GLASS TRANSITION TEMPERATURE OF HYDRATED MIXTURES OF CALCIUM CHLORIDE AND NITRATE, CALCIUM BROMIDE AND NITRATE, AND CALCIUM IODIDE AND NITRATE

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The glass transition temperature depends linearly on the concentration and mole fraction of halide ions, y_X, in the studied concentration range up to $y_X = 0.95$. The behaviour of the three studied systems was compared.

An increased attention has been paid to the investigation of the low-temperature region of hydrated inorganic salts, *i.e.*, the region of undercooled solutions and glasses. Sare and Angell[1,2] pointed out the glass-forming ability of many hydrated salts. Their results reveal an interesting fact that certain combinations of cations and anions in electrolyte solutions either do not form undercooled solutions and glass or form them only in a limited concentration interval, whereas other combinations form them very easily. The influence of the character or concentration of individual ions on the glass formation and its concentration range is, however, not clear. This problem can be solved by a systematic study of systems in which one sort of ions is gradually replaced by another one. The mutual replacement of ions the salts of which differ appreciably by their glass-forming concentration regions is from this point of view most interesting. Such an investigation is possible since the multicomponent systems can be more easily undercooled. It is also possible to compare the behaviour of binary systems described earlier[1,2] with the ternary ones which have been studied only sporadically.

In studying the low-temperature regions, the glass transition temperature is most easily experimentally accessible. This quantity, which characterizes the transition from an undercooled liquid to an amorphous phase, is nowadays considered as an important source of information for the structure of liquids and amorphous solids as well as for the determination of the concentration range of glass-forming mixtures. We therefore studied the influence of a gradual replacement of the anion in the model system $Ca^{2+}/NO_3^-/X^-/H_2O$, where $X = Cl$, Br, or I, on the concentration range of the glass-forming region and on the temperature of the glass transition of this system.

EXPERIMENTAL

All chemicals were of reagent grade. The solutions were prepared by dissolving a weighed quantity of calcium halide in a weighed analysed calcium nitrate solution. Samples with a chosen water content were then obtained by diluting or evaporating. Their content of halide ions was checked argentometrically, that of calcium ions complexometrically. The water content in the system was expressed by molar ratio, R, of water to calcium ions. The salt content in the system was expressed by the mole fraction of calcium ions:

$$x = n_{Ca^{2+}}/(n_{Ca^{2+}} + n_{H_2O}) = 1/(R + 1).$$

The content of halide ions was given by their mole fraction, $y_X = n_{X^-}/(n_{X^-} + n_{NO_3^-})$ (X^- denotes halide ion).

The glass transition temperatures were determined by differential thermal analysis with indication of both the temperature and the temperature difference between the sample and standard, *i.e.*, benzene. Copper–constantan thermocouples (0·2 mm in diameter) were placed directly in the samples. Laboratory vessels with the samples were first cooled in liquid nitrogen at a rate of about 17 K/s under formation of glass. The temperature difference between the sample and benzene was measured during heating at a constant rate of 0·1 K/s beginning from the temperature of liquid nitrogen. The experimental setup was described earlier[3]. With samples which could not be transferred in the melted state into the laboratory vessel, the formation of glass was determined in a simplified way. The melt was taken by a warm glass pipette and dropped on a metal spoon dipped in liquid nitrogen, whereby a spherical drop was formed which was studied optically to check the presence of crystals.

RESULTS AND DISCUSSION

The Glass-Forming Concentration Range

The experimental results are summarized in Tables I—III, where the glass-forming concentration regions are indicated for mixtures of calcium nitrate and halides in dependence on the total concentration of the salts in the system. The glass-forming concentration region is limited by the minimum and maximum salt content. Within this region, macroscopic glass samples can be obtained by rapid cooling. The lower concentration limits are usually defined by two concentrations: the lower one for solutions that crystallize distinctly after rapid cooling, the higher one refers to solutions that give glass without detectable crystals after rapid cooling. The high-concentration glass-forming limit should be defined by two limiting concentrations, of which the lower would refer to solutions that form glass after rapid cooling and the higher one to solutions that crystallize. In view of high values of the liquidus for hydrated mixtures of calcium nitrate and halides at higher salt concentrations, their melting and homogenizing required such a high temperature that a considerable evaporation of water from the mixture took place. Since the solutions were very viscous and water evaporated from the surface layer, homogeneity of the system could not be ensured. Therefore, in most cases only the highest concentrations of those solutions which were

indeed homogeneous are given in the Table. All these solutions were glass-forming. It is, however, possible that if homogeneous solutions of higher concentration could be prepared, they would not crystallize during rapid cooling.

