Thermodynamics of Metal Complex Formation in Aqueous Melts of Calcium Dinitrate–Ammonium Nitrate. Part I. Cadmium(II) Chlorides

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The formation constants of $[CdCl]^+$ and $CdCl_2$ complexes in melts of $Ca[NO_3]_2\cdot a[NH_4][NO_3]\cdot xH_2O$ (a = 1.5, 2.3, 5.4, and 11.5; x = 0—8) at selected temperatures in the range 323—433 K, have been determined from e.m.f. measurements in suitable concentration cells. The results are analyzed in terms of two models based on the quasi-lattice concept of the melt. The models predict the dependences of the thermodynamic data for $[CdCl]^+$ formation on the temperature and water content of the melt. A comparison and critical evaluation of the models is presented.

IN our previous paper [1] cadmium(II) chloride complexes in aqueous melts of $Ca[NO_3]_2$ and $Ca[NO_3]_2$–$K[NO_3]$ were studied and a model was proposed which predicts the dependence of the formation constant of $[CdCl]^+$ on the temperature and water content of the melt. The proposed model is based on the quasi-lattice concept of molten salts and should be valid in aqueous melts up to a water content corresponding to complete hydration of the first co-ordination shell of the complex-forming metal ion.

The present paper, which continues our research on metal-complex formation in anhydrous and aqueous molten salts,[1–7] has two purposes: to provide additional thermodynamic data on metal-complex formation in charge-unsymmetrical aqueous melts, and to test and evaluate our model with new data. The present system $Ca[NO_3]_2$–$[NH_4][NO_3]$–H_2O differs from the previous, $Ca[NO_3]_2$–$K[NO_3]$–H_2O, in that the ratio Ca^{2+} : $[NH_4]^+$ is varied (beside the variation of water concentration and temperature). This makes it possible to follow the dependence of some thermodynamic data on the proportions of the 2 : 1 and 1 : 1 salts, which are a measure of charge asymmetry in the quasi-lattice and which contribute to the reciprocal Coulomb effect in mixtures of molten salts.[6] Moreover, an interesting feature of the $Ca[NO_3]_2$–$[NH_4]$-$[NO_3]$–H_2O system is that the ammonium ion, in contrast to potassium ion, can take part in hydrogen bonding, even at low water concentrations in the melt. This might have an influence on the thermodynamics of complex formation.

EXPERIMENTAL

The electromotive force (e.m.f.) of the following concentration cell was measured:

$$\text{Ag,AgCl}\left|\begin{array}{l}Ca[NO_3]_2\cdot a[NH_4][NO_3]\cdot xH_2O\\ [NH_4]Cl\quad (n_{Cl})\\ Cd[NO_3]_2\quad (n_{Cd})\end{array}\right\|\left.\begin{array}{l}Ca[NO_3]_2\cdot a[NH_4][NO_3]\cdot xH_2O\\ [NH_4]Cl\quad (n_{Cl})\end{array}\right|\text{AgCl,Ag}$$

Here (Ag,AgCl) is the silver–silver(I) chloride electrode, a is the number of moles of $[NH_4][NO_3]$, and x is the number of moles of water per mole of $Ca[NO_3]_2$. The total concentration of chloride ligand in both half-cells is n_{Cl}, the total cadmium concentration in the left-hand half-cell being n_{Cd}. Both concentrations are expressed in Tempkin's ionic fractions. The cell and the technique of measurement are described in our previous papers.[1,5]

Aqueous melts of desired composition were prepared from known amounts of carefully dried salts and water. Dry $Ca[NO_3]_2$ was obtained by prolonged heating at 220 °C in a dry atmosphere.

RESULTS

E.m.f. measurements furnished the ΔE values of the concentration cell and their dependence on n_{Cl} and n_{Cd}, on the composition of the salt system (a and x), and on temperature. As our e.m.f. data are too extensive to be tabulated in this paper, they have been deposited in Supplementary Publication No. SUP 21722 (27 pp., 1 microfiche).† Only measurements in anhydrous $Ca[NO_3]_2\cdot 11.5$

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[1] I. J. Gal, R. M. Nikolić, and G. Heraković, *J.C.S. Dalton*, 1976, 104.

