COMPARISON OF SHEAR ULTRASONIC RESULTS
OF ELECTROLYTE-ACETAMIDE MOLTEN MIXTURES

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Shear ultrasonic investigation are presented in sodium trifluoroacetate/CF_3COO-Na/-acetamide molten mixtures as a function of amide concentration. This results are compared with other electrolyte-acetamide molten mixtures investigated previously.

1. Introduction

In the last years we investigated the molten mixtures of electrolyte-acetamide in binary system, which can be easy supercooled to low temperature giving the possibility to measure the phase changing from liquid state to solid state. In the supercooled region this mixtures demonstrate very high dielectric constant [1] and viscoelastic behavior in relaxation region and pure elastic behavior in metastable glassy state. The previously made investigations suggested the polymer structure of amide chain which was joined with metal ions [2] [3].

Last time we investigated tree mixtures:

- acetamide + sodium thiocyanate /NaSCN/ [2]
- acetamide + calcium nitrate /$Ca(NO_3)_2$/ [3]
- acetamide + sodium trifluoroacetate /CF_3COONa/ [6]

To know what is the influence of acetamide concentration on polymer chain creation and the influence on the range of relaxation processes the last mixture was investigated as a function of amide concentration. Tree different concentration was prepared for measurements: a) 8.06 mol/kg b) 11.98 mol/kg and c) 19.48 mol/kg.

2 Measurements

To determine the range of relaxation processes of these mixtures we performed the measurements as follows:

- density measurements as a function of temperature

- steady flow viscosity as a function of temperature
- ultrasonic shear impedance measurements as a function of frequency and temperature
- ultrasonic measurements of shear elasticity in metastable glassy state as a function of temperature and frequency.

For density measurements the vibrating densitometr of PAAR (Austria) was used. The measurements was made in temperature range $10-60°C$. The results may be fitted by linear equation

$$\rho = a + bT,$$

where ρ is in kg/m³ and T — temperature in Kelvin. For the 8.06 mol/kg solution $a = 1693.05$, $b = 1.060$, for 11.98 mol/kg solution $a = 1789.86$, $b = 1.098$ and for 19.48 mol/kg solution $a = 1927.21$, $b = 1.188$.

For steady flow viscosity measurements the Hoeppler viscometer was used. As an example the results for 8.06 mol/kg amide concentration are shown on Fig 1.
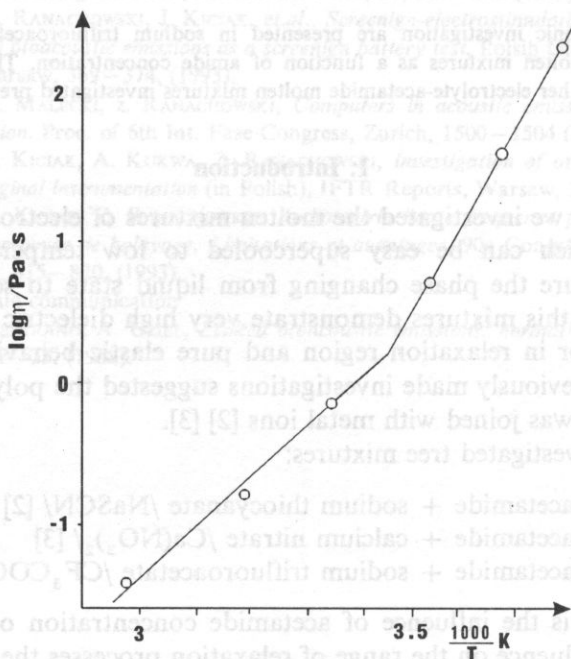

Fig. 1. The changes of viscosity for 8.06 mole/kg solution as a function of temperature.

