Electrical conductivity of molten calcium nitrate and calcium chloride hydrates

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The temperature and calcium ions concentration dependence of the equivalent conductivity Λ was studied in the system $CaCl_2$—$Ca(NO_3)_2$—H_2O at ionic fraction $y_{Cl^-} = [Cl^-]/([Cl^-] + [NO_3^-]) \cong 0.2$. The temperature dependence is described either by the Arrhenius, Vogel, Vogel—Tammann—Fulcher equations, or the second degree polynomial in the form $\ln \Lambda = A + BT + CT^2$. It is shown that the Arrhenius equation is unsuitable to describe the $\Lambda = f(T)$ dependence in the temperature interval studied (293—353 K). The other equations describe behaviour of the system with the sufficient accuracy. The concentration dependence of the conductivity satisfies the relation $\ln \Lambda = a + bx_{Ca} + cx_{Ca}^2 + dx_{Ca}^3$ (x_{Ca} denotes mole fraction of calcium) in the interval of x_{Ca} from 0.05 to 0.20. The comparison is being made also between the presently studied system and the system with $y_{Cl^-} \cong 0.1$.

Была изучена зависимость эквивалентной электропроводности Λ от температуры и от концентрации ионов кальция в системе $CaCl_2$—$Ca(NO_3)_2$—H_2O при ионной доли $y_{Cl^-} = [Cl^-]/([Cl^-] + [NO_3^-]) \cong 0,2$. Температурная зависимость была выражена уравнением Аррениуса, Фогеля, уравнением Фогеля—Тамманна—Фульхера, или полиномом второй степени типа $\ln \Lambda = A + BT + CT^2$. Было показано, что уравнение Аррениуса непригодно для описания температурной зависимости эквивалентной электропроводности в изучаемом интервале (293—353 K). Другие уравнения описывают систему с достаточной точностью. Концентрационная зависимость электропроводности описывается отношением $\ln \Lambda = a + bx_{Ca} + cx_{Ca}^2 + dx_{Ca}^3$ (x_{Ca} обозначает мольную долю кальция) в интервале x_{Ca} с 0,05 до 0,20. Изучаемая система была также сопоставлена с системой, в которой $y_{Cl^-} \cong 0,1$.

The marginal attention has been paid so far to the study of metastable undercooled liquids. Recently, the number of works dealing with indicated subject rapidly increases. In this respect some aqueous ionic melts are of special interest [1—5].

We deal systematically with observing transport phenomena [6] in the framework of quenchable ionic liquid systems. As an introductory model system we have selected the system $Ca(NO_3)_2$—$CaCl_2$—H_2O (system I). Its variables are the temperature (approx. from 293 to 350 K), the mole fraction of calcium x_{Ca} (approx. from 0.05 to 0.2), and the ionic fraction $y_{Cl^-} = [Cl^-]/([Cl^-] + [NO_3^-])$. This work is linked closely to our previous study in which the change of the equivalent conductivity Λ of the system I in both indicated temperature and x_{Ca} intervals and at $y_{Cl^-} = \text{const} \cong 0.1$ (system IA) was observed. Here we describe the behaviour of the system at analogous conditions with y_{Cl} set to 0.2 (system IB).

Experimental

The reagents used and the preparation of solutions are the same as described in [6].

The resistance measurements

0.5 M-KCl solution [7, 8] at 1550 Hz was used for the calibration of conductivity cells. The cell constants were 337.70 and 274.73. The extrapolation of measured resistances to infinite frequency was not applied while the resistance was found to be frequency independent in wide range of a.c. frequencies [9, 10]. The cell constants were checked against the conductivity of molten $Ca(NO_3)_2 \cdot 4H_2O$. The resistance of current leads, 0.02 ohm, was negligible in comparison to the measured resistance (10^3—10^5 ohm). The electrodes were manufactured from platinized Pt foil (dimensions 15 × 17 mm). All measurements were conducted using a bridge of the type R 568 (Mashinpriborimport, Moscow) allowing the precision of ±0.1%. The temperature was kept constant by a water thermostat and measured by mercury thermometer immersed into tempering liquid closed to the conductivity cell. The measured data were processed on a Hewlett—Packard 9830 A computer.

Results and discussion

Temperature dependence of the equivalent conductivity

The equivalent conductivity was calculated using the relation

$$\Lambda_{\text{exp}} = \frac{\varkappa(18\ R_1 + 164.09 - 53.1\ y_{Cl^-}) \cdot 10^3}{2\ h} \qquad (1)$$

in which h is density (kg m^{-3}),
$\varkappa$ is specific conductivity (S cm^{-1}),
R_1 is the ratio of the number of moles of water to the number of moles of calcium.

The density of systems studied was measured by one of the authors (*Z. Kodejš*) and will be published elsewhere.