[2] I. J. Gal, J. Mendez, and J. W. Irvine, jun., *Inorg. Chem.*, 1968, 7, 985.

[3] J. Mendez, I. J. Gal, and J. W. Irvine, jun., *Inorg. Chem.*, 1968, 7, 1320.

[4] I. J. Gal, *Inorg. Chem.*, 1968, 7, 1611.

[5] R. M. Nikolić and I. J. Gal, *J.C.S. Dalton*, 1972, 162.

[6] I. J. Gal, G. Djurić, and L. Melovski, *J.C.S. Dalton*, 1973, 2066.

[7] R. M. Nikolić and I. J. Gal, *J.C.S. Dalton*, 1974, 985.

$[NH_4][NO_3]$ at 433 K and in aqueous $Ca[NO_3]_2{\cdot}5.41[NH_4][NO_3]{\cdot}7.83H_2O$ at 353 K are presented in Table 1 as an example. From the experimental data, the stability constants $K_1 = [CdCl^+]/[Cd^{2+}][Cl^-]$ and $K_2 = [CdCl_2]/[CdCl^+][Cl^-]$ were obtained using the Braunstein–Blander–Lindgren method[8] modified for unsymmetrical charge distribution.[9] Briefly, this method is based on graphical extrapolation of the function exp $(-F\Delta E/RT) - 1$ to zero cadmium and chloride concentration [equations (1) and (2)]. Here, a is the mol ratio of $[NH_4]^+ : Ca^{2+}$ in the system $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$, ΔE is the e.m.f. value of the concentration cell, F is the Faraday constant, R is the gas constant, and T is the absolute temperature. In the above equations, the constants K_1 and K_2 are expressed, as are the concentrations, in ion fractions.[9]

TABLE 1

E.m.f. measurements

(*a*) $Ca[NO_3]_2{\cdot}11.5[NH_4][NO_3]$ (433 K)

$n_{Cl} = 1.40 \times 10^{-4}$		$n_{Cl} = 2.16 \times 10^{-4}$		$n_{Cl} = 3.31 \times 10^{-4}$	
10^4n_{Cd}	ΔE/mV	10^4n_{Cd}	ΔE/mV	10^4n_{Cd}	ΔE/mV
0.95	1.9	0.92	1.9	0.94	1.8
1.91	3.0	1.84	4.1	1.87	3.8
2.83	4.6	2.88	6.2	2.79	5.8
3.82	7.3	3.88	7.8	3.79	7.5
4.79	9.0	4.89	9.5	4.79	9.0
5.75	11.8	5.89	11.2	5.75	10.9
6.71	12.9	6.93	12.9	6.71	13.0

$n_{Cl} = 4.76 \times 10^{-4}$		$n_{Cl} = 6.42 \times 10^{-4}$		$n_{Cl} = 7.95 \times 10^{-4}$	
10^4n_{Cd}	ΔE/mV	10^4n_{Cd}	ΔE/mV	10^4n_{Cd}	ΔE/mV
0.96	2.6	1.06	2.9	0.98	2.0
1.90	4.5	2.02	4.9	2.00	4.3
2.84	6.5	3.14	7.8	3.02	6.7
3.77	8.3	4.15	9.5	3.96	8.7
4.76	10.2	5.23	11.6	4.91	10.6
5.70	12.3	6.27	13.5	5.94	13.0
6.64	14.1	7.27	14.8	6.86	14.2

(*b*) $Ca[NO_3]_2{\cdot}5.41[NH_4][NO_3]{\cdot}7.83H_2O$ (353 K)

