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THE EFFECT OF $FeCl_3$ ON CHANGES IN THE RHEOLOGICAL PROPERTIES OF GLYCEROL DETERMINED BY AN ACOUSTIC METHOD

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The results of the shear mechanical impedance measurements are presented for solutions of $FeCl_3$ in glycerol at frequencies 30 and 500 MHz and over a temperature range from 218-303 K. These results complemented the previous investigations [4] performed at a frequency of 0.5 MHz. A distinct effect of $FeCl_3$ on the range of the viscoelastic relaxation of glycerol and on its molecular structure was found.

1. Introduction

An increasing interest in the rheological properties of liquid has been observed in the recent years, since it is expected that they are essential in the investigations of the liquid state and the principle of intermolecular forces.

In the case of solutions it can be expected that their response to shear stress, particularly over the range of viscoelastic relaxation can reflect the effect of the solute on the structure of the solvent and the molecular rearrangement. In terms of knowledge it is most interesting to note the case when an electrolyte is the solute and alcohol is the solvent, since alcohol can form with electrolyte ions not only specific solvate complexes, but also more developed and arranged molecular regions (clusters).

The above investigations were initiated with the measurements of the shear impedance in solutions of electrolytes in glycerol taken at a frequency of 0.5 MHz

[4]. The present paper complements the results of measurements in solutions of $FeCl_3$ in glycerol with the investigation of the shear impedance performed at frequencies 30 and 500 MHz over a temperature range from 218 to 303 K. The results of this investigation made it possible to determine the curve of the viscoelastic relaxation at high frequencies. It was found to be in good agreement with the theoretical conclusions in [4].

2. Experimental part

2.1 Preparation of samples

Anhydrous ferric chloride (manufactured by British Drug Houses, cz.d.a.) with a content of up to 2 % of ferrous chloride and glycerol (manufactured by POCh, Gliwice, b.f.) dehydrated by boiling under decreased pressure were used in the investigations. The water content in the glycerol determined by the Fischer method was 0.3 %. The solutions of $FeCl_3$ were obtained by solving a specific amount of ferric chloride in glycerol and its concentration was determined by weight [1]. The calculated values of the concentration are given in Table 1.

Table 1. Temperature dependence of the density and viscosity of glycerol with $FeCl_3$

Concentration of $FeCl_3$ in moles in 1 kg^3 of glycerol	Density $[kgm^{-3}]$	Viscosity $[Nsm^{-2}]$
0	$1.43605 \times 10^3 - 6.012 \times 10^{-1} T$	$-3.6344 - 9.3908 \times 10^7 T^{-3}$
0.06715	$1.4284 \times 10^3 - 5.460 \times 10^{-1} T$	$-3.4155 - 9.2425 \times 10^7 T^{-3}$
0.1069	$1.4404 \times 10^3 - 5.702 \times 10^{-1} T$	$-3.3328 - 9.1404 \times 10^7 T^{-3}$
0.1693	$1.4438 \times 10^3 - 5.614 \times 10^{-1} T$	$-3.2573 - 9.1768 \times 10^7 T^{-3}$
0.3058	$1.4707 \times 10^3 - 5.9190 \times 10^{-1} T$	$-3.3343 - 9.9207 \times 10^7 T^{-3}$
0.4015	$1.4904 \times 10^3 - 6.1571 \times 10^{-1} T$	$-3.6218 - 1.1342 \times 10^8 T^{-3}$

2.2. The measurements of density and viscosity

The density of the solutions was determined using a specific gravity bottle in a temperature range from 323 to 243 K with a precision of ± 0.05 K. For lower temperatures the density was extrapolated from the linear equation $\varrho = A + BT$, where A and B are constants and T is the temperature.

The static viscosity η was determined using a Höpler viscometer and capillary viscometers over a temperature range from 323 to 253 K. For lower temperatures the values of the density were extrapolated using the equation proposed by MEISNER [2] $\log \eta = c + D/T^3$, where c and D are constants.

The measured values of the viscosity and density of the solutions investigated are given in Table 1.

