TEMPERATURE AND CONCENTRATION DEPENDENCE OF EQUIVALENT CONDUCTIVITY IN $Ca(NO_3)_2$-CaI_2-H_2O SYSTEM

Jindřich NOVÁK and Ivo SLÁMA

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

Received February 21st, 1979

The dependence of the equivalent conductivity on the temperature and composition of the $Ca(NO_3)_2$-CaI_2-H_2O system was studied. The ionic fraction $[I^-]/([I^-] + [NO_3^-])$ was changed from 0·1 to 0·5, the mole fraction of calcium salts (assumed in anhydrous form in the presence of free water molecules) was 0·075—0·200. The equivalent conductivity was found to be a linear function of the ionic fraction at constant temperature and salt concentration.

Although the fact that some ionic liquids can exist in the liquid state even deep below the liquidus curve has been known since long, systematic studies of various systems in the undercooled state are of a relatively recent date. A number of authors[1-6] began to study the behaviour of ionic liquids such as $Ca(NO_3)_2 + H_2O$, $MgCl_2 + H_2O$, $CaI_2 + H_2O$, especially their transport properties in a broad temperature range and at such high concentrations of the salts at which all the water present can be assumed to be relatively firmly bound in the hydration sphere of the ions. Then we have to speak about aqueous melts rather than aqueous solutions. These contain only hydrated ions, eventually ion pairs, but no free water molecules. These systems are often surprisingly stable in the undercooled state (they do not crystallize), they can be relatively easily prepared and stored. The study of their properties is hence facilitated.

We have studied the change of the transport properties of the $Ca(NO_3)_2$-H_2O system caused by replacing the nitrate ions partially by halide ions[7-9]. Some further results are given in the present work.

EXPERIMENTAL

Chemicals. Calcium nitrate tetrahydrate (Lachema, Brno) and hydrated calcium iodate (Merck) were of reagent grade. Stock solutions of a concentration $y = [I^-]/([I^-] + [NO_3^-]) = 0{\cdot}1$, 0·2, 0·3, 0·4, and 0·5 were prepared in redistilled water. The desired concentration of Ca^{2+} ions was adjusted by addition of water. The concentration of I^- ions was determined argentometrically, that of Ca^{2+} chelatometrically. The concentration of Ca^{2+} ions was expressed as mole fraction x or as the ratio, R, of the number of moles of water to the number of moles of the salts.

Resistance measurement. The constant of the conductivity cell was 273·5 cm^{-1}. The platinum electrodes used were covered with platinum black and their dimensions were 15 × 17 mm. The temperature of the cell was kept constant to within ±0·05 K by means of a water thermostat. The resistance was measured with an R 568 type bridge (Mashinpriborimport, Moscow) with an accuracy of ±0·1%. The data obtained were evaluated on a HP 9830 A computer.

RESULTS

The equivalent conductivity was calculated from the equation

$$\Lambda = 1000\varkappa(M_1(1 - y) + M_2y + M_3R)/2h\,, \tag{1}$$

where M_1, M_2, M_3 denote molar masses of $Ca(NO_3)_2$, CaI_2, and water, respectively, R concentration of calcium salts, h density, kg . m^{-3} and $\varkappa$ specific conductivity. The density was calculated from the formula

$$h = \sum_{i=1}^{3} t^{i-1}\left(\sum_{j=1}^{4} a_{ij}x^{j-1}\right), \tag{2}$$

where t denotes temperature in °C, x mole fraction of Ca salts, and a_{ij} parameters, which are given in Table I (ref.[20]). This equation enables to interpolate the densities for $y = 0{\cdot}1$, $0{\cdot}2$, $0{\cdot}3$, 0.4, and $0{\cdot}5$ in the temperature interval 0 – 50°C and concentration interval $0{\cdot}05 \leqq x \leqq 0{\cdot}20$.

The found values of the equivalent conductivity Λ (in S cm^2 mol^{-1}) for the mentioned systems were fitted by the simple Vogel–Tammann–Fulcher equation:

$$\Lambda = A \exp\left[-B/(T - T_0)\right], \tag{3}$$

where A, B, T_0 are constants and T denotes temperature in K. Usually 15 – 20 measurements were carried out in the temperature interval 0 – 50°C. Eq. (*3*) is obeyed with a satisfactory accuracy; its parameters are given in Table II.