$n_{Cl} = 1.67 \times 10^{-4}$		$n_{Cl} = 2.18 \times 10^{-4}$		$n_{Cl} = 3.42 \times 10^{-4}$	
10^4n_{Cd}	ΔE/mV	10^4n_{Cd}	ΔE/mV	10^4n_{Cd}	ΔE/mV
0.77	0.9	0.78	1.3	0.76	1.4
1.54	1.6	1.57	2.8	1.53	3.7
3.09	4.2	3.13	4.9	3.06	5.2
4.63	6.7	4.70	6.8	4.59	7.0
6.17	8.2	6.26	8.9	6.13	8.4
7.71	10.1	7.83	10.8	7.66	10.4

$n_{Cl} = 6.19 \times 10^{-4}$		$n_{Cl} = 8.28 \times 10^{-4}$		$n_{Cl} = 9.89 \times 10^{-4}$	
10^4n_{Cd}	ΔE/mV	10^4n_{Cd}	ΔE/mV	10^4n_{Cd}	ΔE/mV
0.76	0.8	0.74	1.2	0.78	1.4
1.51	2.1	1.48	2.4	1.57	2.2
3.02	4.3	2.97	4.4	3.13	5.0
4.53	6.1	4.45	6.2	4.70	7.3
6.05	7.9	5.94	8.2	6.27	9.1
7.56	9.6	7.48	10.2	7.83	10.6

$n_{Cl} = 15.92 \times 10^{-4}$	
10^4n_{Cd}	ΔE/mV
0.76	0.9
1.52	1.4
3.05	3.5
4.57	5.5
6.09	7.3
7.62	8.4

$$\frac{1+a}{2+a}.K_1 = \lim_{\substack{n_{Cd}=0\\ n_{Cl}=0}} \partial[\exp(-F\Delta E/RT) - 1]/\partial_{n_{Cd}} \qquad (1)$$

$$\frac{1+a}{2+a}.K_1(2K_2 - K_1) = \lim_{\substack{n_{Cd}=0\\ n_{Cl}=0}} \partial^2[\exp(-F\Delta E/RT) - 1]/\partial_{n_{Cd}}\,\partial_{n_{Cl}} \qquad (2)$$

The stability constants K_1 and K_2 obtained in melts of $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$ are listed in Table 2. The estimated accuracy of the data in Table 2 is *ca.* ±5% for K_1 and *ca.* ±10% for K_2. Measurements in anhydrous systems ($x = 0$) were possible only at a high $[NH_4][NO_3]$ content (Table 2, $a = 11.50$ and 5.41, at 423 and 433 K).

TABLE 2

Consecutive formation constants, K_1 and K_2 (ion-fraction scale) of cadmium(II) chloride complexes in the aqueous molten-salt system $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$

a	x	T/K	K_1	K_2
11.50	0.00	433	616	437
	0.00	423	783	409
5.41	6.73	338	711	396
	7.83	353	607	303
	6.41		650	267
	5.77		708	287
	5.45		742	245
	5.13		775	290
	0.00	423	775	310
	0.00	433	749	522
2.33	5.77	323	852	340
	5.07		1 020	444
	4.39		1 124	501
	4.06		1 218	477
	3.90		1 287	642
	5.06	338	936	340
	4.39		1 030	435
	4.06		1 150	460
	5.77	353	624	221
	4.06		903	401
	3.90		944	429
	3.00		1 144	535
	2.67		1 252	563
1.50	5.77		643	236
	5.00		774	302
	4.50		884	352
	4.13		1 015	377
	3.50		1 134	487
	3.12		1 249	535

When the ratio $a = [NH_4]^+ : Ca^{2+}$ decreases, the melting point of the anhydrous system increases and the sublimation and decomposition of $[NH_4][NO_3]$ prevent accurate e.m.f. measurements. Thus, when $a = 2.33$ and 1.50 it was not possible to experimentally determine the equilibrium constants in the anhydrous system ($x = 0$).

The data in Table 2 show some interesting trends. Thus, at constant salt composition (a) and water content (x) the equilibrium constants decrease with temperature (see, for instance, the K_1 and K_2 values at $a = 2.33$ and $x = 4.06$). At constant salt composition (a) and temperature the equilibrium constants increase when the water content (x) decreases. At constant temperature and water content, the dependence of the equilibrium constants on the salt composition is less clear. Thus, at 353 K and $x = 5.77$ the equilibrium constants at $a = 5.41$ and 1.50 are higher than at $a = 2.33$. A more quantitative interpretation of these experimental data is presented below.

