ELECTRIC CONDUCTIVITY OF DISSOLVED HYDRATES OF CALCIUM NITRATE AND CHLORIDE

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The equivalent conductivity, Λ, was determined for the system $CaCl_2 + Ca(NO_3)_2 + H_2O$, where the ionic fraction $Y_{Cl} = [Cl^-]/([Cl^-] + [NO_3^-]) \approx 0{\cdot}1$, and its changes with the temperature and calcium concentration were studied. The temperature dependence was expressed either as $\ln \Lambda = A + BT + CT^2$ or by the Arrhenius, Vogel, or Vogel–Tammann–Fulcher equation; the results were best correlated by the Vogel or Vogel-Tammann-Fulcher equations. The concentration dependence can be expressed with a sufficient accuracy as $\ln \Lambda = a + bX_{Ca} + cX_{Ca}^2 + dX_{Ca}^3$, where X_{Ca} denotes mole fraction of calcium.

The study of metastable phases has been the subject of increasing interest of different investigators not only for purely scientific reasons but also because discoveries in this until recently neglected field may have a considerable importance in industrial applications. A principal difficulty is usually the complicated preparation of metastable phases. However, there are systems that can be easily brought into a metastable state, namely some of the so-called aqueous ionic melts.

A classical example of such an aqueous ionic melt is $Ca(NO_3)_2.4\,H_2O$. Undercooled aqueous ionic melts consisting of a mixture of water with two or more salts with a common cation (or with a common anion) are in some cases surprisingly stable and they often cannot be brought to crystallization even after several weeks of contact with the corresponding crystals. Different authors[1-5] have studied undercooled ionic melts mostly of the type $MX_i + H_2O$ (we shall call them aqueous binary melts), where $M = Ca^{2+}$, Mg^{2+}, Li^+, *etc.*, $X = NO_3^-$, Cl^-, CH_3COO^-, *etc.*, with regard to their viscosity, conductivity and some other properties at various temperatures and water contents and they attempted to interpret their results theoretically.

On the other hand, no significant attention has been paid to melted hydrates containing two salts with a common cation or anion with emphasis on the dependence of the measured property (electrical conductivity, viscosity, *etc.*) on the concentration of the components or on the kind of the cation or anion. The present work is concerned with the dependence of the equivalent conductivity of the system $Ca(NO_3)_2 + CaCl_2 + H_2O$ at constant ratio $Y_{Cl} = [Cl^-]/([Cl^-] + [NO_3^-]) = 0{\cdot}1$ at various temperatures and calcium concentrations.

EXPERIMENTAL

Chemicals. Calcium chloride and nitrate of reagent grade were products of Lachema, Brno; their solutions in redistilled water were filtered, purified by boiling with active charcoal, again filtered and then used to prepare stock solutions. (The active charcoal was purified by boiling with diluted (1 : 3) HCl and washing with redistilled water.) The stock solutions contained Cl^- and NO_3^- ions in such a ratio that $Y_{Cl} = 0{\cdot}1$; the value found analytically was 0·099. (Cl^- ions were determined argentometrically, Ca^{2+} complexometrically.) Solutions of different calcium content were prepared from the stock solution by changing its water content; their calcium concentration was determined analytically and expressed as mole fraction.

Resistance measurements. The resistance was measured in capillary conductivity cells whose constants were 337·70 and 274·73 cm^{-1}. They were calibrated with 0·5M-KCl at 1 550 Hz (ref.[6,7]). The resistance was independent of the a.c. frequency in a wide range[8,9], hence extrapolation to infinite frequency was not necessary. The platinized Pt foil electrodes had the dimensions 15 × 17 mm. The resistance of the current leads, 0·02 ohm, was negligible against the measured resistance (10^3—10^4 ohm). The cell temperature was maintained by a water thermostat with an accuracy of ±0·05 K; its mercury thermometer was placed close to the cell. The conductance was measured with a bridge of the type R 568 (Mashinpriborimport, Moscow) with an accuracy of ±0·1 per cent. The measured data were processed on a Hewlett-Packard 9830A computer.

RESULTS AND DISCUSSION

Melted calcium nitrate tetrahydrate can be easily undercooled[1-5] and transport phenomena in it can be studied in the region well below the solidus–liquidus curve[10]. A similar situation exists in the calcium nitrate–chloride–water system. To obtain its solidus–liquidus curve, we recalculated the data from the literature[11-14] (given in weight per cent) in terms of the molar fraction of calcium, which we plotted against the ionic fraction $Y_{Cl} = [Cl^-]/([Cl^-] + [NO_3^-])$ (Fig. 1).

