# Glass-transition temperature and molar conductivity of hydrated molten calcium nitrate and calcium chloride mixtures

J. NOVÁK, J. MALÁ, Z. KODEJŠ, and I. SLÁMA

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250 68 Řež near Prague

Received 6 January 1977

Accepted for publication 15 December 1977

Glass-transition temperatures  $(T_s)$  were determined in hydrated molten mixtures of the system calcium nitrate—calcium chloride—water with the ionic fraction of  $y_{\alpha} = [Cl^-]/([Cl^-] + [NO_3^-]) = 0.4$ , in the composition region of 5—23 mole % with respect to calcium salts. The equivalent conductivity\* was measured in the temperature range 293—353 K. A comparison with the system calcium nitrate—water showed that while the replacement of nitrate anions by those of chloride did not influence the glass-transition temperature, the equivalent conductivity decreased in systems with a higher salt content.

В гидратных расплавленных смесях системы  $Ca(NO_3)_2$ — $CaCl_2$ — $H_2O$  при анионной доле  $y_{Cl} = [Cl^-]/([Cl^-] + [NO_3^-]) = 0,4$  были определены температуры стеклообразования  $(T_y)$  в области концентрации кальциевых солей 5—23 мол. % и эквивалентная проводимость в температурном интервале 293—353 К. Сравнением с системой  $Ca(NO_3)_2$ — $H_2O$  было найдено, что замещение нитратных ионов хлоридными ионами не влияет на температуру стеклообразования, в отличие от эквивалентной проводимости, которая понижается в системах с более высоким содержанием солей.

In recent years an increased attention was paid to the investigation of supercooled ionic liquids [1-10]. The expression "ionic liquids" denoted either molten salts or highly concentrated solutions of salts [5]. The terms "undercooling" and "supercooling" are often used as synonyms [4, 11]. Now, however, they have acquired a more specific meaning. Undercooling means the ability of a liquid to exist for a certain time at a somewhat lower temperature (maximally by several Kelvins) than the equilibrium temperature of the liquidus for a given composition,

<sup>\*</sup> Instead of the term molar conductivity recommended by the IUPAC the term equivalent conductivity is used further in the text.

without observable crystallization, and it is used in the field of industrial crystallization [12]. Supercooling, *i.e.* the ability of a liquid to exist at a temperature ranging between the liquidus and the glass-transition temperatures (tens to hundreds of Kelvins), is used in the region of glass formation, *i.e.* for solidified amorphous structures formed by the cooling of melts, at which the first kind of transition did not take place [13].

The condition for the existence of supercooled liquids that cannot be avoided is therefore not only the possibility of its undercooling, but also the ability to form glassy amorphous structures at lower temperatures. Both these properties, however, depend on many factors, especially on the cooling rate. For the study of the properties of supercooled liquids their ability to exist in the whole supercooling range (*i.e.* from the liquidus to the glass-transition temperatures) appears to be of importance for the time required for experimental determination of the investigated properties. In this way it is possible to define the well supercooled liquids.

The supercooled ionic liquids are especially interesting from the point of view of their structure. The usual interpretation of the supercooling ability is based on the assumption of a vehement increase of the relaxation times of a certain configuration of polymer molecules with decreasing temperature. The fundamental structural entities of ionic liquids, however, are simple nonassociated or solvated ions, for which the process of reaching the equilibrium configuration should not be so complicated as it is in the case of chain molecules. Nevertheless many ionic systems exhibit not only glass formation on a macroscopic scale [1] but also a good behaviour from the supercooling point of view [8]. As a typical example we may consider the concentrated solutions of Ca(II) salts [1]; both the solutions of nitrates and of chlorides appear in a certain composition region to be glass-forming. For aqueous solutions of calcium nitrate the glass-forming composition region reaches 6.5-23 mole %, while for the chlorides the region is limited to 5-9 mole % of the salt. Besides, the glass-transition temperatures for chlorides are lower by about 10 K than values for nitrates in the comparable composition range. It appeared therefore to be of interest to investigate how the replacement of calcium nitrate by calcium chloride would affect the various properties of this ternary system.

