

Molar electrical conductivity of the system $\text{Ca}(\text{NO}_3)_2 + \text{CaBr}_2 + \text{H}_2\text{O}$

J. NOVÁK and I. SLÁMA

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

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Molar electrical conductivity λ of the system $\text{Ca}(\text{NO}_3)_2 + \text{CaBr}_2 + \text{H}_2\text{O}$ was studied as a function of temperature and composition. The ratio between ions NO_3^- and Br^- was expressed as anionic fraction y ($y = [\text{Br}^-]/([\text{Br}^-] + [\text{NO}_3^-])$) and it assumed values 0.1, 0.2, 0.3, 0.4, and 1.0. Mole fraction of calcium salts (calculated on the basis of sum of moles of anhydrous calcium salts and moles of water) ranged from 0.06 to 0.125. The dependence of molar electrical conductivity λ on anionic fraction y (in the range 0.0–0.4 at constant temperature and total concentration of salts in the system) was described using the modified Markov—Shumina equation.

В системе $\text{Ca}(\text{NO}_3)_2 + \text{CaBr}_2 + \text{H}_2\text{O}$ была исследована молярная электропроводность λ в зависимости от температуры и состава. Отношение ионов NO_3^- и Br^- выражалось в виде анионной доли y ($y = [\text{Br}^-]/([\text{Br}^-] + [\text{NO}_3^-])$) и составляло 0,1, 0,2, 0,3, 0,4 и 1,0. Молярная доля солей кальция (рассчитанная по сумме молей соли кальция, взятой в виде безводной соли, и молей воды, взятой в виде свободных молекул) составляла 0,06–0,125. Для выражения зависимости молярной электропроводности λ от анионной доли y в интервале 0,0–0,4 при постоянной температуре и концентрации соли было использовано видоизмененное уравнение Маркова—Шуминой.

The experimental study and theoretical interpretation of transport properties of highly concentrated solutions of inorganic salts (or aqueous melts) is one of the possibilities leading to deeper understanding of these systems. Because these liquids can be relatively easily supercooled it is possible to obtain data on their behaviour not only closely under the liquidus curve but rather deep under it. In the series of our works [1–4] we studied electrical conductivity of the model system $\text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$ in which a part of NO_3^- ions had been replaced by Cl^- or I^- ions.

In this work the attention is paid to the dependence of λ on partial replacement of nitrate by bromide ions.

Experimental

Preparation of samples

Chemicals used were of anal. grade: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Lachema, Brno), hydrated CaBr_2 (Merck). The basic solutions having anionic fraction y equal to 0.1, 0.2, 0.3, 0.4, and 1.0 were prepared by dissolution of salts in distilled water. The determination of Br^- ions was done by argentometry, of Ca^{2+} ions by chelatometry. The concentration of calcium salts is expressed either as mole fraction x or as ratio R of number of moles H_2O and number of moles of salts. We did not succeed in preparing supercooled system $\text{CaBr}_2 + \text{H}_2\text{O}$ with $x > 0.125$ stable enough to carry out measurements. Supercooled aqueous melts of this composition transform in movable gels, λ of which considerably changes with the stage of crystallization of CaBr_2 .

Measurement of resistivity

The measuring procedure was the same as in previous works [1–4]. The molar electrical conductivity λ [$0.5(1-y)\text{Ca}(\text{NO}_3)_2 + 0.5y\text{CaBr}_2$] in units $\text{S cm}^2 \text{mol}^{-1}$ was calculated using the relation

$$\lambda = \kappa[M_1(1-y) + M_2y + RM_3]/2d \cdot 10^{-3} \quad (1)$$

Table 1

Coefficients for calculation of density according to eqns (2) and (3)

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	1.01728	6.33735	-15.48990	16.10054
	2.8380×10^{-5}	-5.3713×10^{-3}	0.04817	- 0.07166
	-4.9619×10^{-6}	-2.0139×10^{-5}	- 2.3869 $\times 10^{-4}$	5.2382×10^{-4}
0.2	0.97994	7.68489	-27.08487	53.49541
	2.6870×10^{-3}	-0.07024	0.65443	- 2.02129
	-3.8089×10^{-5}	7.6351×10^{-4}	- 7.2957 $\times 10^{-3}$	0.02320
0.3	0.93145	8.77333	-28.32978	41.77640
	6.9906×10^{-3}	-0.17269	1.36922	- 3.35623
	-1.1494×10^{-4}	2.6449×10^{-3}	- 0.02112	0.05224
0.4	1.01172	6.60112	- 0.85344	-59.23677
	3.4895×10^{-3}	-0.08409	0.57372	- 1.08688
	-6.6802×10^{-5}	1.4468×10^{-3}	- 0.01055	0.02249
1.0	0.66080	15.23777	-42.66502	
	0.01319	-0.24970	1.09738	
	-1.3277×10^{-4}	2.3742×10^{-3}	- 0.01047	

where M_1 , M_2 , and M_3 are the molecular weights of $\text{Ca}(\text{NO}_3)_2$, CaBr_2 , and H_2O , respectively. R is defined above, d is the density in kg m^{-3} , κ is the specific electrical conductivity in S cm^{-1} .