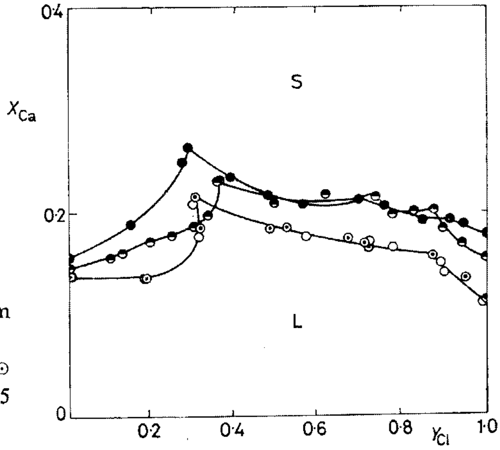

FIG. 1

Solidus–Liquidus Curve for the System $Ca(NO_3)_2 + CaCl_2 + H_2O$

Temperature, K: ○ 298·15 (ref.[11]); ⊙ same (ref.[14]); ◓ 308·15 (ref.[12]); ● 333·15 (ref.[13]).

TABLE I

Differences between Equivalent Conductivities Λ_{exp} Determined Experimentally and Those Calculated from Eq. (*3*) ("pol."), (*2*) ("Arrh."), (*4*) ("Vog."), and (*5*) ("VTF") at Various Temperatures and X_{Ca} Values

Temperature K	Λ_{exp}	% E			
		pol.	Arrh.	Vog.	VTF
		$X_{\text{Ca}} = 0·200$			
299·30	0·184	−1·31	−9·99	0·46	1·53
305·38	0·285	0·90	−0·09	−0·35	0·69
315·10	0·518	1·24	7·52	−0·84	0·06
324·85	0·866	0·73	9·78	0·35	1·07
335·60	1·372	−1·41	5·41	0·01	0·57
342·70	1·784	−1·41	0·38	0·05	0·54
353·25	2·513	1·25	−10·58	−0·09	0·34
		$X_{\text{Ca}} = 0·170$			
294·85	0·634	−0·97	−9·34	−0·04	0·83
305·10	1·089	1·41	2·19	−0·19	0·57
315·60	1·715	0·40	6·33	−0·48	0·11
324·55	2·391	−0·71	6·64	−0·17	0·30
334·15	3·319	0·56	6·11	2·09	2·48
344·00	4·230	−1·77	−1·71	−0·72	−0·34
353·60	5·332	1·07	−8·63	−0·67	−0·26
		$X_{\text{Ca}} = 0·144$			
293·65	1·593	−0·93	−6·35	0·05	0·49
305·30	2·565	1·27	2·43	0·14	0·54
315·10	3·551	0·46	4·58	−0·25	0·06
325·60	4·839	0·07	4·91	0·44	0·67
333·65	5·911	−0·73	2·84	0·20	0·40
342·90	7·204	−1·41	−1·52	−0·67	−0·48
352·00	8·720	2·86	−5·09	0·37	0·60
		$X_{\text{Ca}} = 0·111$			
295·45	4·575	−0·34	−4·15	−0·11	0·38
304·80	6·099	0·37	0·66	−0·40	0·04
314·60	7·892	−0·17	2·75	−0·65	−0·29
325·50	10·350	1·37	5·14	1·68	1·95
335·10	12·229	−1·21	1·58	−0·48	−0·25
343·95	14·298	−0·65	−0·53	−0·25	−0·02
353·35	16·534	0·68	−3·97	−0·33	−0·07

TABLE I

(*Continued*)

Temperature K	Λ_{exp}	%E			
		pol.	Arrh.	Vog.	VTF
		$X_{Ca} = 0{\cdot}076$			
298·70	11·879	−2·26	−6·27	−1·06	−0·54
307·20	15·532	2·91	3·08	2·08	2·51
314·65	18·052	1·04	3·47	0·00	0·35
324·70	21·682	−0·56	3·12	−0·81	−0·59
333·15	24·743	−1·48	1·53	−1·01	−0·84
341·90	28·086	−0·90	−0·36	−0·21	−0·03
352·00	31·932	1·17	−3·52	0·90	1·16
		$X_{Ca} = 0{\cdot}052$			
294·80	20·696	−0·34	−2·56	−0·03	0·36
305·50	26·015	0·44	0·80	−0·05	0·31
316·10	31·559	0·21	2·04	−0·10	0·18
325·20	36·580	0·06	2·25	0·13	0·37
334·75	41·792	−0·43	1·16	−0·05	0·14
343·40	46·667	−0·26	−0·17	0·02	0·21
353·00	52·014	0·33	−2·37	−0·07	0·14

At a temperature of 298·15 K, a solution of $X_{Ca} = 0{\cdot}133$ can exist according to Fig. 1 in the equilibrium state up to $Y_{Cl} = 0{\cdot}2$. Hence, measurements which we carried out in this region at $X_{Ca} > 0{\cdot}133$ correspond to an undercooled liquid. At 308·15 K, the curve is only approximately similar to that at 298·15 K. Its form changes owing to the formation of different solid phases. Nevertheless, also in this case a part of our measurements corresponds to an undercooled liquid.

