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DIPOLE RETARDATION IN A MIXTURE OF ACETAMIDE AND CALCIUM NITRATE

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The results of investigations of the dielectric properties of an acetamide and calcium nitrate mixture ($x_{\mathrm{acetam}} = 0.7644$) are presented. They are to be complementary to ultrasonic and viscoelastic studies made previously [4]. It has been established that two relaxation processes exist. They are referred to the previously described ultrasonic relaxation spectra and retardation in the viscoelastic spectrum.

1. Introduction

Mixtures of acetamide and inorganic salts containing mono- and bivalent cations tend to create high viscosity supercooled liquids. This makes it possible to investigate structures of these systems in metastable, glassy state.

In previous published articles [1, 2] the acoustical and viscoelastic properties of a mixture of acetamide and sodium thiocyanate were investigated. The results of these investigations lead to the separation of the relaxation process of a structural nature. One supposes that this process is connected with the formation of polymeric chains in acetamide "coupled" by ions of metals. Dielectric relaxation measurements, made for the same mixture, support the existence of polymeric structures in glassy state [3]. Two dielectric relaxation times were found. The low-frequency process with a high dielectric increment was interpreted as a result of the cooperative movement of ions along the polymeric chain. The second one, which occurs in the megacycles/s range, was connected with the relaxation of $\mathrm{Na(CH_3CONH_2)_2^+}$ groups in a high-viscosity environment.

Mixtures of acetamide and bivalent ions also form glassy states, but their stability is much lower than similar ones with monovalent ions. It can be expected that, also in this case, polymeric structures connected by metal ions are created. However, investigations of the acoustical and viscoelastic properties of the mixture of acetamide and calcium nitrate have not given a correct answer as to whether the proposed polymerization process occurs in this mixture. In the used frequency range intensive relaxation of the chemical nature has been observed; however it can also be the relaxation connected with the vicinity of the phase transormation, called eutectic relaxation [4]. It can be assumed that the great electric charge of the metal ion leads to a stiffening of the polymer structure and shifting of the structural relaxation into the lower-frequency range. To check this idea dielectric relaxation investigations have been taken up.

In the absence of an external electric field, liquids which consist of molecules with a constant dipole momentum do not indicate spontaneous polarization. Under the influence of the applied electric field, the tendency of molecule rotation and their arrangement in coincidence with the direction of the electric field appears. This means that the resultant polarization originates and coincides with the direction of the field. The energy of the interaction between the dipole and electric field is many times smaller than thermic movement energy. This fact allows only for small deviation from random orientation of the dipole. Electric permeability is defined as

$$e=\frac{1}{e_0}\frac{P}{E}+1, \tag{1}$$

where e is the electric permeability, e_0 is electric permeability in the vacuum, P is the polarization and E is electric field intensity. Electric permeability depends on the frequency of the applied field. At lower frequency, when the dipole reorientation follows changes of the electric field, electric permeability achieves the maximum. When the frequency of the electric field increases, than the dipoles do not follow these field changes and, consequently electric permeability becomes the complex value. The dependence of the complex permeability on frequency for the dielectric relaxation process with single relaxation time is given by Debye's equation:

$$e^*(\omega)=e_\infty+\frac{e_{\mathrm{st}}-e_\infty}{1+j\omega t_D}, \tag{2}$$

where e_∞ and e_{st} are the electric permeabilities measured at high and low frequencies, respectively, ω is the angular frequency and t_D is the time of the dielectric relaxation. Separating the complex permeability in the real and imaginary parts gives

$$\begin{aligned} e'(\omega) &= e_\infty+\frac{e_{\mathrm{st}}-e_\infty}{1+\omega^2 t_D^2}, \\ e''(\omega) &= \frac{e_{\mathrm{st}}-e_\infty}{1+\omega^2 t_D^2}\,\omega t_D, \end{aligned} \tag{3}$$

The frequency dependence of the real and imaginary parts of the permeability is presented in Fig. 1. This dependence is similar to that for a complex compliance