The temperature dependence of Λ_{exp} described by the classical Arrhenius equation (*2*)

$$\Lambda = A_1 \exp(-B_1/RT) \qquad (2)$$

in cases of concentrated salts solutions, or undercooled aqueous melts gives satisfactory results in the narrow temperature range only. In the more extended temperature interval the modified Arrhenius equation, called Vogel equation

$$\Lambda = A_2 \exp(-B_2/[T - T_0]) , \qquad (3)$$

or the Vogel—Tammann—Fulcher equation

$$\Lambda = A_3 \cdot T^{-1/2} \exp(-B_3/[T - T_0]) , \qquad (4)$$

is usually used.

The last from the mentioned equations, as shown by *Angell* [11] approximates well the temperature dependence of Λ_{exp} for a number of aqueous undercooled melts in wide temperature interval. T_0 constant, according to Angell, represents the temperature at which the configuration entropy drops to zero. T_0 is therefore an important constant characterizing the state of the system. At temperature lower than T_0 the system cannot exist in the liquid state any longer. Similar problems are dealt within [12]. The temperature dependence Λ can also be described by the polynomial of an appropriate degree. We used the second degree polynomial in the form

$$\ln \Lambda = A_4 + B_4 T + C_4 T^2 . \qquad (5)$$

The constants A_4, B_4, C_4 at fixed x_{Ca} and y_{Cl^-} values were refined using least squares method. This form of description is found suitable for a number of practical purposes. From the experimental relationship (*5*), however, no inference can be made on the behaviour of the system as a whole, which correspondingly reduced the significance of this manner of data treatment.

In order to decide which form of data interpretation is the most adequate and to be able to make a comparison with our former results [6] the differences between values of the equivalent conductivity calculated according to eqns (*2—5*) (Λ_{calc}) and values of Λ_{exp} are expressed as a relative error in per cent

$$E = \frac{\Lambda_{exp} - \Lambda_{calc}}{\Lambda_{exp}} \cdot 100 . \qquad (6)$$

The comparison of results is summarized in Table 1*a* – *f*, where E values are listed for each series of x_{Ca} at $y_{Cl^-} = 0.202$ (system IB). The constants necessary to calculate the Λ according to eqns (*2—5*) are listed in Tables 2 and 3.

It was ascertained here and in our previous work, too ($y_{Cl^-} = 0.099$, system IA) [6], that eqn (*2*) is entirely unsuitable to describe the system. The agreement between Λ_{exp} and Λ_{calc} according to eqns (*3—5*) is fairly good, none of these three equations, however, gives E values appreciably lower than the remaining two equations.

The dependence on concentration

It is known that for the melt which is a mixture of the two pure ionic compounds Λ can be calculated using *Markov*'s relationship [13]. In our case it would be basically possible to calculate Λ in this way under the assumption that the

Table 1

E Values in the system IB derived from the equivalent conductivities measured and calculated using eqns (*2*—*5*)

a) $x_{Ca} = 0.194$

T, K	*E* (*2*)	*E* (*3*)	*E* (*4*)	*E* (*5*)
295.35	−14.92	0.05	1.16	−1.47
306.30	3.81	−1.08	−0.13	1.85
316.30	10.34	−0.18	0.53	1.42
324.60	11.02	0.96	1.52	0.41
334.20	5.91	0.21	0.67	−2.03
343.05	− 1.81	−0.24	0.18	−1.86
352.55	−13.15	−0.55	−0.09	1.91

b) $x_{Ca} = 0.164$

T, K	*E* (*2*)	*E* (*3*)	*E* (*4*)	*E* (*5*)
296.00	−6.74	−0.06	0.89	−1.89
306.00	2.42	0.54	1.38	1.81
314.65	5.28	0.29	1.00	1.89
324.00	5.26	−0.12	0.46	0.66
334.30	1.88	−1.34	−0.83	−1.69
343.00	−2.65	−2.25	−1.78	−3.06
352.55	−3.02	2.65	3.11	2.55

c) $x_{Ca} = 0.138$

T, K	*E* (*2*)	*E* (*3*)	*E* (*4*)	*E* (*5*)
295.25	−6.30	−0.23	0.26	−1.06
305.90	2.12	0.31	0.81	1.42
314.65	4.17	−0.24	0.19	0.64
324.85	4.60	0.08	0.42	−0.02
333.25	2.62	−0.27	0.00	−1.05
342.40	−0.22	0.04	0.27	−0.69
352.90	−5.39	0.00	0.22	0.84