It is known from the literature that in a certain composition region the addition of a further component to the system supports the glass formation, and the ability of forming supercooled solutions [14, 15]. From the structural point of view we may consider the replacement of salts with a common cation to be an exchange of the anions  $NO_3^-$  by  $Cl^-$  in the system of hydrated ions.

An important property of ionic solutions is their electric conductivity. Its magnitude is the measure of the tendency to rearrange the structure entities of the liquid in the nearest neighbourhood. In diluted electrolytic solutions the ionic mobility is influenced by many factors, especially by the fluidity of the medium. In

concentrated solutions the mechanism of the ionic transport in the electric field is different. A slow rearrangement of the ions might be the reason for an uneasy formation of the periodic structure, necessary for crystal formation. Therefore we directed our interest to the temperature and composition dependences of the equivalent conductivity at the exchange of anions in the system under consideration. As it follows from preliminary observations, the solutions of calcium nitrate and calcium chloride mixtures are more resistant to crystallization even at considerably lower temperatures than the liquidus temperature of the mixtures.

The object of this paper was to study the mutual relationship between the glass-transition temperature and the equivalent conductivity in the liquidus region of the system  $Ca(NO_3)_2$ — $CaCl_2$ — $H_2O$  at the composition given in terms of the mole fraction of chlorides,  $y_{CI} = n_{CaCl_2}/(n_{CaCl_2} + n_{Ca(NO_3)_2}) = 0.4$ , where  $n_A$  denotes the number of moles of the substance A.

## Experimental

#### Glass-transition temperature

All solutions were prepared by weighing the desired amounts of the recrystallized anal. grade chemicals and of distilled water. After homogenization, the samples were analyzed for their chloride content using the argentometric method with potentiometric indication of the equivalent point, and using chelatometry for their Ca(II) content. A standard amount of 0.2 ml of the sample was filled into quartz test tubes, 4 mm in diameter, using a syringe.

In order to determine the glass-transition temperatures the method of DTA with indication of the temperature and the temperature differences between the measured and the standard sample was applied. Benzene was used as reference substance. Copper—constantan thermocouples (0.2 mm in diameter) were placed directly in the samples. The test tubes with the samples were first rapidly cooled in liquid nitrogen to form glass. At the constant heating rate of  $0.1 \text{ K s}^{-1}$  the temperature difference between the investigated sample and benzene was measured from the liquid nitrogen temperature.

The experimental equipment consisted of a cryostat with linear temperature increase, based on the principle of a proportional regulation of cooling by means of nitrogen vapours and resistance heating. The cryostat was made of a copper block of 40 mm in diameter and 90 mm in height, and was provided with an evaporator and an indicator of the liquid nitrogen level in the lower part. This block was placed in a Dewar flask filled with liquid nitrogen so that during the measurement only the evaporating body could be immersed under the nitrogen level. This level was kept constant by pumping liquid nitrogen from a storage tank.

The block had vertical air vents through which the evaporated nitrogen flew from the bottom of the flask. The flow rate of the nitrogen was controlled by the input power of a resistor immersed into the liquid nitrogen. The heating of the block was provided by the resistance heating made of a Pt wire coiled on the jacket of the block. The linear temperature increase was ensured by a proportional regulator controlling the nitrogen evaporation and the resistance heating of the block. The copper—constantan thermocouple

placed in the third test tube in the block served as a sensor of the regulator. By the equipment described above linear heating was made possible in the range 100-400 K.

The temperature changes were recorded by means of two line recorders EZ 11. The calibration of the measuring thermocouple was carried out with a tested copper—constantan thermocouple.

# Equivalent conductivity

The experimental equipment, measuring technique, and the used reagents were analogical as described in the previous paper [9].