2.3. The measurements of the shear impedance

The measurements of the shear impedance of the solutions investigated and of its variation over the temperature range from 218-303 K at a frequency of 500 MHz were taken using a measuring system prepared at the Department of Physical Acoustics, Institute of Fundamental Research, Polish Academy of Sciences [3]. The measured values of the shear resistance are shown in Table 2.

Table 2. The real component of the shear impedance of solutions of $FeCl_3$ in glycerol at a frequency $f = 500$ MHz (in $[Nsm]^{-3}x10^{-5}$)

Temperature [K]	Glycerol	Glycerol – $FeCl_3$ $m = 0.4015$	Glycerol – $FeCl_3$ $m = 0.3058$	Glycerol – $FeCl_3$ $m = 0.1693$	Glycerol – $FeCl_3$ $m = 0.1069$	Glycerol – $FeCl_3$ $m = 0.06715$
218.15	22.2	22.65	22.55	22.35	22.3	22.25
223.15	21.8	22.3	22.15	22.05	22.0	21.95
228.15	21.4	21.95	21.85	21.75	21.65	21.65
233.15	21.0	21.65	21.45	21.4	21.35	21.3
238.15	20.6	21.05	20.75	20.7	20.7	20.7
243.15	20.2	20.4	20.0	19.7	19.9	20.0
248.15		19.8	19.2	18.9	19.2	19.3
253.15	19.4	19.1	18.5	17.8	18.3	18.25
263.15	17.85	17.6	16.9	16.6	16.3	16.3
273.15	15.4	15.8	15.0	14.5	14.3	14.2
283.15	12.9	14.0	12.95	12.3	12.2	12.0
293.15	10.05	12.1	11.1	10.5	10.3	10.0
303.15	7.85	10.1	9.35	8.85	8.68	7.85

3. The presentation of results

The literature proposes presentation of the measurement results of the viscoelastic relaxation range based on the Maxwell model or on the $B-E-L$ model.

3.1. Presentation based on the Maxwell model

Assuming a continuous Gaussian distribution of relaxation times the behaviour of standardized values of the shear impedance can be determined from

the formulae

$$\frac{R}{(\varrho G_\infty)^{1/2}} = \sqrt{\frac{1}{2}\int_0^\infty \frac{g_{(x)}\omega^2\tau_0^2x^2}{1+\omega^2\tau_2^0x^2}\,dx\left\{1+\left[1+\left(\frac{\int_0^\infty \frac{g_{(x)}x}{1+\omega^2\tau_0^2x^2}\,dx}{\int_0^\infty \frac{g_{(x)}\omega^2\tau_0^2x^2}{1+\omega^2\tau_0^2x^2}\,dx}\right)^2\right]^{1/2}\right\}^{1/2}}, \tag{1}$$

$$\frac{X}{(\varrho G_\infty)^{1/2}} = \sqrt{\frac{1}{2}\int_0^\infty \frac{g_{(x)}\omega^2\tau_0^2x^2}{1+\omega^2\tau_0^2x^2}\,dx\left\{\left[1+\left(\frac{\int_0^\infty \frac{g_{(x)}x}{1+\omega^2\tau_0^2x^2}\,dx}{\int_0^\infty \frac{g_{(x)}\omega^2\tau_0^2x^2}{1+\omega^2\tau_0^2x^2}\,dx}\right)^2\right]^{1/2}-1\right\}^{1/2}}, \tag{2}$$

where

$$g_{(x)} = (b/\pi^{1/2}x)\exp-[bln x]^2, \quad 0 < \tau_s < \infty, \tag{3}$$

R and X are the components of the shear impedance (shear mechanical resistance and reactance), ϱ is the density of the medium, G_∞ – is the limiting shear modulus of the liquid, ω is the angular frequency. $g_{(x)}$ represents the distribution of relaxation times, $g_{(x)}dx$ represents the part of the distribution of relaxation times over the range between x and $x+dx$ for the following parameters of the distribution width for b: $b = 0.4$ for glycerol and $b =$ from 0.33 to 0.3 for solutions of $FeCl_3$ in glycerol [4].