DISCUSSION

The $Ca(NO_3)_2$–CaI_2–H_2O system can be derived from the $Ca(NO_3)_2$–H_2O system for constant x and chosen y by replacing the nitrate ions gradually with iodide ions. This change should be manifested by changing transport properties, namely the equivalent conductivity.

We shall denote the $Ca(NO_3)_2$–H_2O system as D_0 and after replacing a part of the nitrate ions with iodide the system will be denoted as D_1 (for $y = 0{\cdot}1$), D_2 ($y = 0{\cdot}2$), and so on. To discuss the influence of y on Λ at constant x, we must know the values of Λ for the systems D_0 through D_5 at constant x and t. These were calculated from Eq. (*3*) for 10, 25, 30, and 50°C (pseudoexperimental values). Then the values of Λ were interpolated by means of the polynomial

$$\ln \Lambda = A_0 + A_1x + A_2x^2 + A_3x^3 + A_4x^4 \tag{4}$$

for x = 0·05, 0·075, 0·100, 0·125, 0·150, and 0·175. Experimental values of Λ from ref.[10] were used for the system D_0.

The dependence of Λ on y at T, x = const. in the temperature range 10–50°C and concentration range $0{\cdot}075 \leqq x \leqq 0{\cdot}175$ has the form

$$\Lambda = a_0 + a_1 y\,. \tag{5}$$

The constants a_0 and a_1 are given in Table III. It is seen that at lower concentrations of the Ca salts partial replacement of NO_3^- ions by I^- ions causes a significant increase of the equivalent conductivity. This effect decreases with increasing content of Ca salts until the equivalent conductivity becomes independent of y in the studied concentration range. On increasing x further, the increase of y has an opposite influence on the equivalent conductivity: it decreases by replacing NO_3^- ions partially with I^-.

To discuss the described behaviour, we must consider the following facts. The equivalent conductivity at constant temperature depends especially on the number

TABLE I

Coefficients of Eq. (2) for Calculation of the Density

y	a_{11}	a_{12}	a_{13}	a_{14}
	a_{21}	a_{22}	a_{23}	a_{24}
	a_{31}	a_{32}	a_{33}	a_{34}
0·1	1·06909	5·38184	−3·86456	−17·01214
	$-1{\cdot}0237\,.\,10^{-3}$	0·01016	−0·11810	0·33788
	$8{\cdot}8637\,.\,10^{-6}$	$-2{\cdot}5690\,.\,10^{-4}$	$2{\cdot}2992\,.\,10^{-3}$	$-5{\cdot}9743\,.\,10^{-3}$
0·2	1·05659	6·73133	−13·21169	8·04440
	$-2{\cdot}2372\,.\,10^{-3}$	0·04716	−0·44501	1·18785
	$2{\cdot}8504\,.\,10^{-5}$	$-8{\cdot}5475\,.\,10^{-4}$	$7{\cdot}5118\,.\,10^{-3}$	−0·01938
0·3	1·05543	7·47482	−15·68326	14·98831
	$-1{\cdot}9861\,.\,10^{-3}$	0·03896	−0·37864	1·04350
	$1{\cdot}8864\,.\,10^{-5}$	$-5{\cdot}6435\,.\,10^{-4}$	$5{\cdot}1141\,.\,10^{-3}$	−0·01368
0·4	0·98442	9·85950	−27·29457	30,74510
	$-1{\cdot}4608\,.\,10^{-4}$	−0·01226	0·04792	−0·03238
	$-2{\cdot}7586\,.\,10^{-6}$	$2{\cdot}3527\,.\,10^{-5}$	$1{\cdot}9811\,.\,10^{-4}$	$-1{\cdot}2398\,.\,10^{-3}$
0·5	0·99130	10·68900	−34·43600	57·70400
	$3{\cdot}0692\,.\,10^{-7}$	−0·01912	0·13634	−0·34159
	$-7{\cdot}5527\,.\,10^{-6}$	$2{\cdot}1080\,.\,10^{-4}$	$-2{\cdot}0167\,.\,10^{-3}$	$6{\cdot}2145\,.\,10^{-3}$

of charged particles in unit volume of the liquid, on their charge and size. In diluted solutions of calcium nitrate, we have to deal with hydrated Ca^{2+} and NO_3^- ions. If we replace (at $T = \text{const.}$) NO_3^- ions partially with I^-, the equivalent conductivity will change in dependence on the ratio of effective radii of these hydrated anions.