For the description of density in the composition range $y = 0.1-0.4$, the twelve-parameter equation was used

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

Density in $\text{CaBr}_2 + \text{H}_2\text{O}$ system was described by nine-parameter equation

Table 2

Coefficients for calculation of molar electrical conductivity λ according to eqn (4) (δ is the mean relative deviation in %)

			$y = 0.1$			
R	3.9	5.2	6.0	7.7	11.0	15.3
T_0	200	211	201	191	187	178
$\ln A$	5.63	4.51	4.71	5.00	5.23	5.64
B	697	398	391	366	315	328
δ	0.13	0.15	0.52	0.52	0.34	0.27
			$y = 0.2$			
R	4.4	5.3	6.2	8.8	12.0	15.6
T_0	194	202	199	146	187	181
$\ln A$	5.76	4.83	4.81	6.10	5.39	5.60
B	699	444	385	636	309	302
δ	0.31	0.63	0.71	0.53	0.26	0.39
			$y = 0.3$			
R	4.5	5.0	5.8	9.4	10.8	15.4
T_0	208	204	199	186	183	173
$\ln A$	5.45	4.95	4.89	5.25	5.38	5.81
B	634	487	421	346	335	346
δ	0.08	0.47	0.71	0.37	0.41	0.32
			$y = 0.4$			
R	4.3	5.1	6.3	7.7	11.1	16.3
T_0	203	205	194	201	182	176
$\ln A$	5.67	4.93	5.18	4.69	5.44	5.79
B	669	467	456	291	330	318
δ	0.20	0.71	0.79	0.57	0.33	0.31
			$y = 1.0$			
R	9.1	12.3	18.8			
T_0	150	139	132			
$\ln A$	6.06	6.27	6.54			
B	522	488	459			
δ	0.19	0.15	0.12			

$$d = \sum_{i=1}^3 t^{i-1} \left(\sum_{j=1}^3 a_{ij} x^{j-1} \right) \quad (3)$$

where t is the temperature in $^{\circ}\text{C}$, i and j are integers, and a_{ij} are constants. The value of these constants are presented in Table 1. These equations may be used for interpolation of density in the studied composition range of y and in the concentration range $0.05 \leq x \leq 0.15$.

The λ values were calculated from experimental data and treated using the simple Vogel—Fulcher—Tammann equation [5—11]

$$\lambda = A \exp \left[-B/(T - T_0) \right] \quad (4)$$

where A , B , and T_0 are the constants characterizing the system, T is the temperature in K. The relationship (4) describes the experimental data with sufficient accuracy in the temperature range $5\text{--}50^{\circ}\text{C}$. The parameters of eqn (4) are given in Table 2.

Discussion

In order to appreciate the influence of y on λ at constant t and x we used eqn (4) for calculating values λ at temperatures 10, 20, 30, and 50°C . In the next step we obtained by extrapolation or interpolation the pseudoexperimental values λ at $x = 0.05, 0.075, 0.100, 0.125$, and 0.150 at given temperatures. For the system $\text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$ the literature data were used [5]. The pseudoexperimental values at temperature 20°C are plotted vs. y in Fig. 1. In Fig. 2 λ vs. y at $x = 0.10$ and at temperatures 10, 20, 30, 40, and 50°C is presented.

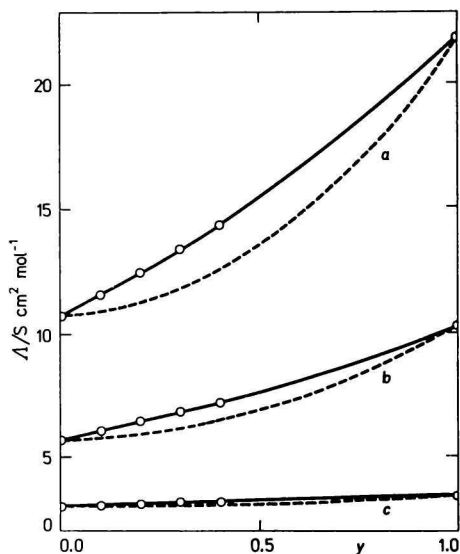


Fig. 1. Dependence of molar electrical conductivity in the system $\text{Ca}(\text{NO}_3)_2 + \text{CaBr}_2 + \text{H}_2\text{O}$ on ionic fraction of bromides at 20°C .

a) $x = 0.075$; b) $x = 0.100$; c) $x = 0.125$.
 - - - Molar electrical conductivity calculated according to relationship (7); — molar electrical conductivity calculated according to relationship (9); \circ the pseudoexperimental data.