3.2. Presentation based on the *B—E—L* model

The $B-E-L$ model consists of two parallel acoustic impedances for the solid Z_S and for the Newtonian liquid Z_N

$$\frac{1}{Z^*} = \frac{1}{Z_N} + \frac{1}{Z_S}. \tag{4}$$

By transforming (4) one can derive the formula for the shear compliance J^* as a function of the characteristic constants of the medium investigated

$$\frac{J^*}{J_\infty} = \frac{1}{G_\infty} + \frac{1}{j\omega\eta} + 2k\left(\frac{1}{j\omega\eta G_\infty}\right)^\beta. \tag{5}$$

The components of the acoustic shear impedance of the liquid, R and X, determined from formula (5) are

$$\frac{R}{(\varrho G_\infty)^{1/2}} = \frac{(\omega\eta/2G_\infty)^{1/2}[1+(2\omega\eta/G_\infty)^{1/2}]}{[1+(\omega\eta/2G_\infty)^{1/2}]^2+\omega\eta/2G_\infty}, \tag{6}$$

$$\frac{X}{(\varrho G_\infty)^{1/2}} = \frac{(\omega\eta/2G_\infty)^{1/2}}{[1+(\omega\eta/2G_\infty)^{1/2}]^2+\omega\eta/2G_\infty}. \tag{7}$$

Formula (5) sufficiently well describes the results of the measurements taken of simple liquids for $k = 1$ and $\beta = 1/2$. In the case of complex liquids or their mixtures this formula is modified by the coefficients k and β which fit the curves to the measurement results [4]. Using formula (5) and the coefficients $k = 1.56$, $\beta = 0.4$ the effect of electrolytes on the viscoelastic relaxation curves of glycerol (Fig. 6) was described.

4. Discussion of the results and conclusions

The measurement results are shown in Figs. 1-5. They show that $FeCl_3$ widens distinctly the range of the viscoelastic relaxation time of glycerol. The changes observed in the distribution of the relaxation times induced by the presence of electrolyte reflect its effect on the cooperativeness of molecular rearrangements in the solvent [6]. Investigations of the structural and viscoelastic relaxation in associated liquids (polyhydroxide alcohols, hexachlorodiphenyl) [2, 6, 7], showed that an explanation of the changes in molecular moduli (i.e. bulk modulus and shear modulus) requires a wide spectrum of relaxation times to be assumed.

The width of the range of the viscoelastic relaxation of solutions of $FeCl_3$ in glycerol increases with increasing concentration of electrolyte (Fig. 6). This did not occur in other solutions [6]. It seems probable that a wider spectrum of the viscoelastic relaxation times is in the case of solutions of $FeCl_3$ in glycerol connected with formation of stable solvate complexes involving orbitals $3d$ of the ion Fe^{+3}.

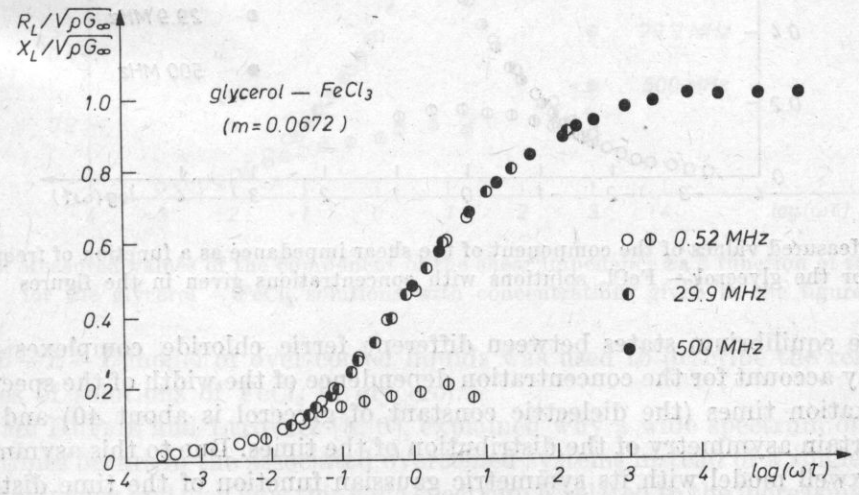

Fig. 1. Measured values of the component of the shear impedance as a function of frequency for the glycerol – $FeCl_3$ solutions with concentrations given in the figures