TABLE II

Coefficients of Eq. (3) for Calculation of A and the Average Relative Error in Percent, δ

			$y = 0{\cdot}1$			
R	4·2	4·8	5·9	7·7	11·4	17·2
T_0	195	207	190	189	181	182
$\ln A$	5·65	4·57	4·97	5·04	5·41	5·62
B	703	427	473	372	344	295
δ	0·41	1·17	1·13	0·14	0·13	0·35
			$y = 0{\cdot}2$			
R	3·8	4·9	5·9	7·7	9·7	15·7
T_0	205	205	196	184	182	178
$\ln A$	5·46	4·64	4·90	5·11	5·32	5·68
B	696	445	431	387	360	319
δ	0·11	0·97	0·50	0·40	0·29	0·21
			$y = 0{\cdot}3$			
R	5·3	6·1	7·8	11·2	15·7	
T_0	198	194	195	182	181	
$\ln A$	4·97	4·98	4·89	5·41	5·63	
δ	499	439	329	329	304	
B	0·75	0·46	0·45	0·29	0·20	
			$y = 0{\cdot}4$			
R	4·3	4·9	6·1	8·0	11·6	17·3
T_0	209	180	186	191	178	186
$\ln A$	5·16	6·07	5·42	5·03	5·51	5·65
B	609	781	526	345	335	263
δ	0·20	0·34	0·74	0·52	0·31	0·39
			$y = 0{\cdot}5$			
R	4·9	6·4	8·0	11·9	17·0	
T_0	185	184	185	180	171	
$\ln A$	5·92	5·33	5·17	5·49	5·94	
B	740	512	374	317	330	
δ	0·29	0·42	0·43	0·32	0·18	

The effective radius of hydrated I^- ions is smaller than for NO_3^- ions[11], hence the partial replacement of NO_3^- with I^- under the mentioned conditions should result in an increase in Λ, which was indeed observed. While both cations and anions are hydrated in diluted solutions, at higher concentrations the anions loose their water of hydration preferentially. It is therefore questionable whether the radius of I^- ions will be smaller than that of NO_3^- ions also at higher concentrations. According to Högfeldt and Leifer[12], Cl^- and Br^- ions are hydrated up to the concentration of 12 mol/kg. Berecz and coworkers[13] assume the existence of hydrated Cl^- ions with 2 H_2O molecules in saturated $LaCl_3$ solution. According to Högfeldt[14], ClO_3^- and HSO_4^- ions are hydrated up to a concentration of 7 mol/kg more than NO_3^- ions, which are according to Peleg[15] hydrated in aqueous solutions of NH_4NO_3 at $R > 1$. Accordingly, the anions are probably hydrated in the concentration range where a partial replacement of NO_3^- with I^- ions causes an increase of the equivalent conductivity.

In aqueous solutions of calcium nitrate, however, associates or complexes are formed. According to Hester and Plane[16], $CaNO_3^-$ particles are formed in which the bond between calcium and nitrate ions has at least partly a covalent character. The existence of $CaNO_3^-$ was later substantiated[17,18]. The following equilibrium was