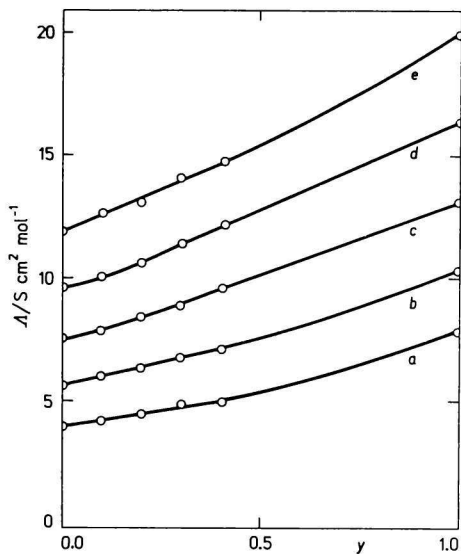


Fig. 2. Dependence of molar electrical conductivity in the system $\text{Ca}(\text{NO}_3)_2 + \text{CaBr}_2 + \text{H}_2\text{O}$ on ionic fraction of bromides at $x = 0.100$ and following temperatures: a) 10°C; b) 20°C; c) 30°C; d) 40°C; e) 50°C.

From Fig. 1 it follows that a partial replacement of nitrate by bromide ions in the system $\text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$ having $x = 0.05$ leads to a fast increase of λ with increasing y . However, with increasing concentration of salts in the system this effect diminishes and at $x = 0.13$ (i.e. $R \approx 6.7$) the partial replacement of NO_3^- ions by Br^- ions has no influence on the value of parameter λ . This phenomenon is in agreement with the behaviour of similar system in which nitrate ions are replaced by iodide ions [4]. In the latter case when $x = 0.127$ the partial replacement of NO_3^- by I^- ions also does not influence the value of λ .

If we consider that hydrated cations of the type $\text{Me}(\text{H}_2\text{O})_m^{+i}$ [6–11], anions $\text{X}(\text{H}_2\text{O})_n^{-j}$ (i, j, m, n being integers), and water molecules are basic building units in the system under discussion then a decrease in concentration of water should result first in the loss of free water followed by removing of water from hydrated shells of anions. From the works of *Džidić* and *Kebarle* [12] and *Arshadi et al.* [13] the following conclusions can be drawn. In the system of halogenides of alkali metals it can be assumed for $R < 9$ that most of water is contained in hydration shells of cations. In these conditions the anions are hydrated less or not at all. If the concentration of water in the system were so low that only hydrated cations and unhydrated anions would be present then the molar electrical conductivity of the systems in which nitrate ions are replaced by Br^- or I^- ions should (at constant x) depend on y and this change should be inverse to ionic radii. Therefore the relation of molar electrical conductivity λ_{Br^-} of the system $\text{Ca}(\text{NO}_3)_2 + \text{CaBr}_2 + \text{H}_2\text{O}$ and λ_{I^-} of the system $\text{Ca}(\text{NO}_3)_2 + \text{CaI}_2 + \text{H}_2\text{O}$ (x, y, t being the same) should be $\lambda_{\text{I}^-} < \lambda_{\text{Br}^-}$ because it holds $r_{\text{Br}^-} < r_{\text{I}^-}$ ($r_{\text{Br}^-} = 1.95, r_{\text{I}^-} = 2.16$). Similar effect should be

observed in the concentration range where the first coordination shell about calcium is filled incompletely or if anions are hydrated by 1—2 water molecules. Obviously it is not the case. Up to the concentration of calcium salts $x < 0.127$ — 0.130 it holds $\lambda_{I^-} > \lambda_{Br^-}$ and thus $R > 8.1$ — 8.3 . At concentration of calcium salts $x \doteq 0.127$ — 0.130 the partial replacement of NO_3^- ions by ions I^- or Br^- does not influence the value of λ or the influence is only negligible. The observed behaviour of the studied systems is therefore in contradiction with their assumed structure. According to [14—17] the solutions and aqueous melts of calcium nitrate contain species $CaNO_3^+$ or $CaNO_3^+ \cdot aq$. It can be assumed that partial replacement of nitrate by bromide or iodide ions leads also to partial replacement of NO_3^- which is associated in the particle $CaNO_3^+ \cdot aq$ or it can result in a change of number of water molecules forming hydration shell of this associate. Final conclusions concerning the structure of studied aqueous melts (or concentrated solutions) cannot be yet drawn because there is not still sufficient amount of information at disposal.