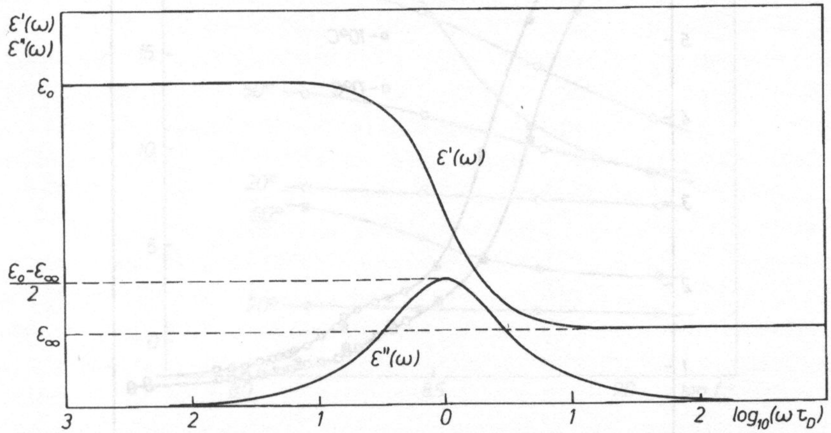

Fig. 1. The dependence of the complex electrical permeability on frequency for the monodispersive relaxation process.

$J^*(\omega)$. It should be underlined that this is only a formal similarity and results from a uniform description of the relaxation phenomena. Nevertheless, the process called dielectric relaxation can, through nomenclature analogy used in mechanical investigations, be called dielectric retardation.

2. Results of measurements

The electric permeability of the mixture of acetamide and calcium nitrate ($x_{\text{acetam}}=0.7644$) was measured in the ranges of temperature from -5 to 20°C and frequency from 0.5 kHz to 300 MHz. In the range of high temperature (20–110°C), the measurements were made only for frequencies 150–200 MHz. In the frequency ranges 0.5–10 kHz and 15 kHz–4.788 MHz the Semiautomatic Tesla Bridge and Wayn-Kerr Radio Frequency Bridge type B601 were used respectively. In measurements at higher frequencies the wave-guide methods were applied; at 150 and 300 MHz the coaxial concentric line was used, while the waveguide with a rectangular section was applied at 600 and 1200 MHz.

The results of measurements are shown in Tables 1–3 and in Figs. 2–4. In the low-frequency range, the dielectric losses were calculated from the formula: $e''=1.8\,\delta(f)$ where $\delta(f)$ is the specific conductivity, f is the frequency. In Figs. 2 and 3 the black points marek the results of measurements carrried out in the same system at Prof. R. Petrhrick's lab at the Strathclyde University of Glasgow (Great Britain) [5], which covered the low-frequency range 10^{-2}–10^5 Hz.

Accuracy of the measured permeability and dielectric losses was estimated at 5%.

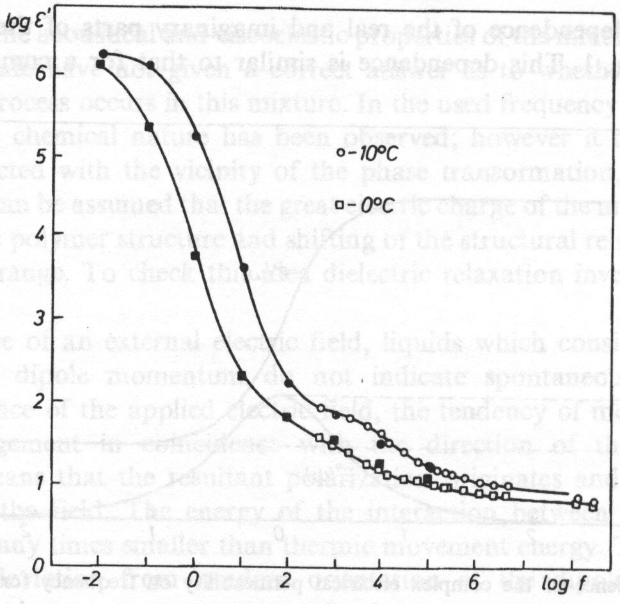

Fig. 2. The dependence of the real part of electrical permeability on frequency at the temperatures 0°C (–□–) and 10°C (–○–). The black points represent the values from Ref. [5].

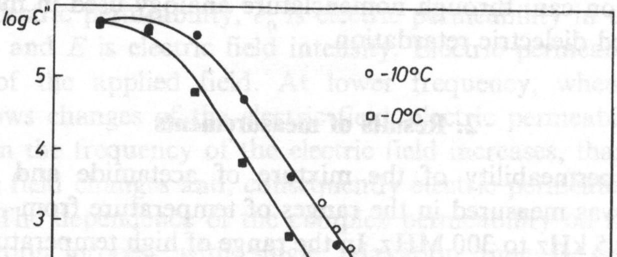

Fig. 3. The dependence of the imaginary part of electrical permeability on the frequency at the temperatures 0°C (–□–) and 10°C (–○–). The black points represent the values from Ref. [5].