DISCUSSION

As mentioned earlier, we have developed a model[1] which, for ionic association (complex formation) of the type $Cd^{2+} + Cl^- \longrightarrow [CdCl]^+$, gives expression (3) for the standard free-energy change $\Delta G_T^{\ominus}$ (or the equilibrium

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[8] J. Braunstein, M. Blander, and R. M. Lindgren, *J. Amer. Chem. Soc.*, 1962, **84**, 1529.

[9] H. Braunstein, J. Braunstein, A. S. Minano, and R. E. Hagman, *Inorg. Chem.*, 1973, **12**, 1407.

TABLE 3

Comparison of experimental and predicted values of $\Delta G^{\ominus}$

			$-\Delta G^{\ominus} = RT\ln K_1/\text{kJ mol}^{-1}$		
x	y [equation (4)]	T/K	expt. (Table 2)	[equations (3)—(6)]	Parameters [equation (3)]
(a) $Ca[NO_3]_2{\cdot}5.41[NH_4][NO_3]{\cdot}xH_2O$					
5.77	6.00	353	19.3	(19.3)	$\Delta E_1 = -17.24$ kJ mol^{-1}
5.45	5.67		19.4	18.4	$\Delta E_2 = -14.01$ kJ mol^{-1}
5.13	5.33		19.5	18.1	$Z = 6$
0.00	0.00			22.4	
0.00	0.00	423	23·4	(23.4)	
0.00	0.00	433	23·8	(23.8)	
(b) $Ca[NO_3]_2{\cdot}2.33[NH_4][NO_3]{\cdot}xH_2O$					
5.77	6.00	323	18.1	18.3	$\Delta E_1 = -18.56$ kJ mol^{-1}
5·07	5.28		18.6	17.8	$\Delta E_2 = -13.47$ kJ mol^{-1}
4.39	4.57		18.9	18.9	$Z = 6$
4.06	4.22		19.1	19.4	
3.90	4.06		19.2	19.6	
0·00	0·00			23.4	
5.06	5.26	338	19.2	18.0	
4.39	4.57		19.5	18.9	
4.06	4.22		19.7	19.4	
0.00	0.00			23.6	
5.77	6.00	353	18.9	18.8	
4.06	4.22		20.0	19.5	
3.90	4.06		20.1	19.7	
3.00	3.12		20.7	20.9	
2.67	2.77		20.9	21.2	
0.00	0.00			23.8	
(c) $Ca[NO_3]_2{\cdot}1.50[NH_4][NO_3]{\cdot}xH_2O$					
5.77	6.00	353	19.0	(19.0)	$\Delta E_1 = -19.46$ kJ mol^{-1}
5.00	5.20		19.5	18.7	$\Delta E_2 = -13.76$ kJ mol^{-1}
4.50	4·68		19.9	19.6	$Z = 6$
4.13	4.29		20.3	20.2	
3.50	3.64		20.7	21.2	
3.12	3.25		20.9	21.7	
0.00	0.00			24.7	
(d) $Ca[NO_3]_2{\cdot}11.5[NH_4][NO_3]$ (anhydrous)					
0.00	0.00	423	23·9	(23.9)	$\Delta E_1 = -16.91$ kJ mol^{-1}
0.00	0.00	433	23.1	(23.1)	

constant K_1) in an aqueous melt mixture. Here, Z is the quasi-lattice co-ordination number (usually $Z = 6$ in nitrate melts) and y is the hydration number of the complex-forming cation. It has been shown that for Cd^{2+} in a melt of the type $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}xH_2O$, if $x \leqslant Z$, the hydration number y is given approximately[1] by equation (4) (x is the number of moles of H_2O per mole of calcium nitrate, as defined earlier).