From the measured specific conductivity, $\varkappa$ (S cm^{-1}), we calculated the equivalent conductivity, Λ_{exp}, as

$$\Lambda_{exp} = 10^3\varkappa(18R + 164{\cdot}09 - 53{\cdot}1\,Y_{Cl})/2\,h\,, \qquad (1)$$

where h denotes density (kg/m^3) and R ratio of the number of mols of water to the number of mols of calcium. The temperature dependence of the equivalent conductivity Λ in salt solutions can be expressed by the Arrhenius equation

$$\Lambda_{Arrh} = A_1 \exp\left(-B_1/RT\right). \qquad (2)$$

only in a narrow temperature interval. As found by Angell[15,16], in a wider temperature range this equation does not hold. This statement applies also for aqueous melts and concentrated aqueous solutions.

Another possibility is to approximate the temperature dependence of Λ as

$$\ln \Lambda = A_2 + B_2 T + C_2 T^2 \,, \tag{3}$$

where the constants A_2, B_2, and C_2 for constant X_{Ca} and Y_{Cl} can be found by the least squares method. Although this procedure would lead to the desired degree of accuracy especially if polynomials of a higher degree were chosen, the empirical constants would have no physical significance and therefore we consider more appropriate to use the modified Arrhenius equation (the Vogel equation):

$$\Lambda_{\mathrm{Vog}} = A_3 \exp\left(-B_3/(T - T_0)\right) . \tag{4}$$

Besides it was shown by Angell[17] that the dependence of Λ on the temperature in concentrated electrolyte solutions or aqueous melts fits with a sufficient accuracy the Vogel–Tammann–Fulcher equation:

$$\Lambda_{\mathrm{VTF}} = A_4 T^{-1/2} \exp\left(-B_4/(T - T_0)\right) . \tag{5}$$

Here the characteristic constant T_0 has the meaning of the temperature at which the configurational entropy of the system drops to zero[17]. This means that at lower temperatures than T_0 the system cannot be in the liquid state.

The difference between the calculated values (Λ_{cal}) from Eqs (*2*)–(*5*) and Λ_{exp} was expressed as the relative error in per cent:

$$\% E = 100(\Lambda_{\mathrm{exp}} - \Lambda_{\mathrm{cal}})/\Lambda_{\mathrm{exp}} . \tag{6}$$

TABLE II

Constants A_2, B_2, C_2 in Eq. (*3*) and A_1, B_1 in (*2*) for Various X_{Ca} Values

X_{Ca}	A_2	B_2	$C_2 \,.\, 10^4$	$A_1 \,.\, 10^{-3}$	$B_1 \,.\, 10^{-3}$
0·200	−59·854	0·3184	−4·145	5 598·0	10·18
0·170	−42·266	0·2301	−2·996	245·0	7·48
0·144	−30·261	0·1679	−2·156	44·8	5·94
0·111	−22·148	0·1287	−1·644	11·9	4·59
0·076	−20·504	0·1271	−1·678	7·2	3·77
0·052	−12·398	0·0829	−1·037	5·6	3·26

The constants for Eqs (*2*)–(*5*) are summarized in Tables II and III for $Y_{Cl} = 0{\cdot}099$ and various values of X_{Ca}. The agreement between Λ_{exp} and Λ_{cal} from Eqs (*4*) and (*5*) is mostly very good (Table I) and either of these equations is equally well applicable. Eq. (*3*) is, however, less suitable since the relative error, $\% E$, is larger than with (*4*) or (*5*). A polynomial of a higher degree than the second would, no doubt, give more accurate values. The Arrhenius equation is not adequate (Table I).

To judge quantitatively the influence of the addition of $CaCl_2$ to the $Ca(NO_3)_2 + H_2O$ system on its equivalent conductivity, we calculated the equivalent conductivity Λ_I for $Ca(NO_3)_2 + H_2O$ ("system I") from the published data[5], and the equivalent conductivity Λ_{II} for our system ("system II") at temperatures $T = 293{\cdot}15 + 10\,i$, $i = 0, 1, \ldots, 6$ for different values of X_{Ca} (Table IV). The values of Λ_I and Λ_{II} were fitted by the equation

$$\ln \Lambda_{cal} = a + bX_{Ca} + cX_{Ca}^2 + dX_{Ca}^3 \qquad (7)$$

TABLE III

Constants T_0, A_3, B_3 in Eq. (*4*) and T_0, A_4, B_4 in (*5*) for Various X_{Ca} Values