TABLE III

Coefficients of Eq. (*5*)

x	Constant	t, °C			
		10	25	30	50
0·075	a_0	8·305	12·454	14·013	20·631
	a_1	7·386	10·483	11·400	15·054
0·100	a_0	4·140	6·730	7·732	12·147
	a_1	3·229	4·636	5·446	7·480
0·125	a_0	1·991	3·659	4·292	7·268
	a_1	0·194	0·317	0·446	0·963
0·150	a_0	0·888	1·863	2·270	4·252
	a_1	−0·626	−1·160	−1·329	−1·834
0·175	a_0	0·322	0·810	1·038	2·277
	a_1	−0·374	−0·831	−1·006	−1·689

derived from calorimetric measurements[19] in aqueous cadmium nitrate solutions:

$$\begin{tikzcd}
\mathrm{Cd(H_2O)_n^{2+}} \arrow[r, phantom, "+"] \arrow[d, shift left] & \mathrm{NO_3^-} \arrow[d, shift left] \\
\mathrm{Cd(H_2O)_nNO_3^+} \arrow[u, shift left] \arrow[r, shift left] & \mathrm{CdNO_3^+ + nH_2O} \arrow[u, shift left] \arrow[l, shift left]
\end{tikzcd}$$

It is possible that in aqueous calcium nitrate solutions the situation is analogous: a part of NO_3^- ions enters the first coordination sphere of calcium and replaces some water molecules, a part of NO_3^- associates in the second coordination sphere through a water molecule and the remaining nitrate ions remain free. During partial replacement of NO_3^- with I^- ions, the value of Λ will be influenced not only by the ratio of their effective ionic radii but also by the capability of I^- ions to form complexes or associates with calcium ions. As long as the addition of I^- into the calcium nitrate –water system leads to an increase of the number of complex particles (hence a decrease of the total number of charged particles in the system and increase in the size of positively charged particles), the equivalent conductivity diminishes. Changes in a_1 in Eq. (5) during increasing concentration of Ca salts would then be due to two counteracting effects: increase of Λ caused by replacement of the less mobile hydrated NO_3^- ion by the more mobile I^- ion, and decrease of Λ caused by the formation of more complex particles or associates and by lowering the cation charge. The latter effect would be enhanced by increasing concentration of Ca salts, therefore also a_1 would decrease with increasing x, which is in accord with our results.

In spite of this agreement, the conclusions about the effect of the partial replacement of NO_3^- by I^- ions must be taken with care since our knowledge about the interaction between Ca^{2+}.aq or $CaNO_3^+$.aq with I^- ions in concentrated solutions or aqueous melts is unsatisfactory. A further study of this problem is therefore necessary.

REFERENCES

1. Angell C. A.: J. Electrochem. Soc. *112*, 1224 (1965).
2. Moynihan C. T., Smalley C. R., Angell C. A., Sare E. J.: J. Phys. Chem. *73*, 2287 (1969).
3. Breslau B., Miller I.: J. Phys. Chem. *74*, 1056 (1970).
4. Angell C. A., Sare E. J.: J. Chem. Phys. *52*, 1058 (1970).
5. Angell C. A., Bressel R. D.: J. Phys. Chem. *76*, 3244 (1972).
6. Sharma R. C., Gaur H. C.: Electrochim. Acta *21*, 997 (1976).
7. Novák J., Sláma I., Kodejš Z.: This Journal *41*, 2838 (1976).
8. Novák J., Sláma I., Kodejš Z.: Chem. Zvesti *31*, 29 (1977).
9. Malá J., Novák J., Kodejš Z., Sláma I.: This Journal *43*, 183 (1978).
10. Bressel R.: *Thesis.* Purdue Univ., Lafayette 1972.
11. Nightingale E. R., jr: J. Phys. Chem. *63*, 1381 (1959).
12. Högfeldt E., Leifer L.: Acta Chem. Scand. *17*, 338 (1963).

13. Berecz E., Báder I., Török T.: Acta Chim. (Budapest) *91*, 119 (1976).
14. Högfeldt E.: Acta Chem. Scand. *14*, 1627 (1960).
15. Peleg M.: J. Phys. Chem. *75*, 2060 (1971).
16. Hester R. E., Plane R. A.: J. Chem. Phys. *40*, 411 (1964).
17. Hester R. E., Krishnan K.: J. Chem. Phys. *46*, 3405 (1967).
18. Balshaw B., Smedley S. I.: J. Phys. Chem. *79*, 1323 (1975).
19. Vasilev V. P.: Zh. Neorg. Khim. *7*, 555 (1962).
20. Kodejš Z.: Unpublished results.

Translated by K. Micka.