$$\Delta G_T^{\ominus} = -RT\ln K_1 = \Delta E_1 + \frac{(\Delta E_2 - \Delta E_1)y}{(Z-y)\exp\left(\dfrac{\Delta E_2 - \Delta E_1}{RT}\right) + y} - RT\left[\frac{(Z-y)\ln(Z-y)}{(Z-y) + y\exp\left(\dfrac{\Delta E_1 - \Delta E_2}{RT}\right)} + \frac{y\ln y}{(Z-y)\exp\left(\dfrac{\Delta E_2 - \Delta E_1}{RT}\right) + y}\right] \tag{3}$$

$$y = 1.04x \tag{4}$$

The two energy parameters ΔE_1 and ΔE_2 are the Helmholtz free bond-energy increases when the ligand (in the present case, Cl^-) replaces a nitrate ion and a water molecule, respectively, in the co-ordination sphere of cadmium. These parameters can be determined independently: ΔE_1 in the anhydrous melt $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]$, when Cd^{2+} is surrounded only by nitrate ions, from the equilibrium constant K_1 at $y = 0$; similarly, ΔE_2 is obtained from K_1 in an aqueous melt where

$$\Delta E_1 = RT(\ln Z - \ln K_1) \quad (y = 0) \tag{5}$$

$y = Z$ (when Cd^{2+} is surrounded by $y = Z$ water molecules). Thus, the model is valid in the range $0 \leqslant y \leqslant Z$,

$$\Delta E_2 = RT(\ln Z - \ln K_1) \quad (y = Z) \tag{6}$$

or from anhydrous $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]$ up to about $Ca[NO_3]_2{\cdot}a[NH_4][NO_3]{\cdot}5.77H_2O$ [as calculated from equation (4) when $y = Z = 6$]. It should also be mentioned that ΔE_1 is, according to an earlier model of Blander,[10] temperature independent, whereas ΔE_2, as shown in our previous paper,[1] varies slightly with temperature. Taking into account the possible error of *ca.* ±0.5 kJ mol^{-1} in the energy parameters, within a range of *ca.* 40 K, ΔE_2 can also be considered as temperature independent. However, according to the model, both ΔE_1 and ΔE_2 depend on a, *i.e.* the $[NH_4]^+ : Ca^{2+}$ mol ratio of the salt mixture.

The application of the model [equation (3)] to the experimental data in Table 2 is illustrated in Table 3, where the experimental and calculated $\Delta G^{\ominus}$ values are compared. A few explanations are necessary concerning the calculation of the ΔE_1 and ΔE_2 parameters in the

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[10] M. Blander, *J. Chem. Phys.*, **1961**, **34**, 432.

last column. For the system $Ca[NO_3]_2 \cdot 5.41[NH_4][NO_3] \cdot xH_2O$, the ΔE_2 value was obtained from equation (6) using the K_1 value at $x = 5.77$ (or $y = Z = 6$). The ΔE_1 parameter was calculated from equation (5) applied to the K_1 values at 423 and 433 K at $y = 0$, *i.e.* in the anhydrous melt. (It was assumed that ΔE_1 is temperature independent.) In the system $Ca[NO_3]_2 \cdot 2.33[NH_4][NO_3] \cdot xH_2O$, the ΔE_2 parameter was determined by applying equation (6) to the K_1 values at 323 and 353 K when $y = 6$, then taking the mean value. As mentioned earlier, in the anhydrous system $Ca[NO_3]_2 \cdot 2.33[NH_4][NO_3]$ no e.m.f. measurements could be made and therefore direct determination of ΔE_1 at $y = 0$ was not possible. However, ΔE_1 was obtained by a trial and error method of fitting equation (3) to the data at 323 and 353 K. The same method was used to obtain the ΔE_1 value for the $Ca[NO_3]_2 \cdot 1.50[NH_4][NO_3] \cdot xH_2O$ system, whereas ΔE_2 in that system was calculated from equation (6). As seen from Table 3, the agreement between the experimental and calculated $\Delta G^{\ominus}$ values is fairly good. Only in two cases is the difference above 1 kJ mol^{-1}; in all other cases the agreement is within 1 kJ mol^{-1}, or *ca.* $\pm 5\%$ of the $\Delta G_T^{\ominus}$ value. Moreover, with two bond-energy parameters (ΔE_1 and ΔE_2) all experimental $\Delta G_T^{\ominus}$ values for $Ca[NO_3]_2 \cdot 2.33[NH_4][NO_3] \cdot xH_2O$ are reproduced over a temperature range of 30 K.