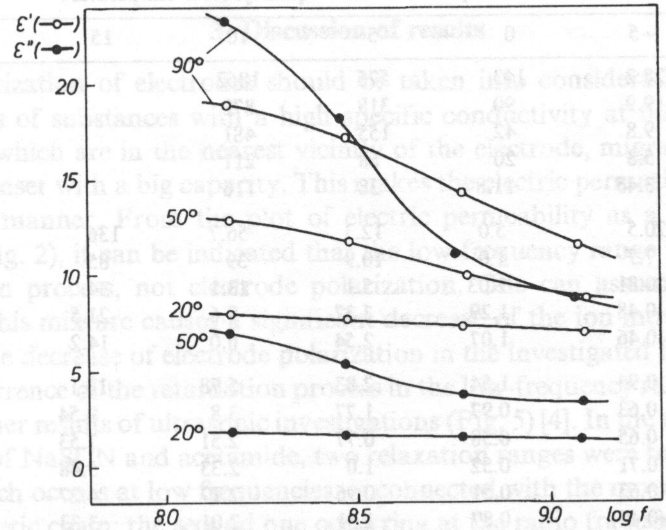

Fig. 4. The dependence of real and imaginary parts of electrical permeability on the frequency at high temperature.

Table 1. The real part of electrical permeability for the acetamide and calcium nitrate mixture as a function of temperature and frequency. Low temperature

f [kHz]	−5	0	5	10	15	20* °C
0.5	19	37	63	89.5		
1.0	15.5	30	53	75.5		
2.0	13	24	42	66		
5.0	11.5	18	31.5	52.5		
10	10	15	24.5	42		
15	9.5	13	19	33	57	75
30	9.2	11.5	16	25	41	65
60	9.2	11.5	14.5	19	29	52
120	8.5	10	12.5	16.5	26	43
240	8.5	9.5	11.5	15	22	33
149	8.5	10	12.2	15.4	22	33.3
300	8.1	9.4	11.1	13.8	18.6	29.5
596	7.6	8.8	10.3	12.2	15.4	21.2
1211	7.4	8.4	9.8	11.1	13.5	17.5
2382	7.0	8.0	9.7	11.0	12.8	15.5
4788	6.9	7.7	9.0	10.4	12.0	14.2
150000	6	6.5	6.9	7.3	7.8	8.2
300000	5.6	6.1	6.4	6.7	7.1	7.4

* — extrapolated

Table 2. The imaginary part of electrical permeability for the tested mixture dielectrtic losses as a function of temperature and frequency. Low temperature

f [kHz]	−5	0	5	10	15	20	°C
0.5	28.2	143	575	1862			
1	19.9	90	318	872			
2	9.8	42	155	481			
5	5.3	20	68	211			
10	3.45	11.8	38	116			
15	20.5	5.0	12.3	56.7	136	258	
30	7.7	1.0	10.9	39	85	147	
60	0.81	2.03	5.1	13.1	34	90	
120	0.48	1.29	3.37	8.6	21.5	52.5	
240	0.46	1.07	2.54	6.0	14.2	34	
149	0.94	1.54	2.83	5.78	13.1	33.4	
300	0.63	0.97	1.77	3.8	9.54	28.2	
594	0.65	0.58	0.77	2.51	7.53	17.5	
1211	0.71	0.52	1.0	2.33	5.48	11.4	
2382	0.63	0.51	0.96	2.17	4.27	7.38	
4788	(0.47)	0.87	1.31	2.01	3.33	5.65	
150000	0.34	0.5	0.7	0.96	1.24	1.56	
300000	0.6	0.74	0.94	1.15	1.4	1.64	

* — extrapolated

Table 3. The real and imaginary parts of electrical permeability for the tested mixture as a function of temperature and frequency. High temperature

T/°C	e'	e''	T/°C	e'	e''
	f=150 MHz			f=600 MHz	
101.7	19.6	31.7	108.3	14.9	13.4
91.4	18.8	25.4	98.3	14.5	11.8
80,9	16.8	18.6	86.0	13.4	9.1
70.1	15.8	13.4	74.8	12.2	7.0
59.3	14.3	8.6	63.5	11.0	5.3
49.3	12.2	5.8	53.5	9.9	3.9
39.5	10.6	4.0	43.9	8.8	2.7
30.2	8.9	2.7	31.2	7.7	1.2
22.8	7.9	1.8	22.8	7.3	1.0
8.9	6.6	1.0	12.1	6.3	0.8
	f=300 MHz			f=1200 MHz	
102.2	18.4	22.7	109.5	12.5	11.2
92.2	17.1	18.5	98.5	11.8	10.0
80.6	16.2	13.3	87.0	11.3	7.5
70.1	14.5	10.1	74.5	10.0	5.9
59.6	13.0	7.3	63.0	9.4	4.4
49.8	11.3	5.1	52.7	8.7	3.3
40.0	9.9	3.5	41.7	7.8	2.3
30.7	8.7	2.3	32.9	7.2	1.8
22.8	7.5	1.7	21.4	6.5	1.3
9.8	6.4	0.9	13.8	6.1	1.0

