GLASS TRANSITION TEMPERATURE OF CALCIUM NITRATE–POTASSIUM NITRATE–WATER SYSTEM

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The glass-forming concentration region of the calcium nitrate–potassium nitrate–water system was determined. The glass transition temperature can be in the studied region approximated by a linear function of the salt concentrations. A comparison of the properties of the studied system with the hydrated calcium nitrate and chloride mixture revealed important differences in the effect of different salts on the undercoolability of aqueous calcium nitrate solutions.

The glass-forming capability of very concentrated solutions of hydrated salts has been studied mainly by Angell and Sare[1,2]; subsequent publications[3–5] were concerned with the glass transition temperatures of the hydrated salt mixtures, especially with regard to the effect of the composition (replacement of cations or anions) and the limits of the glass-forming region.

The effect of the composition of ionic liquids on the glass-forming capability is related to the effect of the structure of the solution to diminish the nucleation frequency and/or the rate of crystal growth below the liquidus temperature. It is of interest from this point of view to compare the influence of the solvation agent and of another salt on the structure of a single salt solution. In the case of two salts with a common anion, it is possible to compare the interaction between the cation and the solvation molecule as well as between two cations.

The present work deals with the glass transition temperature of the calcium nitrate–potassium nitrate–water system, where it is possible to compare the effects of K^+ ions and water on the degree of undercooling.

EXPERIMENTAL

All chemicals were of reagent grade. The solutions were prepared in two steps. First, solutions of a given cation concentration, z, were prepared by weighing potassium nitrate dried at 150°C, which was then added to a filtered, weighed and analysed calcium nitrate solution. Then the concentration of water was adjusted by dilution or evaporation. Its value, R, was expressed as the ratio of the number of mols of water to the number of mols of the salts in the system. Accordingly, the mole fraction of the salts, x, is equal to $1/(R + 1)$. The content of K^+ ions was expressed as their ionic fraction $z = n_K/(n_K + n_{Ca})$.

For the investigation of the glass-forming region, the solutions were pressed out by a syringe from a heated glass pipette into small reagent glasses of 4 mm diameter, which were rapidly immersed into liquid nitrogen. The solution from the glass pipette was analysed.

To check the glass-forming capability in a nonaqueous system, we prepared a mixture of about 50 mol% potassium nitrate dried for 2 h at 200°C and 50 mol% calcium nitrate dried in a vacuum oven (0·1 MPa underpressure) for 48 h at 180°C. The substances were weighed in air atmosphere. The mixture was put into a reagent glass, closed with a rubber stopper protected with a Teflon foil, and bubled for 4 h with nitrogen dried with magnesium perchlorate at 250°C. The sample, which was taken off and cooled in nitrogen atmosphere, was dropped into a titrated Carl Fischer reagent without causing a change in the titre of the solution. The sample prepared in this way did form glass.

The glass transition temperature was determined by differential thermal analysis with an indication of both the temperature and the temperature difference between the sample and standard[6].

RESULTS AND DISCUSSION

Glass-Forming Region

The glass-forming concentration region is the region of concentrations of the individual components in which macroscopic glass samples can be obtained by cooling the system rapidly. The composition of the ternary system under study is schematically shown in Fig. 1 by the closed region in the triangular diagram (JKLMNRPJ). This glass-forming region is approximately delimited by connecting lines led through

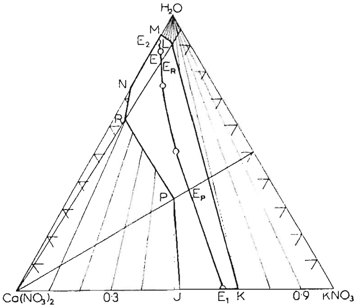

FIG. 1

Glass-Forming Region for $Ca(NO_3)_2$–KNO_3–H_2O System

The ionic fraction of K^+ ions is given on the abscissa, the salt concentration is given in mol%.

the glass-forming concentration limits of the binaries calcium nitrate–water and calcium nitrate–potassium nitrate. The potassium nitrate–water system does not form glass at normal pressure.

To evaluate the results, the concentrations of KNO_3 and water were referred to 1 mol $Ca(NO_3)_2$ as a base. Thus, hydrated calcium nitrate forms glass by rapid cooling of solutions containing $3-14$ mol H_2O per mol $Ca(NO_3)_2$ (ref.[1,2]). The same applies for nonaqueous mixtures of KNO_3 and $Ca(NO_3)_2$ containing more than 1 and not essentially more than 2 mol KNO_3 per mol $Ca(NO_3)_2$ (ref.[7]). We see that the limits for binaries are different. The ternary system can be obtained by gradually replacing water with KNO_3 in the aqueous calcium nitrate, or by gradually replacing KNO_3 with water in the KNO_3–$Ca(NO_3)_2$ system. The ternary solutions can be characterized also by the molar ratio of both KNO_3 and water per 1 mol $Ca(NO_3)_2$.