In systems where the nitrate ions were gradually replaced by chloride, the probable values of the low-concentration glass-forming limit are in the range of the values found with solutions of calcium nitrate and chloride[1]. At a higher content of Cl^- ions in the ternary mixture, the glass-forming limit approached gradually the value found with binary calcium chloride solutions. A similar course of the low-concentration glass-forming limit was found with other ternary systems under study.

The high-concentration limit of the glass formation is with all ternary systems under study characterized by a sudden drop during replacement of $90-100 \text{ mol}\%$ of nitrate with halide ions. This finding is interesting from the point of view of the difference between binary calcium nitrate solutions on the one hand and calcium halides on the other hand. Calcium nitrate forms a tetrahydrate as the first crystalline phase in the water–salt system. However, solutions of this composition form easily glass and can be readily undercooled. For example, Ambrus and coworkers[4] mea-

TABLE I

Range of Glass-Forming Concentration Region and Parameters A, B for the Dependence (1) of Glass Transition Temperature T_g (K) on Mole Fraction x of Ca^{2+} Ions in $Ca(NO_3)_2$–$CaCl_2$– –H_2O System

y_{Cl}	Low-concentration limit x	High-concentration limit x	N	A	S_A	B	S_B
0	0·066	0·256	21	141	0·5	383	3·0[a]
0·098	0·055−0·068	0·202	6	133	1·6	435	10·1
0·196	0·061−0·076	0·225	7	137	1·0	427	6·9
0·308	0·057−0·072	0·250	7	132	1·6	443	8·5
0·398	0·053−0·076	0·227	7	132	1·8	466	14·1
0·500	0·054−0·070	0·275	9	128	4·1	455	25·8
0·625	0·054−0·076	0·225	8	124	3·7	489	24·7
0·720	0·054−0·062	0·205	6	124	3·0	474	24·0
0·800	0·048−0·064	0·228	17	126	2·1	460	16·6
0·850	−0·057	0·185	6	125	6·2	469	6·1
0·900	0·054−0·062	0·225	11	123	4·4	458	41·2
0·950	0·050−0·054	0·081−0·093	9	122	1·5	460	21·9
1·000	−0·053	0·087−0·094	10	123	0·8	471	11·6[a]

y_{Cl} Mole fraction of Cl^- ions, N number of measured data, S_A and S_B standard deviations of A and B; [a] the constants A, B were calculated from experimental data in ref.[1].

sured the viscosity of these solutions up to 148 K, *i.e.*, 68 K below the liquidus temperature. Sare[1] succeeded in determining the temperature of the glass transition even for solutions more concentrated than correspond to calcium nitrate trihydrate. In contrast, for calcium halides, where the first crystalline phase in the water-salt system is hexahydrate, the high-concentration glass-forming limit is at most 10 mol% salt. This means that solutions with $R < 9$ have a marked tendency to form crystalline hexahydrate. We expected that the addition of calcium chloride to hydrated calcium nitrate will cause a lowering of the high-concentration limit, which is however not the case. On the contrary, we obtained glass with nitrate–halide–water mixtures at higher salt concentrations than with the binary calcium nitrate–water system. The high-concentration limit was lowered only when more than 90 mol% of nitrate ions was replaced by halide. Conversely, when halide ions are replaced by nitrate, crystallization in calcium halide solutions is effectively suppressed already by small additions of calcium nitrate.