It is interesting to compare our model with Braunstein's aqueous quasi-lattice model of ionic association which was originally developed for 1 : 1 salt systems with a very low water content.[11] Braunstein's model can be expressed in our notation as in equation (7). Here,

$$Z/K_1 = \exp(\Delta E_1/RT) + R_{H_2O} \exp(\Delta E_2/RT) \quad (7)$$

R_{H_2O} is the mol ratio of water to the nitrate ion ($H_2O : [NO_3]$), whereas all other symbols have the same meaning as in our model. Equation (7) can be easily tested: a plot of Z/K_1 against R_{H_2O} should give a straight line, from the gradient and intercept of which ΔE_2 and ΔE_1 can be obtained. Application of this equation to our data (Table 2) is illustrated in Figure 1. It can be seen that, except in one case, the linear relation of Z/K_1 against R_{H_2O} does not hold when R_{H_2O} is greater than 1. Below this limit (a few points in Figure 1) we used the apparently linear relation and calculated the ΔE_1 and ΔE_2 values. These values are listed in Table 4 and compared with those obtained by our model. It can be seen that the ΔE_1 values are in excellent agreement, well within the accuracy of ± 0.5 kJ mol^{-1} for a bond-energy parameter. The agreement between the ΔE_2 values is less good, which is, indeed, expected if Braunstein's model [equation (7)] is valid only at low water concentrations.

TABLE 4

Comparison of the ΔE_1 and ΔE_2 values

		$-\Delta E_1$/ kJ mol^{-1}		$-\Delta E_2$/ kJ mol^{-1}	
Salt system	T/K	(3)	(7)	(3)	(7)
$Ca[NO_3]_2 \cdot 5.41[NH_4][NO_3] \cdot xH_2O$	353	17.3	17.2	14.0	14.5
$Ca[NO_3]_2 \cdot 2.33[NH_4][NO_3] \cdot xH_2O$	323	18.6	18.8	13.5	14.4
	338		18.9		15.2
	353		19.1		15.3
$Ca[NO_3]_2 \cdot 1.50[NH_4][NO_3] \cdot xH_2O$	353	19.5	19.6	13.8	16.2

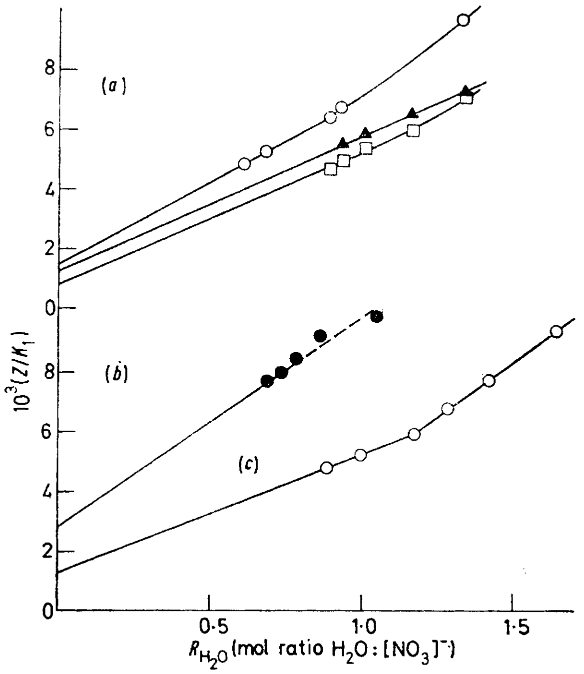

FIGURE 1 Dependence of Z/K_1 on the ratio R_{H_2O} [equation (7)] for (*a*) $Ca[NO_3]_2 \cdot 2.33[NH_4][NO_3] \cdot xH_2O$ at 323 (□), 338 (▲), and 353 K (○), (*b*) $Ca[NO_3]_2 \cdot 5.41[NH_4][NO_3] \cdot xH_2O$ at 353 K, and (*c*) $Ca[NO_3]_2 \cdot 1.50[NH_4][NO_3] \cdot xH_2O$