X_{Ca}	T_0	A_3	B_3	T_0	A_4	B_4
0·200	210·4	187·61	615·95	207·2	4 738·8	672·9
0·170	198·6	177·48	542·24	194·7	4 482·4	602·8
0·144	188·0	187·61	503·88	182·7	4 863·5	574·8
0·111	182·7	203·39	427·70	175·9	5 341·1	504·1
0·076	222·7	126·02	178·68	216·5	2 997·6	219·5
0·052	170·0	375·93	361·81	159·4	10 295·0	455·8

TABLE IV

Differences between Equivalent Conductivities Calculated from Eq. (*7*) and Those Interpolated or Extrapolated to the Given Temperatures (K) from Experimental Data According to Eq. (*3*)

X_{Ca}	$\% E$						
	293·15	303·15	313·15	323·15	333·15	343·15	353·15
0·200	−0·12	−0·50	−0·69	−0·42	−0·65	−0·44	−0·22
0·170	0·73	1·67	2·11	1·48	2·23	1·48	0·75
0·144	−0·63	−0·66	−0·71	−0·88	−1·51	−0·81	−0·02
0·111	0·27	−1·47	−2·27	−0·80	−1·05	−0·98	−1·15
0·076	−8·96	1·91	2·79	1·27	1·84	1·45	1·26
0·052	−0·09	−0·86	−1·22	−0·60	−0·86	−0·67	−0·55

for all the mentioned temperatures. The constants a, b, c, d for $\Lambda_{cal(I)}$ and $\Lambda_{cal(II)}$ calculated by the computer are summarized in Table V. Further we introduce the relative difference

$$\% D = 100(\Lambda_{cal(I)} - \Lambda_{cal(II)})/\Lambda_{cal(I)} . \tag{8}$$

TABLE V

Constants in Eq. (7) for the System $Ca(NO_3)_2.4\ H_2O$ (upper values) and for $Ca(NO_3)_2 + CaCl_2 + H_2O$ (lower values)

Temperature, K	*a*	*b*	*c*	*d*
293·15	4·312	−29·514	79·966	−388·502
	5·054	−51·123	281·941	−1 028·964
303·15	4·507	−29·762	86·996	−359·123
	5·025	−43·439	215·762	−791·364
313·15	4·678	−29·849	91·576	−330·593
	5·029	−37·711	165·792	−605·513
323·15	4·827	−29·774	93·706	−302·913
	5·037	−33·315	130·213	−471·842
333·15	4·952	−29·537	93·387	−276·083
	5·232	−35·083	146·497	−477·718
343·15	5·054	−29·139	90·619	−250·104
	5·245	−31·623	115·671	−365·600
353·15	5·132	−28·580	85·400	−224·974
	5·334	−31·235	115·482	−345·545

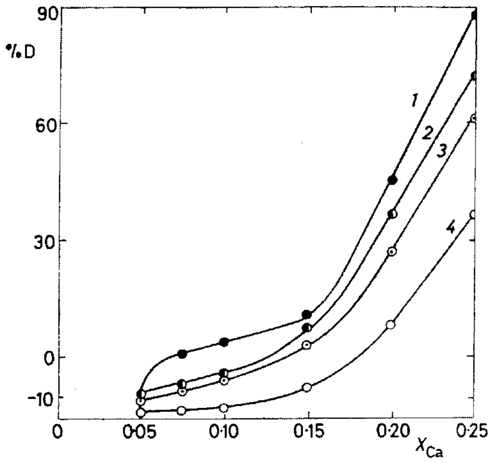

FIG. 2

Dependence of % D on Molar Fraction of Calcium X_{Ca}

The value of % D is defined by Eq. (8). Temperature, K *1* 293·15; *2* 313·15; *3* 333·15; *4* 353·15 K.

TABLE VI
Values of % D at Various Temperatures (K) and X_{Ca} Values

X_{Ca}	% D						
	293·15	303·15	313·15	323·15	333·15	343·15	353·15
0·050	−9·01	−10·79	−11·43	−10·85	−11·67	−12·22	−13·79
0·075	1·28	−3·52	−6·39	−8·16	−8·10	−10·21	−12·86
0·100	3·90	−0·62	−3·17	−5·33	−5·65	−8·11	−12·36
0·150	11·00	9·03	8·34	6·76	3·66	0·73	−7·62
0·200	46·45	40·80	36·42	32·26	27·22	20·33	8·66
0·250	87·05	79·95	71·98	64·42	60·84	48·75	37·24

The values of % D calculated for various values of X_{Ca} are given in Table VI; they vary from negative to positive reaching several tens per cent. In Fig. 2 is shown the dependence of % D on X_{Ca} at various temperatures. It is apparent that a partial replacement of the nitrate by the chloride in the system I has a large influence on the equivalent conductivity. The influence of Y_{Cl} on the equivalent conductivity in the system II will be the subject of a further work.

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