For shear ultrasonic measurements the MATEC (USA) set was used. The normal incidence technique and the superposition method was applied in measurements [4] on frequency 10.30 and 90 MHz. The special attention was paid on dry atmosphere during the measurements, specially in low temperatures because of influence of humidity on the shear impedance value. The results of ultrasonic
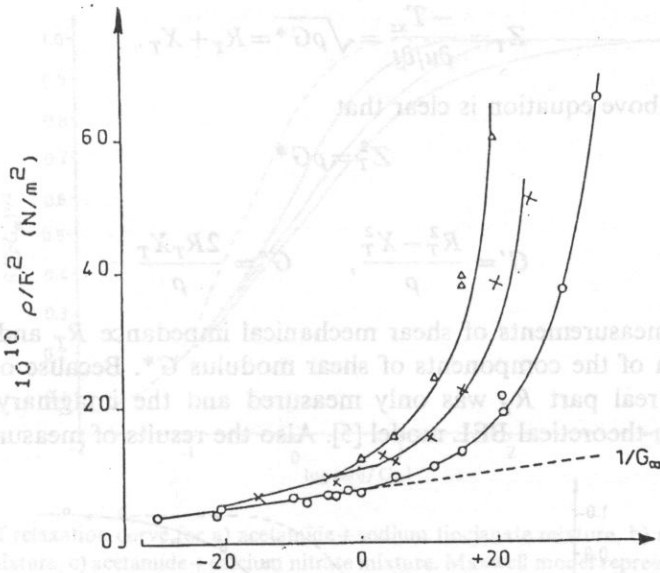
Fig. 2. The run of ρ/R^2 as a function of temperature and frequency for the 8.06 mole/kg solution.
($\Delta = 10$ MHz, x = 30 MHz, o = 90 MHz).

measurements of shear elasticity in metastable glassy state are shown on Fig. 2 as an example for 8.06 mol/kg solution and are given by equation

$$1/G_\infty \; (N/m^2) = 2.83 \cdot 10^{-10} + 1.575 \cdot 10^{-11} \; (T - T_g),$$

where T_g is the glass transition temperature and is equal 240 K for 8.06 mole/kg solution.

3. Theory

If the element of liqiud of density ρ is shearing in the plane xy with the transversal motion u as a result of the shear stress T_{xz} the motion equation is

$$\rho \, dxdydz = \frac{\partial T_{xz}}{\partial z^2} \, dxdydz.$$

When the shear wave is propagated in z direction then

$$\rho \, \frac{\partial^2 u}{\partial t^2} = G^* \, \frac{\partial^2 u}{\partial z^2},$$

where the complex shear modulus $G^* = G' + j \, G''$

The mechanical impedance is the magnitude which characterize the mixture to be measured under shearing stress. It is definited as a ratio of shearing stress T to the acoustic velocity $(\partial u/\partial t)$

$$Z_T = \frac{-T_{xz}}{\partial u/\partial t} = \sqrt{\rho G^*} = R_T + X_T.$$

From the above equation is clear that

$$Z_T^2 = \rho G^*$$

and

$$G' = \frac{R_T^2 - X_T^2}{\rho}, \qquad G'' = \frac{2R_T X_T}{\rho}$$

Then, the measurements of shear mechanical impedance R_T and X_T permit to determine both of the components of shear modulus G^*. Because of the technical limitation the real part R_T was only measured and the imaginary part X_T was calculated from theoretical BEL model [5]. Also the results of measurements, which
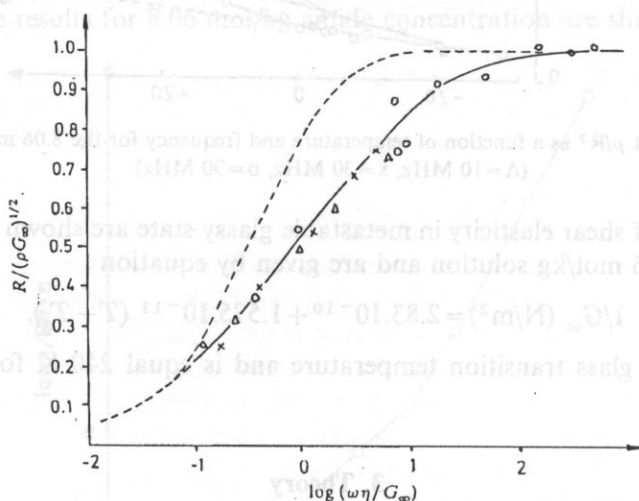

Fig. 3. The relaxation curve for acetamide+sodium trifluorooctane solution in normalised scale. ($\Delta = 10$ MHz, $x = 30$ MHz, $o = 90$ MHz).

show both Fig. 3 and 4 are presented in normalize scale, it means that the real part of impedance R_T is related to the highest impedance in glassy state $Z_T = \sqrt{\rho G_\infty}$ (and the frequency used in measurements is related to the maxwell relaxation frequency or relaxation time ($\tau_m = \eta_0/G_\infty$).