Table 1 (Continued)

d) $x_{Ca} = 0.124$

T, K	E (2)	E (3)	E (4)	E (5)
292.50	−5.22	−0.13	0.57	−0.53
306.10	2.11	−0.30	0.31	0.73
314.10	3.74	−0.18	0.35	0.42
325.05	4.05	0.33	0.76	0.00
333.60	2.12	−0.06	0.30	−0.83
343.00	−0.57	0.05	0.39	−0.41
352.05	−4.63	−0.36	−0.01	0.57

e) $x_{Ca} = 0.077$

T, K	E (2)	E (3)	E (4)	E (5)
296.05	−2.75	−0.05	0.33	−0.17
306.25	0.68	0.03	0.31	0.41
315.25	1.84	−0.08	0.12	0.04
324.25	2.05	0.00	0.16	−0.27
333.75	1.16	−0.05	0.09	−0.60
340.95	1.34	1.27	1.43	0.88
352.45	−3.46	−0.93	−0.67	−0.21

f) $x_{Ca} = 0.051$

T, K	E (2)	E (3)	E (4)	E (5)
294.35	−2.51	−0.05	0.38	−0.36
305.35	0.81	0.01	0.41	0.49
314.05	1.77	−0.11	0.23	0.26
323.70	1.83	−0.16	0.12	−0.16
333.20	1.21	0.00	0.23	−0.32
342.25	0.00	0.11	0.34	−0.16
352.30	−2.30	−0.09	0.13	0.25

Table 2

Constants of eqns (*2*) and (*3*) to calculate the Λ for the system IB

x_{Ca}	(*2*)		(*3*)		
	$A_1 \cdot 10^3$	$B_1 \cdot 10^3$	T_0	A_2	B_2
0.194	4991.0	9.970	213.4	155.9	−553.9
0.164	194.2	7.206	185.8	291.9	−641.3
0.137	35.0	5.668	192.0	175.0	−456.7
0.124	20.6	5.115	178.7	230.8	−495.9
0.077	6.4	3.654	167.6	327.4	−419.3
0.051	5.8	3.252	165.7	420.0	−380.0

Table 3

Constants of eqns (*4*) and (*5*) to calculate the Λ for the system IB

x_{Ca}	(*4*)			(*5*)		
	T_0	A_3	B_3	A_4	B_4	$C_4 \cdot 10^4$
0.194	210.7	3797.4	−601.5	−62.622	0.3390	−4.493
0.163	181.4	7629.2	−715.5	−34.448	0.1842	−2.307
0.137	185.9	4598.7	−530.0	−29.030	0.1624	−2.087
0.124	172.1	6165.6	−578.4	−24.674	0.1405	−1.794
0.077	159.9	8673.0	−503.2	−15.194	0.0954	−1.201
0.051	154.8	11640.0	−479.1	−11.964	0.0807	−1.005

Table 4

Constants of eqn (*7*) to calculate the Λ for the system IB

T, K	a	b	c	d
293.15	4.529	−33.00	125.68	−643.56
303.15	4.413	−22.82	33.30	−321.45
313.15	4.740	−27.47	76.17	−377.33
323.15	4.804	−24.65	52.12	−266.77
333.15	4.914	−23.75	45.15	−213.08
343.15	4.935	−20.52	18.68	−119.12
353.15	5.039	−20.66	21.28	−100.88

equivalent conductivities for x_{Ca} from the interval 0.05—0.20 were known. Since we were unable to measure the system at indicated concentrations owing to the easy crystallization of $CaCl_2$ from its solution and since the relevant data were not available in the literature, we could not apply Markov's relationship and we decided to calculate the dependence $\Lambda = f(x_{Ca})$ according to the empirical equation (7)

$$\ln \Lambda = a + bx_{Ca} + cx_{Ca}^2 + dx_{Ca}^3 \quad (7)$$

analogously as it was done in [6]. The dependence of Λ on concentration was obtained by calculation of equivalent conductivities Λ_I (system IB) at temperatures $T = 293.15 + 10\, i$ (where $i = 0, 1, 2, ..., 6$) for corresponding x_{Ca} values using eqn (5) and fitting individual Λ_I values by the polynomial (7). The constants a, b, c, d used to calculate the Λ_I are listed in Table 4.

In order to be able to express the difference between the equivalent conductivity of the system I ($y_{Cl^-} \neq 0$) and the system in which $y_{Cl^-} = 0$ (system II) at both constant temperature and x_{Ca} it is necessary to calculate the corresponding equivalent conductivity of the system II according to eqn (7) (the constants are listed in [6]) and to compare these values (denoted as Λ_{II}) with Λ_I values. The difference can be expressed in per cent as follows

$$D = \frac{\Lambda_{II} - \Lambda_I}{\Lambda_{II}} \cdot 100 \,. \quad (8)$$

The dependence $D = g(x_{Ca}) = f(R_I)$ for the system IB ($x_{Ca} = 1/[1 + R_I]$) at temperatures $T = 293.15 + 10\, i$ ($i = 0, 2, 4, 6$) is shown in Figs. 1*a*—*d*.

To make the comparison possible the same dependence characteristic of the system IA is shown in these figures, too (using the data from [6]).