# **Results and discussion**

## Glass-transition temperature

In order to verify the function of the equipment the glass-transition temperatures in the binary system calcium nitrate—water were determined. The experimental results showed a good agreement with literature data [1] (Table 1). The relative deviations were less than 1%. The experimentally determined values of the glass-transition temperature  $T_g$  are shown in Fig. 1, plotted in dependence on the mole fraction of Ca(II) salts

$$x_{\rm Ca} = (n_{\rm Ca(NO_3)_2} + n_{\rm CaCl_2}) / (n_{\rm Ca(NO_3)_2} + n_{\rm CaCl_2} + n_{\rm H_2O})$$

at a constant chloride composition  $y_{CI} = 0.398$ . It is evident that the glass-transition temperature in the given composition range of Ca(II) salts is a linear function of the content of these salts. Such a dependence in this system is not surprising, since the concentrated solutions of calcium nitrate similarly as of calcium chloride exhibit in the glass-forming region a similar dependence. Though

	(T <sub>g.e</sub>	$_{*p}$ ) with the literature data	$[1, 3](T_{g, Ref})$	
9.601 X	X <sub>Ca</sub>	T <sub>g.exp</sub> K	T <sub>s. Ref</sub> K	Difference K
	0.08	168.1	169	- 0.9
	0.11	180.6	181	+0.4
	0.14	193.2	193	+0.2
	0.17	205.8	207	-1.2
	0.20	218.4	220	- 1.6
	0.23	230.9	230	+ 0.9

Table 1

Comparison of the glass-transition temperatures of hydrated calcium nitrate found experimentally  $(T_{e,ren})$  with the literature data [1, 3]  $(T_{u,Ref})$ 

for binary systems this relationship is not generally valid, yet in all systems investigated thus far it is possible to approximate the glass-transition temperature as a linear function of the salt content. Deviations usually appear in the boundary regions of glass formation.

Also for other types of liquid mixtures the temperature of glass transition was found to be a linear function of the composition. Thus, for example, for mixtures of dimethyl sulfoxide (DMSO) with water the dependence of  $T_g$  vs. composition is linear in the whole glass-forming region (40—80 mole % DMSO) [14]. Such a dependence was also found for calcium nitrate solutions in DMSO and in other solvents [15], in a wide range of glass formation (4—32 mole %). On the other hand, however, for metal alloys the curve expressing the dependence  $T_g$  vs. composition [16] exhibits a bend, though in limited composition regions it is possible to approximate the composition dependence of  $T_g$  to a linear function.

A simple composition dependence of glass-transition temperature would have a great significance in those cases, where it would be possible to predict the value of  $T_g$  of the mixture from the glass-transition temperatures of the components as an additive property. In multicomponent mixtures of silica and lead glasses the additivity of the glass-transition temperatures was determined [17]. Therefore, it would be of interest to find out, whether this phenomenon occurs also in ionic liquids. Unfortunately, however, the components themselves are for the most part not glass-forming, so that the values of  $T_g$  for pure substances are not known.

Another question under discussion is the glass-forming composition region. For solutions of calcium nitrate the glass-forming ability was found to be in the range 6.5–23 mole % of the salt, while for calcium chloride solutions it was the range



Fig. 1. Dependence of glass-transition temperature  $T_a$  (in K) on the mole fraction of calcium salts,  $x_{ca}$ , in the binary mixtures of a) CaCl<sub>2</sub>—H<sub>2</sub>O (line 1), b) Ca(NO<sub>3</sub>)<sub>2</sub>—H<sub>2</sub>O (line 2), and in the ternary mixture Ca(NO<sub>3</sub>)<sub>2</sub>—CaCl<sub>2</sub>—H<sub>2</sub>O (rings) with the ionic fraction of chlorides  $y_{ca} = 0.398$ .

5—9 mole % [1]. In the investigated mixture the value of  $T_g$  could be determined in the composition region of 8—23 mole % of the salts, practically representing the glass-forming ability region of calcium nitrate solutions. Though it cannot be generally stated that the glass-forming region of ternary mixtures should be an average of the starting binary systems, regarding the influence of the structure of solution on the glass-transition temperature, this appears to be probable. Thus it may be assumed that the replacement of the NO<sub>3</sub> ions by Cl<sup>-</sup> ones does not cause any principal structural change in the solution and that the mixture of calcium chloride and calcium nitrate will behave like a calcium nitrate solution with respect to glass-transition temperatures.