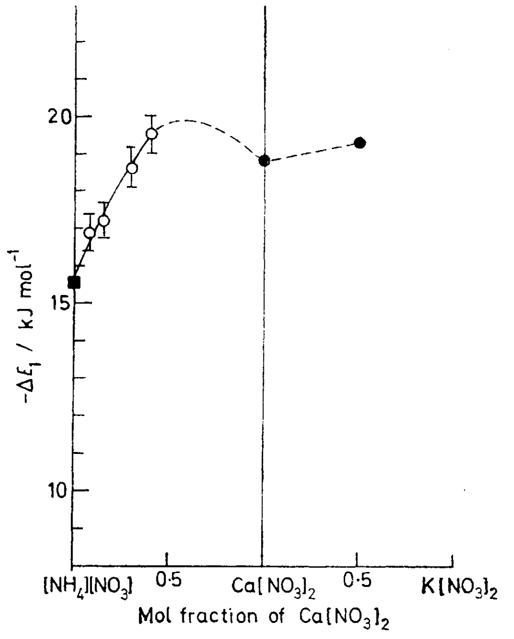

FIGURE 2 Dependence of ΔE_1 (for $[CdCl]^+$ formation) on the mol fraction of calcium nitrate in the molten-salt mixtures $Ca[NO_3]_2$–$[NH_4][NO_3]$ and $Ca[NO_3]_2$–$K[NO_3]$: (■), calculated value from ref. 5; (●), from ref. 1; (○), this work

It is interesting to analyse the dependence of ΔE_1 on the charge asymmetry of the molten-salt system.

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[11] J. Braunstein, *J. Phys. Chem.*, 1967, **71**, 3402.

Previously[6] we have shown that ΔE_1 for AgCl formation in anhydrous $Ca[NO_3]_2 \cdot aK[NO_3]$ depends on the mol fraction of the 2 : 1 salt. Qualitatively, the trend of this dependence was in agreement with the anticipated reciprocal Coulomb effect. In Figure 2 we have plotted all the available ΔE_1 data for $[CdCl]^+$ formation against the mol fraction of calcium nitrate in $Ca[NO_3]_2$–$K[NO_3]$ and $Ca[NO_3]_2$–$[NH_4][NO_3]$ mixtures. (The mol fraction of calcium nitrate can be taken as a measure of the electrical charge asymmetry of the melt.) It can be seen that the available data are incomplete, especially for the system $Ca[NO_3]_2$–$K[NO_3]$ and for higher calcium nitrate contents in the system $Ca[NO_3]_2$–$[NH_4][NO_3]$. The reciprocal Coulomb effect[6] requires more negative ΔE_1 values when the fraction of the 1 : 1 salt increases. Qualitatively, this trend is in agreement with the fact that ΔE_1 values are more negative in $Ca[NO_3]_2 \cdot 1.50$-$[NH_4][NO_3]$ and $Ca[NO_3]_2 \cdot K[NO_3]$ than in pure $Ca[NO_3]_2$. However, the increase in ΔE_1 from $Ca[NO_3]_2 \cdot 1.50$ $[NH_4][NO_3]$ to pure $[NH_4][NO_3]$ in Figure 2 is opposite to the above trend and indicates that other effects are probably important (for example, polarization of ions, hydrogen bonding with ammonium ions, the number of cation vacancies, *etc.*). So far, only one model deals with the dependence of the bond-energy parameters on the composition of the salt mixtures, and then only in 1 : 1 salt mixtures.[12] This is a topic which requires more experimental data and considerable efforts in theoretical work.

[5/2141 *Received*, 3*rd November*, 1975]

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[12] G. Bombi and G. A. Sacchetto, *J. Electroanalyt. Chem.*, 1972, **34**, 319.