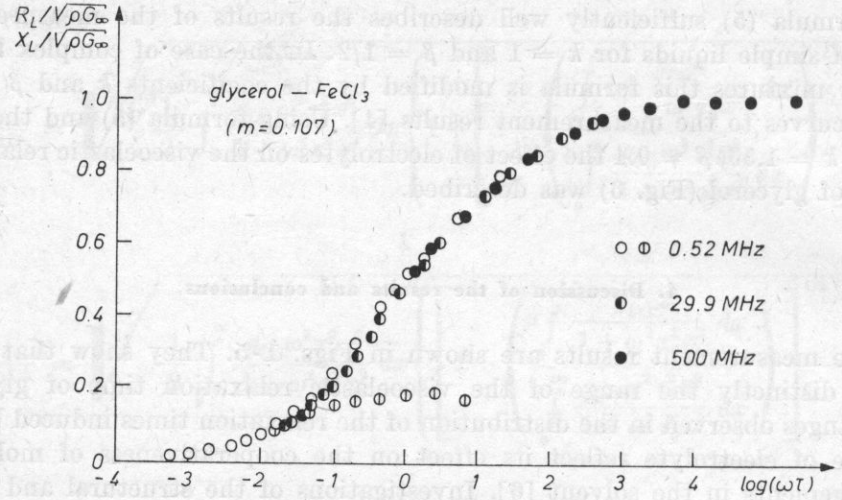

Fig. 2. Measured values of the component of the shear impedance as a function of frequency for the glycerol — $FeCl_3$ solutions with concentrations given in the figures

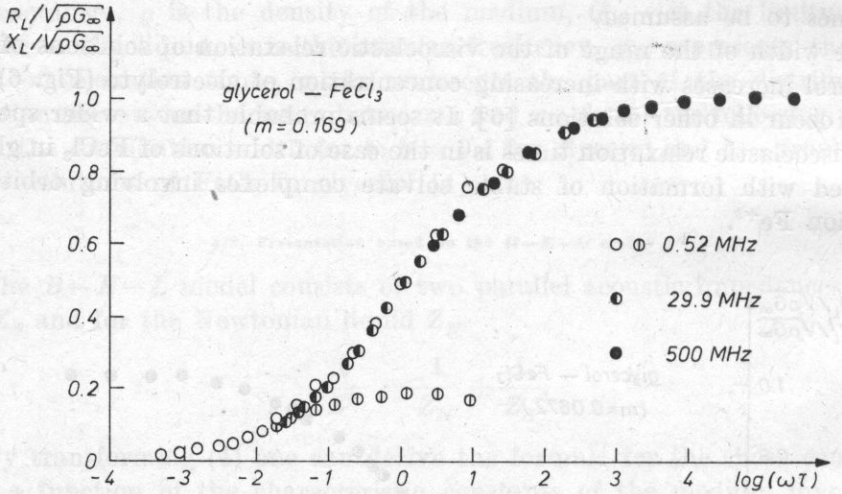

Fig. 3. Measured values of the component of the shear impedance as a function of frequency for the glycerol — $FeCl_3$ solutions with concentrations given in the figures

The equilibrium states between different ferric chloride complexes (III) probably account for the concentration dependence of the width of the spectrum of relaxation times (the dielectric constant of glycerol is about 40) and also for a certain asymmetry of the distribution of the times. Due to this asymmetry the Maxwell model with its symmetric gaussian function of the time distribution describes insufficiently the behaviour of the reduced relaxation curves, particularly in the lower temperature region (higher frequencies). Therefore