Further it is interesting that also the determined  $T_g$  values of the mixture are practically the same as the glass-transition temperatures of calcium nitrate. This is evident from Fig. 1, where the composition dependences of the  $T_g$  values for calcium nitrate and calcium chloride solutions are plotted as full lines. These dependences can be approximately described by the relations  $T_g = 135 + 420x_{ca}$ and  $T_g = 127 + 430x_{ca}$ , respectively. In the comparable composition region (7—9 mole % of salts) the values of glass-transition temperatures of chlorides are lower roughly by about 10 K than those for calcium nitrate. The fact that the values of  $T_g$  for calcium nitrate and for calcium chloride solutions are the same, even in the case when 40 mole % of calcium nitrate is replaced by calcium chloride, indicates that the  $T_g$  value of the mixture is not an additive property of the starting systems.

Table 2 presents literature data [18–20] on the liquidus temperatures  $T_1$ , the experimentally determined glass-transition temperatures  $T_g$ , the corresponding differences  $(T_1 - T_g)$ , and their ratio  $T_1/T_g$ . The technique used, *i.e.* heating of the

$Ca(NO_3)_2$ — $CaCl_2$ — $H_2O$					
	T <sub>I</sub> K	T <sub>s</sub> K	$\begin{array}{c} T_1 - T_g \\ \mathbf{K} \end{array}$	$T_{\rm i}/T_{\rm g}$	
		$y_{\rm CI} = 0.398$			
0.100		177.8	_	_	
0.125	—	189.3	_	_	
0.150	270.5	201.0	69.5	1.346	
0.175	288.0	212.8	75.2	1.353	
0.200	305.0	224.0	81.0	1.360	
0.225	322.0	235.4	86.6	1.367	

Table 2

Comparison of the liquidus temperatures and glass-transition temperatures of the ternary mixtures  $Ca(NO_3)$ ,—CaCl,—H<sub>2</sub>O

 $x_{ca}$  — mole fraction of calcium salts;  $T_1$  — liquidus temperature;  $T_8$  — glass-transition temperature;  $y_{c1}$  — mole fraction of chloride ions.

glassy samples at the rate of 0.1 K s<sup>-1</sup> did not allow to determine the liquidus temperature of the ternary mixture, because no crystallization took place at increased temperature. At the glass-transition temperature the glass turned into a supercooled liquid, which did not crystallize, not even when seeded with various substances. In discussing the ratio of  $T_1/T_g$  we used the assumptions of Angell and Sare [1], who found this ratio to have the value of 1.65 for calcium chloride and 1.53 for calcium nitrate solutions. For the investigated system this value appeared to be less than 1.37 and, consequently, it has not an additive character.

In [1] the ratio of  $T_{\rm l}/T_{\rm g}$  has also been calculated for a series of nitrates and chlorides of bivalent cations. It reaches the average values of 1.68 and 1.86 for the water-rich composition limit of glass-forming ability and the salt-rich composition limit, respectively, in the case of chlorides, while for nitrates these values are 1.58 and 1.62. The above-mentioned ratios are significant for the orienting prediction of  $T_{\rm g}$  for salt solutions. For the studied ternary mixture, however, these values are lower, so that for salt mixture solutions the rule of a constant ratio of  $T_{\rm l}/T_{\rm g}$  cannot be applied.

The maximum supercooling  $T_1 - T_g$  [16] is lower than that for calcium nitrate solutions, however, with respect to the comparison of the systems, this difference has no signification.

## Equivalent conductivity

The temperature dependence of the equivalent conductivity in electrolytic solutions appears as a deviation from the Arrhenius relation in the vicinity of the liquidus temperatures [6]. Thus it may be stated that the apparent activation



Fig. 2. Dependence of the activation energy of conductivity on temperature in the system  $Ca(NO_3)_2$ — $CaCl_2$ — $H_2O$ . Ionic fraction of chlorides :  $y_{c1} = 0.398$ .

Content of calcium salts in mole fraction,  $x_{ca}$ : 1. 0.198; 2. 0.165; 3. 0.139; 4. 0.102; 5. 0.075; 6. 0.052. energy, when formally using the Arrhenius relation, is not constant, but it considerably increases with decreasing temperature. The apparent activation energy may be calculated by derivation of the temperature dependence of the equivalent conductivity, *i.e.* 

$$E = -R \, \mathrm{d} \ln \Lambda / \mathrm{d}(1/T) \tag{1}$$

The values of the apparent activation energy of the samples under investigation are shown as functions of temperature for different salt content in Fig. 2.