3. Discussion of results

The polarization of electrodes should be taken into consideration in dielectric investigations of substances with a high specific conductivity at the low-frequency range. Ions, which are in the nearest vicinity of the electrode, migrate to it forming a layer condenser with a big capacity. This makes the electric permeability increase in an apparent manner. From the plot of electric permeability as a function of the frequency (Fig. 2), it can be indicated that the low-frequency range is dominated by the relaxation process, not electrode polarization. One can assume that the high viscosity of this mixture causes a significant decrease of the ion movement. In turn, this causes the decrease of electrode polarization in the investigated frequency range.

The occurrence of the retardation process in the low-frequency range corresponds with the former results of ultrasonic investigations (Fig. 5) [4]. In the work concerning the mixture of NaSCN and acetamide, two relaxation ranges were found [1–3]. One of them, which occurs at low frequencies, is connected with the movement of cations in the polymeric chain; the second one occurring at the radio frequencies — with the reorientation $Na(CH_3CONH_2)_2^+$ groups. It seems that the low-frequency retardation, observed in the mixture of $Ca(NO_3)_2$ and acetamide, is caused by the cooperative movement of the solvated cations in the limits of the forming polymeric chains. From the measurements of $e'(f)$ and $e''(f)$, the relaxation time of this process can be estimated as $t_{(0°C)}=8$ s and $t_{(10°C)}=0.8$ s. These values are bigger nearly one order than those received in the mixture of NaSCN and acetamide ($t_{(0°C)}=0.13$ s and $t_{(10°C)}=0.06$ s) [3]. This increase of relaxation times is clear on the basis of the proposed mechanism of relaxation. The relaxation time can be connected with the ionic charge (Ze) and their mobility (K) in the following way [3]:

$$t=Ze\xi^2/nKT, \tag{4}$$

Thus the relaxation time grows when the charge of the ion, which "couples" the polymer chains, also grows. The dielectric increment, which is the difference between permeability measured at low and high frequencies, can be connected with the ion charge [3]:

$$\Delta e=e_{st}-e_{\infty}=\frac{4\pi nN}{6kT}(\xi Ze)^2. \tag{5}$$

Assuming the constancy of the correlation coefficient n, the ratio of the dielectric increments equals the ration of squares of the ion charges:

$$\frac{\Delta e(Na^+)}{\Delta e(Ca^{+2})}=\frac{Z^2(Na^+)}{Z^2(Ca^{+2})}=\frac{1}{4} \tag{6}$$

The estimation above corresponds with the experimental results:

$$\Delta e(Na^+)\simeq 4\cdot 10^6 \text{ [3]}, \qquad \Delta e(Na^+)/\Delta e(Ca^{+2})=1/4,$$

$$\Delta e(Ca^{+2})\simeq 16\cdot 10^6 \quad \text{(Fig. 2)},$$

It confirms the existence of the proposed model of the cation movement in the polymeric chain as a phenomenon which is responsible for retardation in the low-frequency range.

In the mixture of NaSCN and acetamide, the existence of the additonal relaxation process with a relatively high dielectric increment at the megacycles/s range ($\Delta e = 40$ at $T = 1.6°C$) [3] was established. In the mixture investigated here, the existence of this kind of process has not been found. Only for a temperature higher than 20°C can one observe a significant increase of electric permeability and losses (Fig. 4). It seems that this relaxatoin process may be hidden in the low-frequency one with a high dielectric increment. The shift of this relaxation to the low-frequency range may result from a cross linking of the polymer with the help of great-charge ions.

4. Conclusions

The electric permeability measurement, which were made for the mixture of acetamide and calcium nitrate, enable to support the polymeric structure model proposed for this liquid. Also it was indicated that low-frequency retardation is connected with the cooperation movement of Ca^{+2} ions in the polymeric chain. In the higher-frequency range the high dielectric increment of this process dominates the second relaxation, the existence of which was established by acoustical methods [4].

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