition temperature T_g for this alcohols is: 166K, 162K, 165K, 156K, respectively,

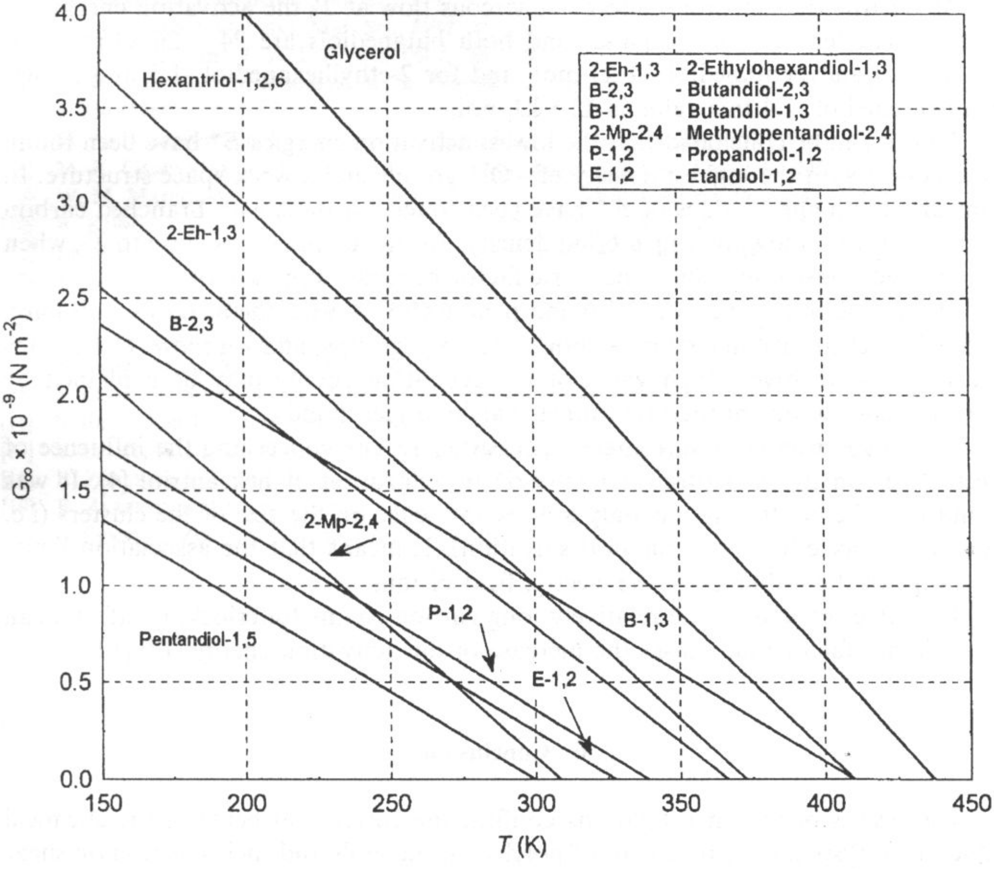


Fig. 4.

c) ethanediol -1.2 and propanediol -2.3 are diols with the lovest viscosities (0.052, 0.141 Pa·s) and the lowest activation energies (36.5, 36.0 kJ/mol). Their shear elasticity modulus G_∞ is 0.487 and 0.611 N/m^2 and the potential barriere are 2.73 10^3 and 2.82 10^3 J/mol. They differ from each other in the – OH group density (1 : 1 and 2 : 3) and the number of methyl groups (0 and 1). Their glass transition temperature is 146 K and 147 K, respectively.

Such division into three groups show the influence of – OH groups (hydrogen bonds) and alkyl groups -CH_3, -C_2H_5 or C_3H_7 on the results of measurements. The – OH groups may create a big associates (clusters), which limit the rotation and translation degrees of freedom of the molecules (i.e. the hydrogen bond model of MADIGOSKY, MCDUFFY and LITOVITZ [9] [10].

The alkyl groups may block the free space in a cluster structure. This suggestion is confirmed by other investigations of the elasticity and shear compressibility of other mixtures of alcohols [11]. Larger deviations of the compressibility for glycerol -2 methyl-pentanediol-2.4 mixture than for glycerol-butanediol -1.3 were found in this mixtures.

As regards the activation energy of viscous flow at T_0 the activation energy for glycerol, ethylene glycol, propanol and both butanediols are 24 – 26 kJ/mol, for hexanetriol and pentanediol 34 kJ/mol, and for 2-ethylhexanediol -1.3 and 2 methylopentanediol -2.4 this value is 42.5 kJ/mol.

Thus it can be concluded that the lowest activation energies E^* have been found for alcohols with the highest density of – OH groups and a week space structure. In contrary, the highest values of E^* have been found for diols with branched carbon chains and with a low hydrogen bond density. At the temperatures close to T_0, when the ordered phase diminishes, the steric factor becomes more important.

In the case of hexanetriol -1.2.6 and pentanediol -1.5 i.e. the alcohols with long, and unbranched carbon chains (without side alkyl groups) and with low -OH groups densities, the relatively high value of the activation energy may be explained by a strong association through intermolecular hydrogen bonds.

This suggestion is in agreement with earlier results concerning the influence of electrolytes on the structural and viscoelastic relaxation of heksantriol [4]. It was found that the electrolyte has only a week influence on the size of the clusters (i.e. there are weak effects of structural solvation). It means that the association limits the range of the influence of the electric field of ions.

The effect of joining the relatively long carbon chains (interlocking effects) can be the other factor that causes the increase of the activation energy [12] [13].

6. Conclusion

The results of this investigations confirm the correlation between the chemical structure and spatial arrangement of polyhydric alcohols and their reaction on shear ultrasonic strain in the viscous range (viscosity, activation energy) and elastic range (shear elastic modulus). The results are in agreement with earlier results of investigation of alcohols and electrolyte solutions, according to that the concentration of hydrogen bonds correlates with the reaction on shear stress [14-20].

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