4. Results and discussion

The run of relaxation curve as a function of frequency (in normalised scale) for amide concentration 8.06 is shown on Fig 3. The points are the results measured on frequency 10, 30 and 90 MHz. The continuous line present the theoretical BEL model of relaxation with the parameter $\beta = 0.5$ and $K = 0.66$ in the equation
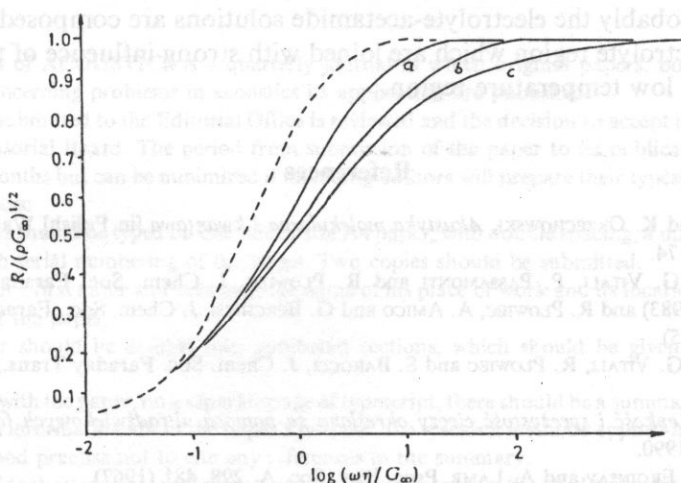
Fig. 4. The run of relaxation curve for a) acetamide+sodium tiocjanate mixture, b) acetamide+sodium trifluoroacetate mixture, c) acetamide+calcium nitrate mixture. Maxwell model represents the dotted line.

$$\frac{1}{G^*} = \frac{1}{G_\infty} + \frac{1}{j\omega\eta} + \frac{2K}{G_\infty\,(j\omega\tau_m)^\beta}.$$

The dotted line on Fig. 3 present the Maxwell model with one relaxation time ($K=0$). The scattering of results is caused by high hygroscopic of the investigated mixtures, specially in low temperature range.

We must say that the run of the relaxation curve for the 11.98 and 19.48 solution was exactly the some ($\beta=0.5$, $K=0.66$), it means that the concentration of amide have no influence on the relaxation processes in this mixtures.

There is another question for electrolyte-acetamide molten mixtures that the run of relaxation curves is close to the theoretical BEL model ($\beta=0.5$, $K=1$) which was created rather for the simple liquid [5], and it is difficult to say that the investigated mixtures the simple liquids are.

On Fig 4 you can see the relaxation curves of the last investigated electrolyte-acetamide molten mixtures i.e. of acetamide $+NaSCN$ (a), acetamide $+CF_3COONa$ (b) and acetamide $+Ca(NO_3)_2$. The range of relaxation times for curve (a) ($\beta=0,5$, $K=0,875$) and curve (b) ($\beta=0,5$, $K=0,66$) are even more narrow then BEL model curve which exactly follow the results of mixture (c) ($\beta=0.5$, $K=1$).

5. Conclusion

The measurements of electrolyte-acetamide solution with shear ultrasonic waves in relaxation region made clear that there is any influence of the amide concentration on the character of relaxation curve. This fact, the run of the relaxation curve close to the theoretical BEL model curve, dielectric [1] and NMR [6] results may

sugests that probably the electrolyte-acetamide solutions are composed of acetamide region and electrolyte region which are joined with strong influence of the metal ions tightly only in low temperature region.

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