The glass-forming concentration region is in the ternary diagram delimited by lines with a higher and lower content of $Ca(NO_3)_2$. The glass-forming limit with a higher content of $Ca(NO_3)_2$ can be characterized by three portions. In the range of the molar ratio of water to KNO_3 from 0 to 1 (JP), the mentioned limit can be approximated by the symmetry axis of the abscissa $Ca(NO_3)_2$–KNO_3. Hence, in this region the addition of water has no effect on the ionic fraction, z, of K^+ ions at which the glass formation appears. At a molar ratio of water to KNO_3 from 1 to 20 (PR), the glass-forming limit can be approximated by a line parallel to the triangle side KNO_3—H_2O. In this concentration region, the glass-forming limit is shifted toward lower values of z and is given by the ratio $N = (n_K + n_{H_2O})/n_{Ca} = 2$. The third portion of the glass-forming limit at a very low content of KNO_3(RN) is characterized by $N = 2-3$.

The glass-forming limit with a low content of $Ca(NO_3)_2$ can be approximated by two portions. For the ratio $M = n_{H_2O}/n_K = 0-20{\cdot}2$ (KL), the content of water in the ternary mixture strongly increases, so that N attains its maximum value of 20. It is seen from Fig. 1 that in this region at an equimolar ratio of K^+ and Ca^{2+} ions, glass formation takes place even with relatively diluted salt solutions. In the other portion of the low-concentration limit, at low concentrations of K^+ ions (LM) the value of N decreases down to 14.

The glass-forming region of the studied system is formed roughly by a band between the glass-forming regions of the $Ca(NO_3)_2$–H_2O and $Ca(NO_3)_2$–KNO_3 systems of an unequal width. This dimension can be expressed as the difference between the limits with a higher and lower concentrations of Ca^{2+} ions. Then it is seen that the band of the glass formation is narrowest in the region of nonaqueous salts $(2-1)$. After replacement of one half of the potassium nitrate with water ($M = 1$), the concentration range of the glass formation increases only slightly (from 1 to 2); it attains its maximum value of 18 at $M = 20$.

The principle of the glass-forming capability is a decrease of the nucleation frequency and/or the crystal growth rate of the corresponding crystalline phase. Hence, in multicomponent systems we must know what crystalline phase can be formed at the given composition. In the studied ternary system, the line joining the eutonic points passes through the glass-forming region. This is in accord with the behaviour of salt–water binary systems, in which the glass-forming region is close to the eutectic composition. The position of this line (E_1EE_2) suggests that the composition of the glass-forming limits with a higher and lower content of calcium nitrate must be discussed separately.

The glass-forming limit with a higher content of calcium nitrate corresponds to solutions in which the nucleation frequency and/or the crystal growth rate of $Ca(NO_3)_2$ is lowered. This effect, however, must exist at least up to the corresponding eutonic or eutectic point. We can conclude that calcium nitrate will not crystallize rapidly from solutions containing per mol $Ca(NO_3)_2$ on the average $1-2$ mol KNO_3 in the region JE_1 or $2-10$ mol of both KNO_3 and water in the region PE_pE_RR or $3-12$ mol water in the region NE_2. It is apparent that the replacement of KNO_3 with water broadens considerably the concentration region in which the nucleation frequency and/or the crystal growth rate of calcium nitrate is effectively lowered.

At low water concentrations, mainly from the anhydrous melt, crystals of the compound $4\,KNO_3.Ca(NO_3)_2$ are formed[7]. The nucleation frequency or the crystal growth rate is lowered only in a narrow concentration range near to 2 mol KNO_3 per mol $Ca(NO_3)_2$.

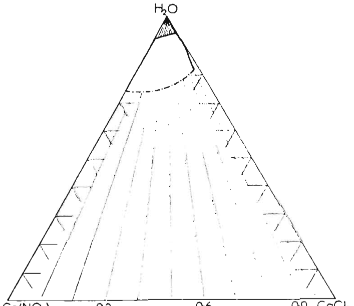

FIG. 2

Glass-Forming Region for $Ca(NO_3)_2$–$CaCl_2$–H_2O System

The ionic fraction of Cl^- ions is given on the abscissa, the salt concentration is given in mol%.

The prevailing part of the glass-forming limit with a lower content of calcium nitrate is related to the crystallization of KNO_3. In this case, the influence of the composition is more limited. Potassium nitrate will not crystallize rapidly enough from solutions containing 3 – 20 mol of both KNO_3 and water per mol $Ca(NO_3)_2$.

Another crystalline phase which can be formed during cooling is ice. A decrease of the nucleation frequency and/or the growth rate is manifested only in diluted solutions close to the eutonic points.

The glass-forming region of the $Ca(NO_3)_2$–KNO_3–H_2O system can be compared with the $Ca(NO_3)_2$–$CaCl_2$–H_2O system studied earlier[5] (Fig. 2), since the basic binary system $Ca(NO_3)_2$–H_2O is in both cases the same. In the first case the cation is varied, in the second the anion.