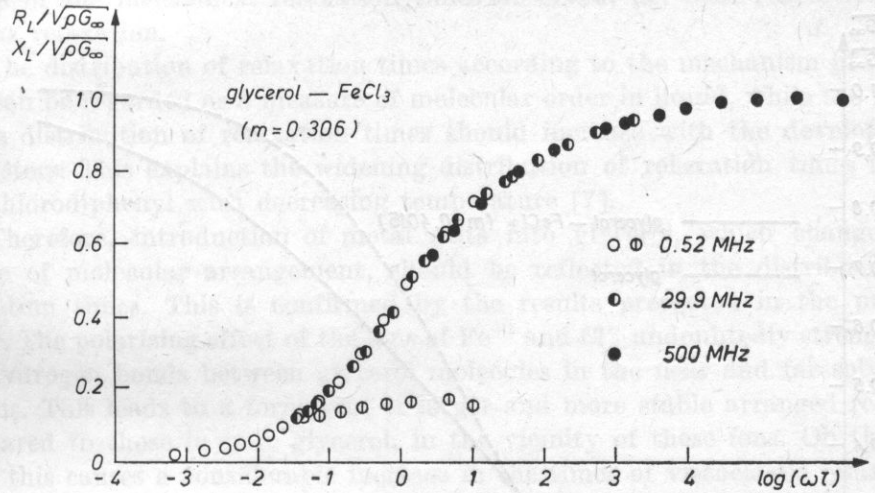

Fig. 4. Measured values of the component of the shear impedance as a function of frequency for the glycerol — $FeCl_3$ solutions with concentrations given in the figures

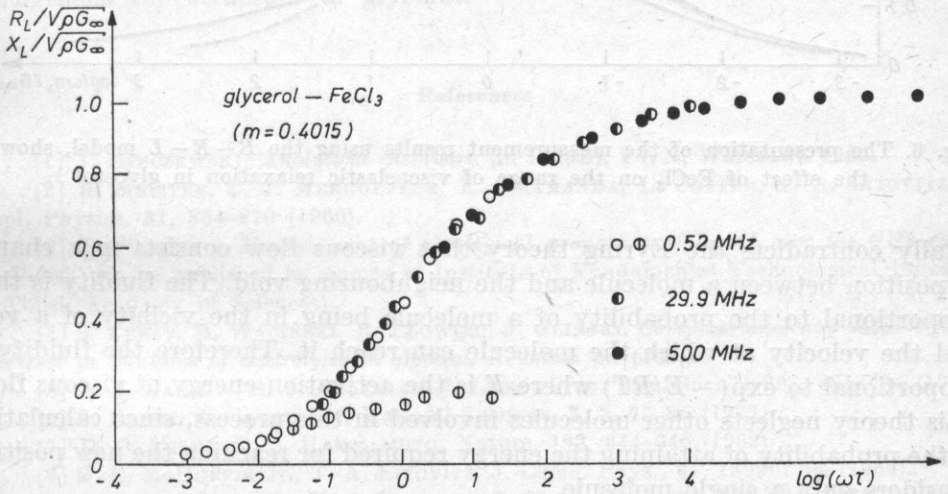

Fig. 5. Measured values of the component of the shear impedance as a function of frequency for the glycerol — $FeCl_3$ solutions with concentrations given in the figures

the $B-E-L$ model of over-cooled liquids was used to describe the relaxation curves of solutions of $FeCl_3$ in glycerol.

Mc DUFFIE and LITOVITZ [8, 9], explained why a wide spectrum of relaxation times occurs in the associated overcooled systems instead of a single relaxation frequency and also how this wide spectrum is related to the increasing temperature. They found that at temperatures of up to about 100 K above the glassy state temperature over-cooled liquids show a temperature dependence that