As can be seen from Figs. 1*a*—*d*, three regions are noticeable on curves expressing the dependence $D = g(x_{Ca}) = f(R_I)$ (in systems IA, IB). In the first place it is the region in which the increase of y_{Cl^-} causes relatively great changes, but their magnitude is practically the same in both systems (region α). Secondly, there is the region (denoted as β) in which changes of D are relatively low, but there is the appreciable difference in the conductivities of the systems. By lowering of x_{Ca} (increase of R_I), the difference in the conductivities decreases. The point at which the curves intersect, or cease to approach each other, indicates the beginning of the third region (γ). The α region ends at temperature 283.15 K and x_{Ca} approx. at 0.143 ($R_I \simeq 6$), which corresponds to the number of water molecules taking part in $CaCl_2$ hydrate formation. By increasing the temperature the beginning of the region α is shifted to the x_{Ca} value 0.2 ($R_I = 4$). The front of this α region and its temperature dependence shift mentioned indicate the relevancy of α region to the ionic melt rather than to the water solution. So far it is not possible to explain

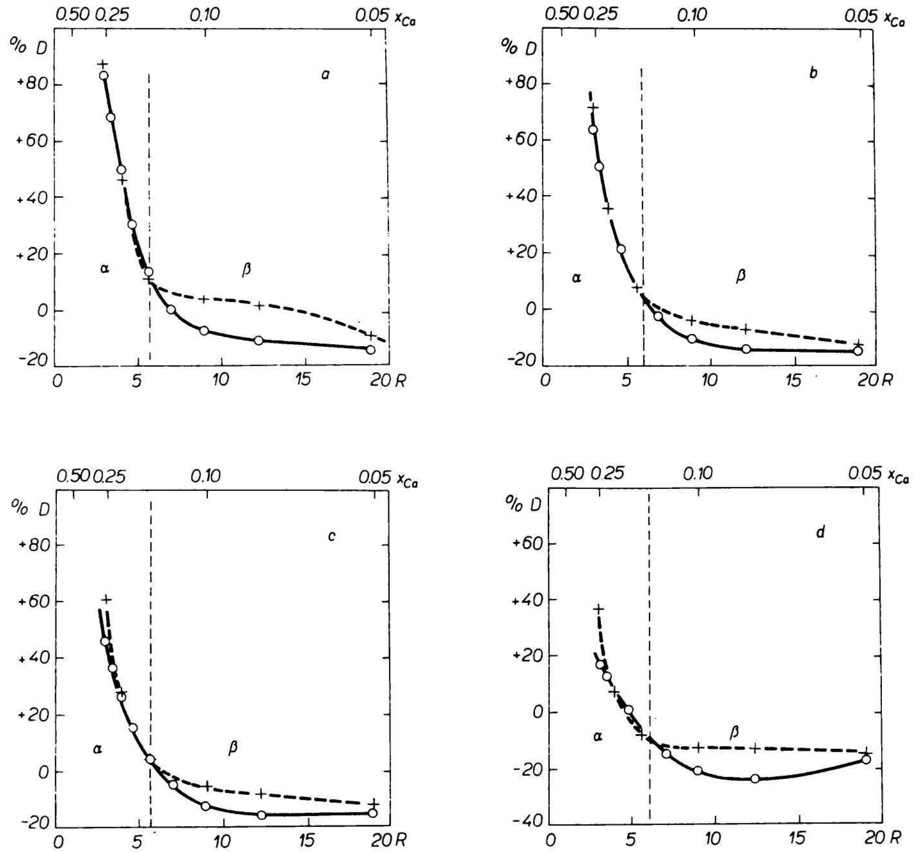

Fig. 1. The difference in D values calculated for the systems IA (+), or IB (○), and values calculated for the system II using eqn (7).
a) $T = 293.15$ K; *b*) $T = 313.15$ K; *c*) $T = 333.15$ K; *d*) $T = 353.15$ K.

reliably the resemblance in magnitudes of equivalent conductivities of systems IA and IB in the region α. In this respect it will be necessary to know the behaviour of the system in a wider range of y_{Cl^-} values.

At certain ratios of equivalent conductivity of the pure $Ca(NO_3)_2 \cdot xH_2O$ and $CaCl_2 \cdot xH_2O$, however, this result can be expected, under the assumption that Markov's equation holds its validity in the system I. The β region most probably represents the transitive region between the solution and the aqueous ionic melt. In the region γ we already have encountered the solution. By increasing the temperature the shift of β region to the higher x_{Ca} (lower R_1) values should occur correspondingly to the shift of liquidus curve of the system [14—17]. As Figs. 1*a*—*d* illustrate this shift positively takes place.

To explain the behaviour of systems IA and IB in the region α further information on changes of the equivalent conductivity in this relation at increasing y_{Cl^-} is necessary. This will be the subject of our next work.

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