The characteristics of the glass-forming region is in both ternaries similar in that a band between two binaries is formed. If we assume in the triangular diagram equal substances in equal apexes of the triangle and calcium chloride instead of potassium nitrate, then the glass formation band of the $Ca(NO_3)_2$–$CaCl_2$–H_2O system is roughly perpendicular to that of the $Ca(NO_3)_2$–KNO_3–H_2O system. The lines joining the limiting glass-forming concentrations of both binaries, $CaCl_2$–H_2O and $Ca(NO_3)_2$–H_2O, delimit the $Ca(NO_3)_2$–$CaCl_2$–H_2O system from the side of lower concentrations of Ca^{2+} ions by the low-concentration limit and from the side of higher Ca^{2+} concentrations by the high-concentration limit. The course of the glass-forming concentration limits is different. On replacing the nitrate ions

TABLE I

Dependence of Glass Transition Temperature (K, denominator) on Mole Fraction of Salts (numerator) in $Ca(NO_3)_2$–KNO_3–H_2O System for Different Ionic Fractions of K^+ Ions

0·1		0·2		0·3		0·4		0·5	
0·2674	227·8	0·2097	202·1	0·2585	215·4	0·2342	200·2		
0·2551	224·9	0·2041	203·2	0·2075	196·8	0·2336	197·5	0·2519	195·1
0·2160	214·2	0·1900	197·9	0·1889	190·5	0·2024	193·1	0·2265	191·0
0·2021	208·7	0·1653	192·0	0·1670	185·8	0·1886	191·7	0·2075	184·0
0·1745	195·0	0·1419	182·9	0·1456	176·4	0·1720	186·5	0·1763	176·4
0·1654	195·0	0·1401	180·8	0·1343	173·7	0·1401	175·1	0·1760	175·6
0·1461	189·2	0·1126	173·5	0·1188	167·7	0·1299	166·7	0·1572	168·8
0·1221	179·4	0·1003	165·4	0·1024	163·6				
0·1213	176·8	0·0940	164·1						
0·0991	166·1								
0·0958	164·5								
0·0788	159·9								

gradually with chloride, the glass formation begins already in more diluted solutions than with the system under study.

Also the high-concentration limit has a different course characterized only by an abrupt change of concentrations of the substances toward higher water content when more than 90 mol% nitrate ions are replaced with chloride.

Glass Transition Temperature

The experimental data, *i.e.*, the mole fraction of salts, x, and the glass transition temperature, T_g, were fitted by the following regression line:

$$T_g = A + Bx \,, \qquad (1)$$

where A and B are coefficients which depend on the cation fraction z as follows:

z	0·1	0·2	0·3	0·4	0·5
A	131·7	133·3	129·0	134·4	126·4
B	370·9	340·5	331·4	284·5	278·4

The obtained data are summarized in Table I. The value of x was varied from 9 to 25 mol% and up to 50 mol% Ca^{2+} ions were replaced with K^+ ions. The glass transition temperature increases with the concentration of salts in the system. A similar dependence was found with most binaries and with the ternary systems studied earlier[5].

Angell and Sare[1] interpreted physically the parameter A in Eq. (*1*) describing the concentration dependence of T_g for binaries as the approximate glass transition temperature of water, although the extrapolation for zero concentration of the salt was carried out through the region that is not experimentally accessible. The extrapolated values of T_g were in the interval 128 – 141 K in good agreement with the value of 138 K found experimentally[1] as the glass transition temperature of water. If we compare this with the values of A for ternary systems (with exchange of anions or cations), we see that also here the approximated glass transition temperatures are close to the glass transition temperature of water, although the values tend to be lower than with the binaries. For example, for the $Ca(NO_3)_2$–$CaCl_2$–H_2O system the values of A are in the range 123 – 137 K, for $Ca(NO_3)_2$–$CaBr_2$–H_2O in the range 109 – 129 K, and for $Ca(NO_3)_2$–KNO_3–H_2O 123 – 134 K (ref.[5]). The value of A for all mentioned ternaries decreases with increasing content of the replacing ion beginning from the value of 141 valid for the $Ca(NO_3)_2$–H_2O system.

The slope of the straight line, B (Eq. (*1*)), for all the studied cases increases slightly with the anion fraction of the added anion. The above data show a distinct drop in the values of B when proceeding from $z = 0·1$ to $z = 0·5$ with the $Ca(NO_3)_2$–

-KNO_3–H_2O system. To show this more clearly, we determined from Eq. (*1*) the values of T_g for chosen salt concentrations in hydrated nitrate mixtures and arrived at the approximate equation

$$T_g = C + Dz\,, \qquad (2)$$

where C and D are constants depending on the chosen salt concentrations and z is the ionic fraction of K^+ ions. Their values are:

x	0·09	0·12	0·15	0·18	0·21	0·24
C	171·1	183·2	195·3	207·4	219·6	231·7
$-D$	37·53	45·23	52·97	60·71	68·44	76·19

It is seen that the values of C increase with the salt content, which is in accord with all the discussed ternary systems; they are very close to those for the $Ca(NO_3)_2$–$CaCl_2$–H_2O system.

The values of D are negative similarly as in the case of systems with exchange of anions; the absolute values of D are however by an order of magnitude lower. Whereas for anionic systems the parameter D increases slightly with the total salt concentration, in the cationic system under study it increases by a factor of 2 when the value of x inxreases from 0·09 to 0·24.

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