For a correlation between equivalent conductivity and temperature in this region several modified equations were suggested as *e.g.* the Vogel equation

$$\Lambda = A_1 \exp(-B_1/(T - T_0))$$
 (2)

or the Vogel-Tammann-Fulcher equation

$$\Lambda = A_2 T^{-1/2} \exp\left(-\frac{B_2}{(T-T_0)}\right)$$
(3)

or the polynomial in the form

$$\ln \Lambda = A_3 + B_3 T + C_3 T^2 \tag{4}$$

where A, B, and C are empirical constants. The parameter  $T_0$  is considered to be the limiting value of the glass-transition temperature.

As seen in Fig. 2, the Arrhenius equation is unapplicable for the definition of the temperature dependence in the given region. On the other hand, the agreement of eqns (2-4) with the experimental data appears to be very good, since the deviations are less than 1%. This is in accordance with the data of other authors [4-8] who studied the transport phenomena in aqueous ionic melts and high-concentrated salt solutions. The constants for the calculation of  $\Lambda$  using eqns (2-4), which were obtained by means of the least square method, are listed in Table 3.

		Eqn (2)			Eqn (3)			Eqn (4)	
Х <sub>Са</sub>	To	<i>A</i> <sub>1</sub>	<i>B</i> <sub>1</sub>	To	<i>A</i> <sub>2</sub>	B 2	A 3	Β,	C <sub>3</sub> 10 <sup>4</sup>
0.198	214.1	205.4	610.0	210.7	5 228.3	668.4	-60.672	0.3210	-4.152
0.165	199.0	215.7	556.9	194.7	5 560.9	622.5	- 44.633	0.2439	- 3.190
0.139	222.1	91.1	285.0	217.1	2 236.3	331.9	- 37.608	0.2133	-2.838
0.102	172.9	291.3	466.3	164.7	7 956.9	557.8	- 19.489	0,1152	- 1.452
0.075	170.0	334.1	402.1	159.6	9 284.8	501.0	- 14.734	0.0932	-1.168
0.052	159.4	495.5	409.9	147.6	14 058.0	519.5	-11.635	0.0792	-0.982

Table 3 Constants for eqns (2-4) used in the calculation of  $\Lambda$  in the system Ca(NO<sub>3</sub>)<sub>2</sub>-CaCl<sub>2</sub>-H<sub>2</sub>O;  $y_{Cl} \doteq 0.4$ 

The composition dependence of the equivalent conductivity at a constant temperature can be approximated by the polynomial

$$\ln \Lambda = a + bx_{Ca} + cx_{Ca}^{2} + dx_{Ca}^{3}$$
(5)

For the computation of the polynomial constants the interpolated values of the equivalent conductivity were taken using eqn (4). The values of the constants a, b, c, d for the different temperatures are given in Table 4.

Table 1

Т,К –	а	b		d
303.15	4.6978	- 28.66	82.97	- 488.14
313.15	4.6692	-21.92	17.66	- 226.00
323.15	4.8297	- 22.45	27.50	-210.35
333.15	4.9165	-21.02	17.24	- 148.33
343.15	5.0399	-21.14	20.48	- 127.59
353.15	5.1499	-21.10	20.45	- 100.45

In order to appreciate the deviations of the equivalent conductivity for the studied system compared with calcium nitrate solutions the values of

$$F = \Lambda_{\text{melt}} / \Lambda_{\text{Ca(NO_3)_2}} \tag{6}$$

were calculated for different salt content and different temperatures. The results are summarized in Table 5. The values of (F-1) vary in dependence on the salt content from positive to negative. This behaviour of the calcium nitrate and calcium chloride mixture differs from the viscosity data [21] where always positive

	Magnitude of $F - 1$ for different temperatures and $x_{ca}$ values						
	Т, К						
	293.15	303.15	313.15	323.15	333.15	343.15	353.15
0.050	0.233	0.245	0.240	0.239	0.241	0.253	0.277
0.075	0.205	0.217	0.238	0.244	0.257	0.275	0.304
0.100	0.078	0.140	0.160	0.180	0.200	0.230	0.271
0.125	-0.080	0.013	0.031	0.066	0.093	0.138	0.198
0.150	-0.250	-0.156	-0.122	-0.073	-0.039	0.021	0.103
0.175	-0.378	-0.350	-0.278	-0.219	-0.175	-0.100	-0.085

Table 5

deviations of the viscosity were found for the mixture, compared with that of calcium nitrate solution.