Influence of Salt Concentration on Glass Transition Temperature

The dependence of the glass transition temperature on the salt concentration at a constant ratio of nitrate to halide ions can be within the limits of experimental errors

TABLE II

Range of Glass-Forming Concentration Region and Parameters A, B for the Dependence (*1*) of Glass Transition Temperature T_g (K) on Mole Fraction x of Ca^{2+} Ions in $Ca(NO_3)_2$–$CaBr_2$–H_2O System

y_{Br}	Low-concentration limit x	High-concentration limit x	N	A	S_A	B	S_B
0	0·066	0·256	21	141	0·5	383	3·0
0·100	0·056−0·074	0·199	12	129	2·6	461	16·1
0·200	0·054−0·076	0·206	6	127	1·4	464	9·1
0·300	0·056−0·080	0·194	6	126	6·3	493	42·2
0·400	0·055−0·079	0·188	5	126	4·5	476	31·4
0·500	0·053−0·076	0·187	5	127	5·2	492	37·8
0·610	0·055−0·074	0·220	8	120	4·1	517	29·1
0·704	0·050−0·057	0·213	7	118	4·0	506	27·1
0·790	0·050−0·056	0·199	10	119	2·1	488	14·5
0·893	0·049−0·058	0·229	6	109	5·9	548	44·6
1·000	0·05	0·091−0·110	12	124	0·4	434	6·2

y_{Br} Mole fraction of Br^- ions, other symbols see Table I.

approximated as

$$T_g = A + Bx_{Ca},\qquad(1)$$

where A and B are constants, which were calculated by the least squares method for different solution compositions (Tables I–III) and x_{Ca} is mole fraction of calcium ions.

With ionic liquids, the linear dependence of the glass transition temperature is a rather usual case. A practically ideal additive system was found in the case of mixtures of calcium and cadmium nitrate tetrahydrate[5]. Unfortunately, the range of the glass-forming concentrations is in aqueous salt solutions always limited, so that experimental values can be determined only within a certain concentration range. The mentioned linear dependence is generally a good first approximation also in these systems. An exception is, for example, the system LiCl–H_2O whose dependence of the glass transition temperature shows distinct breaks at different salt concentrations.

Generally, however, most extrapolations of the glass transition temperature to zero salt concentration lead to the temperature of glass transition of water in the interval 128–139 K, close to the experimentally determined value for pure water[2].

TABLE III

Range of Glass-Forming Concentration Region and Parameters A, B for the Dependence (1) of Glass Transition Temperature T_g (K) on Mole Fraction x of Ca^{2+} Ions in $Ca(NO_3)_2$–CaI_2––H_2O System

y_I	Low-concentration limit x	High-concentration limit x	N	A	S_A	B	S_B
0	0·066	0·256	21	141	0·5	383	3·0
0·100	0·054–0·078	0·195	5	130	2·9	410	19·9
0·200	0·058–0·089	0·191	5	121	5·4	497	37·8
0·300	0·054–0·077	0·181	6	127	4·2	458	28·8
0·400	0·053–0·078	0·185	6	119	1·8	523	12·0
0·500	0·054–0·078	0·165	4	109	6·7	599	53·1
0·600	0·062–0·071	0·163	6	118	1·1	528	97·8
0·694	0·063–0·071	0·179	5	105	8·1	624	66·6
0·827	0·056–0·062	0·172	7	107	10·3	674	89·7
0·940	0·048–0·054	0·160	6	130	17·6	268	16·3
0·950		0·079–0·117					
1·000	0·050	0·050–0·117	13	129	0·4	307	5·4

y_I Mole fraction of I^- ions, other symbols see Table I.

The parameter A has the physical meaning of the approximate temperature of glass transition of water in the studied ternary systems. Its values (Table I) are for the calcium nitrate–calcium chloride–water system practically in the expected range of temperatures found with most salt–water systems. The value of A decreases with increasing content of chloride in the system, which is in accord with the values of A for binary systems calculated from the values of the glass transition temperature[1], namely 141 for calcium nitrate and 123 for calcium chloride solutions. This agreement suggests that also in ternary mixtures of calcium nitrate and chloride it is possible to obtain a probable value of the glass transition of water by extrapolation of the concentration dependence of the glass transition temperature. The situation is somewhat different in the case of ternary systems with bromides or iodides. The found values of A are in some cases lower than those calculated from the values of T_g for binary systems, namely $A = 124$ for bromide and 129 for calcium iodide. This disagreement can be attributed either to a larger scatter of the experimental values or to a nonlinear course of T_g values in the experimentally inaccessible range of low salt concentrations.