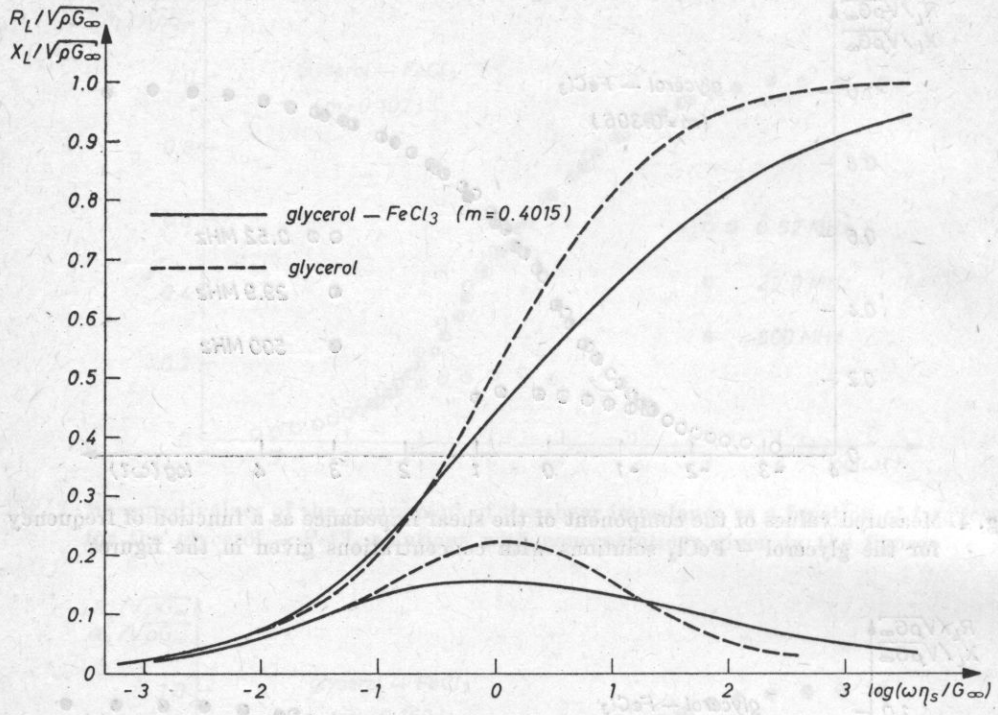

Fig. 6. The presentation of the measurement results using the $B-E-L$ model, showing the effect of $FeCl_3$ on the range of viscoelastic relaxation in glycerol

totally contradicts the Eyring theory that viscous flow consists in a change of position between a molecule and the neighbouring void. The fluidity is thus proportional to the probability of a molecule being in the vicinity of a void and the velocity at which the molecule can reach it. Therefore the fluidity is proportional to $\exp(-E/RT)$ where E is the activation energy of viscous flow. This theory neglects other molecules involved in this process, since calculation of the probability of attaining the energy required for reaching the new position considers only a single molecule.

The model of McDuffie and Litovitz is based on the following assumptions:

1. In liquid there are small arranged regions which disintegrate and reintegrate continually. (This is confirmed by investigations of diffraction of X-rays and neutrons.)

2. The disintegration of such a structure is cooperative in character, i.e. when a molecule changes its position, other molecules "cooperate" with it in order to provide the necessary space. Thus the degree of arrangement changes nonexponentially as a function of time.

3. This cooperative nonexponential behaviour is the cause of the distri-

bution of the mechanical relaxation times observed, i.e. bulk relaxation and viscous relaxation.

The distribution of relaxation times according to the mechanism proposed here can be regarded as a measure of molecular order in liquid, while the width of the distribution of relaxation times should increase with the development of clusters. This explains the widening distribution of relaxation times in the hexachlorodiphenyl with decreasing temperature [7].

Therefore, introduction of metal salts into glycerol, which changes the degree of molecular arrangement, should be reflected in the distribution of relaxation times. This is confirmed by the results presented in the present paper. The polarizing effect of the ions of Fe^{+3} and Cl^- undoubtedly strengthens the hydrogen bonds between glycerol molecules in the near and far solvation regions. This leads to a formation of larger and more stable arranged regions, compared to those in pure glycerol, in the vicinity of these ions. On the one hand this causes a considerable increase in the times of viscoelastic relaxation and on the other hand a considerable widening of the distribution of these times as a result of increasing cooperativeness of molecular groups. It can be stated, therefore, in terms usually used for aqueous electrolyte solutions, that $FeCl_3$ strengthens the structure of glycerol.

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