The different response of the equivalent conductivity and viscosity or fluidity, respectively, with respect to the replacement of the anions of nitrate by chloride, may be explained by the different influence of the chloride anion on the investigated transport properties. The equivalent conductivity of calcium nitrate and calcium chloride solutions in their infinitely diluted state is not too different (135.8 and 130.9, respectively, S cm<sup>2</sup> val<sup>-1</sup> at 298.15 K). In more concentrated solutions, however, the difference between the equivalent conductivity of calcium chloride and calcium nitrate becomes considerably greater. Denoting the ratio of the conductivities of calcium chloride and calcium nitrate as

$$F_{\max} = \Lambda_{\text{CaCl}_2} / \Lambda_{\text{Ca(NO}_3)_2} \tag{7}$$

it is possible to approximate the experimental data of the conductivity in the composition region of 0.5-5 N using the relation [22]

$$\ln \Lambda = \ln \Lambda^{\circ} - c V'' \tag{8}$$

where  $\Lambda^{0}$  is a parameter calculated from experimental data and has the meaning of the numerically extrapolated value of the equivalent conductivity to zero salt content with respect to relation (8); c is the normal concentration of solution, and V" is the equivalent volume of the inhibiting zones of electrolyte. If we denote the values of calcium nitrate and calcium chloride, respectively, with indices "1" and "2", then combining and adapting eqns (7) and (8) we obtain

$$\ln F_{\max} = \ln \left( \Lambda_2 / \Lambda_1 \right) = c \left( V_1'' - V_2'' \right) + \ln \left( \Lambda_2^0 / \Lambda_1^0 \right) \tag{9}$$

Inserting the known values [22] ( $\Lambda_1^0 = 78.4$ ;  $\Lambda_2^0 = 82.4$ ;  $V_1'' = 0.264$ ,  $V_2'' = 0.156$ ), it is possible to calculate  $F_{\text{max}}$  at 298.15 K and c = 5 N. The found value of  $F_{\text{max}}$  is 1.72. Assuming that the conductivity of the calcium nitrate and calcium chloride mixture is additive, we obtain for  $y_{CI} = 0.4$  the value of F = 1.3. Since in the mentioned composition range the numerical value of the concentration, expressed in normalities, is nearly equal to the value in mole %, this value of F is applicable for the salt composition, expressed by the mole fraction of  $x_{Ca} = 0.05$ . The viscosity of the studied mixture is practically the same as that of the calcium nitrate solution. Therefore, in the composition region of  $x_{Ca} = 0.05$  positive deviations of the conductivity of the mixture can be observed, compared with the calcium nitrate conductivity.

With increasing salt content the steeply increasing viscosity of the ternary system shows a growing influence. The value of (F-1) passes through the maximum and at a higher salt content usually negative deviations of the conductivity of the mixture are observed with respect to the conductivity of calcium nitrate solutions. This tendency is especially expressed at lower temperatures.

It is difficult to evaluate quantitatively the influence of the salt content in the system and of the replacement of nitrate by chloride anions on the conductivity and viscosity, because these two influences are not independent. The orientation values can be derived from the product  $\Lambda\eta$ . The dependences of both the equivalent conductivity and fluidity on the salt content at a constant temperature were approximated using the polynomials of the same order. Thus the value of the product  $\Lambda\eta$  can be calculated from the relation

$$\ln (\Lambda \eta) = (a - a_1) + (b - a_2)x + (c - a_3)x^2 + (d - a_4)x^3$$
(10)

where a, b, c, d are constants of the composition dependence of the equivalent conductivity and  $a_1-a_4$  are constants of the same dependence of fluidity, taken from the previous paper [21]. The values of the product  $\Lambda\eta$  increase with increasing salt content and they indicate a steeper composition dependence of viscosity than that of conductivity. Analogous results were obtained for binary systems Ca(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O [3]. In order to evaluate the influence of the replacement of the anions on this dependence, the values of the  $\delta$  coefficient were calculated for different temperatures and salt content of the system

$$\delta = (\Lambda \eta)_{\text{mixt}} / (\Lambda \eta)_{\text{Ca(NO_3)}_2} - 1$$