The physical sense of the other parameter, B, in the concentration dependence of T_g for binary salt–water systems can be derived from the extrapolation of this dependence to a salt concentration of 100%. While the parameter A gives the value of T_g for water, B gives ΔT_g, the difference between the hypothetical T_g value for the anhydrous salt and that for water. The hypothetical T_g values thus found for melted calcium halides and nitrate are by $300 - 600$ K lower than the corresponding melting points. These values appear plausible since they do not exceed the melting points of the pure salts and are comparable with the values of T_g obtained analogously in a binary system of anhydrous salts.

With ternary systems of hydrated calcium nitrate and chloride, the value of B is in the range of binary systems with a slightly increasing trend in dependence on the

TABLE IV

Parameters C, D for the Dependence (2) of T_g (K) on Mole Fraction of Halide Ions y_X in Hydrated Mixtures of $Ca(NO_3)_2$ with I) $CaCl_2$, II) $CaBr_2$, and III) CaI_2 at Mole Fraction x of Ca^{2+} Ions

x	I		II		III	
	C	D	C	D	C	D
0·08	171	−10·96	169	−13·87	166	−13·08
0·11	183	−9·59	182	−10·78	178	−5·83
0·14	196	−8·22	195	−7·69	191	−1·48
0·17	209	−6·85	208	−4·60	203	−8·66
0·20	222	−5·48	222	−1·52	216	−15·90
0·23	235	−4·12				

chloride content. The same applies within the limits of experimental errors also for the mixture of calcium nitrate and bromide. With iodide-containing mixtures, however, a considerable increase and scatter of the parameter B is observed. The scatter is probably due to inaccuracy of the determination of T_g for iodide systems at high salt concentrations.

Influence of Anion Exchange on Glass Transition Temperature

To judge this influence at constant salt concentration in hydrated mixtures of calcium nitrate and halide, we calculated the values of T_g for chosen salt concentrations from Eq. (*1*). A comparison of these values showed that the influence of anion exchange can be approximately expressed as

$$T_g = C + D y_X , \qquad (2)$$

where the parameters C and D are constants at chosen salt concentrations and y_X is the mole fraction of halide ions. The constants C and D are given in Table IV for different halide systems.

The values of C are for chloride and bromide-containing mixtures practically equal, for iodide slightly lower, and preserve an increasing trend with increasing content of calcium salts.

The values of D, on the other hand, increase with the total salt concentration, but the dependence in the order Cl^-, Br^-, and I^- is more pronounced. The substitution of nitrate for chloride leads with chloride mixtures in the accessible concentration always to a decrease of the value of T_g although this effect is not very marked with concentrated systems. In $Ca(NO_3)_2$–$CaBr_2$ mixtures, the influence of anion exchange is in the most concentrated solutions not observed. With nitrate–iodide mixtures, the substitution of I^- for NO^- ions causes a decrease of T_g for more diluted solutions and an increase for more concentrated ones.

In the case of anion exchange, the influence of the composition on T_g can be followed practically in the whole concentration range, *i.e.* from zero to 95 mol% halide at constant water content. This is similar to the $Ca(NO_3)_2.4 H_2O$–$Cd(NO_3)_2.4 H_2O$ system, where an ideal behaviour, *i.e.*, an additivity of the T_g values as function of the molar composition was found[5]. In the mentioned system, however, we have to deal with a gradual exchange of cations, whereas in the systems under study anions are gradually exchanged. It is interesting that in both cases the systems behave within the limits of experimental errors ideally with respect to the glass transition temperatures, *i.e.*, additively. In addition to the conclusions in ref.[5], we conclude that with the studied ternary systems the additivity of T_g values is preserved at various water concentrations. It can be hence assumed that the exchange of ions in ternary systems

leads to hydrated ionic mixtures which are ideal with respect to the additivity of the glass transition temperatures.

This conclusion is important since informations about ionic ternary systems are up to now insufficient to deduce a more general concept of these systems. The prediction of additivity of glass transition temperatures during exchange of cations or anions at constant concentration of the solvent can be of great value for further study of undercooled systems.

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