For the calculation of λ in binary mixtures (melts) the Markov—Shumina equation [18, 19] has been derived

$$\lambda = x_1^2 \lambda_1 + x_2^2 \lambda_2 + 2x_1 x_2 \lambda_{12} \quad (5)$$

where λ_1 and λ_2 are the molar electrical conductivities of pure components of the melt, x_1 and x_2 are their mole fractions and $2x_1 x_2 \lambda_{12}$ is the interaction term of eqn (5). Its magnitude can be determined only experimentally, *i.e.* on the basis of measuring conductivity of system in question. In the case when $\lambda_1 < \lambda_2$ the above quoted authors assume that $\lambda_{12} \doteq \lambda_1$ and the relationship (5) reads

$$\lambda = x_1^2 \lambda_1 + x_2^2 \lambda_2 + 2x_1 x_2 \lambda_1 \quad (6)$$

We tested if the relation (6) can be applied to calculation of molar conductivity of the systems studied in this work. For $x, t = \text{const}$, the system may be regarded as aqueous melt composed of two components, namely hydrated calcium nitrate and calcium bromide. The relation (6) is rewritten as

$$\lambda = (1 - y)^2 \lambda_{s1} + y^2 \lambda_{s2} + 2y(1 - y) \lambda_{s1} \quad (7)$$

where λ_{s1} and λ_{s2} are the molar electrical conductivities of the corresponding binary solutions of salts at chosen x, t . The calculation was done for $x = 0.125, 0.100, 0.075$, and 0.05 and $t = 20^\circ\text{C}$. The results were unsatisfactory (Fig. 1). Therefore we made an assumption that in relationship (5) it holds $\lambda_{12} = f(\lambda_1, \lambda_2)$. We found that for the systems under discussion it is advantageous to write

$$\lambda_{12} = (\lambda_1 \lambda_2)^n \quad (8)$$

After introducing eqn (8) eqn (7) can be modified to the form

$$\lambda = (1 - y)^2 \lambda_{s1} + y^2 \lambda_{s2} + 2y(1 - y)(\lambda_{s1} \lambda_{s2})^n \quad (9)$$

where n is the constant. If we choose $n = 0.5$ the results are far more satisfactory than if we used the unmodified eqn (7). For $x = 0.125$ ($R = 7$) and $t = 20^\circ\text{C}$ the difference between pseudoexperimental and calculated λ is less than 1%. At higher concentrations of water when we deal with highly concentrated solution and not with aqueous melt the agreement is worse. In order to keep the difference between the pseudoexperimental and calculated data on the level 1% the parameter n should be taken 0.49 (see Fig. 1).

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References

1. Novák, J., Sláma, I., and Kodejš, Z., *Collect. Czech. Chem. Commun.* 41, 2838 (1976).
2. Novák, J., Sláma, I., and Kodejš, Z., *Chem. Zvesti* 31, 29 (1977).
3. Malá, J., Novák, J., Kodejš, Z., and Sláma, I., *Collect. Czech. Chem. Commun.* 43, 183 (1978).
4. Novák, J. and Sláma, I., *Collect. Czech. Chem. Commun.*, in press.
5. Bressel, R., *Thesis*. Purdue University, Lafayette, 1972.
6. Angell, C. A., *J. Electrochem. Soc.* 112, 1224 (1964).
7. Angell, C. A., *J. Phys. Chem.* 69, 2137 (1965).
8. Angell, C. A., *J. Phys. Chem.* 70, 3988 (1966).
9. Angell, C. A. and Gruen, D. M., *J. Amer. Chem. Soc.* 86, 5192 (1966).
10. Angell, C. A. and Bressel, R. D., *J. Phys. Chem.* 76, 3244 (1972).
11. Moynihan, C. T., *J. Phys. Chem.* 70, 3399 (1966).
12. Džidič, I. and Kebarle, P., *J. Phys. Chem.* 74, 1466 (1970).
13. Arshadi, M., Yamadagni, R., and Kebarle, P., *J. Phys. Chem.* 74, 1475 (1970).
14. Balshaw, B. and Smedley, S. I., *J. Phys. Chem.* 79, 1323 (1975).
15. Hester, R. E. and Plane, R. A., *J. Chem. Phys.* 40, 411 (1964).
16. Hester, R. E. and Krishnan, K., *J. Phys. Chem.* 46, 3405 (1967).
17. Irish, D. E. and Walrafen, G. E., *J. Chem. Phys.* 46, 378 (1967).
18. Markov, B. F. and Shumina, L. A., *Dokl. Akad. Nauk SSSR* 110, 411 (1956).
19. Markov, B. F. and Shumina, L. A., *Zh. Fiz. Khim.* 31, 1767 (1957).

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