The values are listed in Table 6. From these data it is evident that the increase of the value  $\Lambda\eta$  with increasing salt content in the system is much greater for the ternary system than for the system Ca(NO<sub>3</sub>)<sub>2</sub>—H<sub>2</sub>O. This tendency is the more significant, the lower is the temperature.

Concluding it may be stated that the replacement of the nitrate anions by chloride anions in the system exhibits also for the value of  $y_{CI} = 0.4$  a different effect on the conductivity, viscosity, and glass-transition temperature. It is, however, interesting that the temperature dependence of the transport properties in the liquidus region of the ternary system can be also quantitatively described by

Table 6 Values of the coefficient $\delta$							
Т, К							
$x_{Ca}$ –	293.15	303.15	313.15	323.15			
0.050	0.076	0.106	0.111	0.107			
0.075	0.112	0.174	0.169	0.209			
0.100	0.148	0.213	0.186	0.232			
0.125	0.215	0.256	0.198	0.216			
0.150	0.356	0.343	0.241	0.207			
0.175	0.635	0.528	0.359	0.252			
0.200	1.189	0.906	0.622	0.409			

equations of the same type as for calcium nitrate solutions, the value of the  $T_0$  parameter being close to the experimentally determined glass-transition temperature.

Acknowledgements. We express our gratitude to Dr M. Smíšek for the construction of the equipment used for determination of the glass-transition temperatures.

# References

- 1. Angell, C. A. and Sare, E. J., J. Chem. Phys. 32, 1058 (1970).
- 2. Vuillard, G., Ann. Chim. (Paris) 2, 233 (1957).
- 3. Bressel, R., Thesis. Purdue University, Lafayette, 1972.
- 4. Angell, C. A., J. Phys. Chem. 70, 2793 (1966).
- 5. Moynihan, C. T., J. Phys. Chem. 70, 3399 (1966).
- 6. Angell, C. A., J. Phys. Chem. 70, 3989 (1966).
- 7. Angell, C. A., J. Phys. Chem. 68, 2137 (1965).
- 8. Angell, C. A. and Bressel, R. D., J. Phys. Chem. 76, 3244 (1972).
- 9. Novák, J., Sláma, I., and Kodejš, Z., Collect. Czech. Chem. Commun. 41, 2838 (1976).
- 10. Novák, J., Sláma, I., and Kodejš, Z., Chem. Zvesti 31, 29 (1977).
- 11. Uhlmann, D. R., Non-Cryst. Solids 7, 337 (1972).
- 12. Matuchová, M. and Nývlt, J., Chem. Prům. 22, 537 (1972).
- 13. Šatava, V., Czech. J. Phys. A23, 565 (1973).
- 14. Rasmussen, D. H. and Mac Kenzie, A. P., Nature 220, 1315 (1968).
- 15. Sare, E. J. and Angell, C. A., J. Solution Chem. 2, 53 (1973).
- 16. Chen, H. S., Acta Met. 22, 1505 (1974).
- 17. Frieser, G. B. and Tummala, R. R., Glass Technol. 16, 149 (1975).
- 18. Gmelin's Handbuch der anorganischen Chemie, Syst. No. 28; Calcium, Teil B, p. 555, 1957.
- 19. Vereshchagina, V. S. et al., Zh. Neorg. Khim. 18, 507 (1973).
- 20. Vereshchagina, V. S. et al., Zh. Neorg. Khim. 14, 3390 (1969).
- 21. Kodejš, Z., Horsák, I., and Sláma, I., Rev. Roum. Chim., in press.
- 22. Čeleda, J., Sborník VŠCHT, Praha. (Proc. Univ. Chem. Techn.) B11, 5 (1967).

Translated by M. Uhrová