

COMPLEX FORMATION IN MOLTEN SALTS : THERMODYNAMIC ASSOCIATION CONSTANTS OF CADMIUM-CHLORO COMPLEXES IN MOLTEN NITRATES

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Thermodynamic association constants for the formation of CdCl^+ and CdCl_2 species in molten KNO_3 - $\text{Ba}(\text{NO}_3)_2$ (87.6 : 12.4 mol per cent) eutectic in the temperature range 568.2-628.2 K have been determined by the emf method using Pd-PdO-CdO as the indicator electrode. The temperature coefficients of the association constants were predictable from equations based on quasi-lattice model.

Keywords : Molten Salts; Association Constant; Complex Formation; Concentration Cell; Quasi-Lattice Model; Specific Helmholtz Free Energy.

INTRODUCTION

Of the different electroanalytical techniques (Hsu *et al.*, 1967) used for the study of complex formation in molten salts, the emf method is convenient when suitable reversible electrodes are available. Precision of data enables extrapolation and computer evaluation. In molten nitrates, Ag/Ag^+ and $\text{Ag}/\text{AgX}(s)$ ($X = \text{Cl}, \text{Br}, \text{I}$) electrodes have been used as indicator electrodes for the study of association equilibria of halide complexes (Marcus, 1977). When the solubility of silver halide is relatively high, such that silver ions from it compete with complexing metal ions (e.g., Cd^{2+}) in the formation of associated species, the Pd-PdO-MO ($M = \text{Cd}, \text{Pb}$) electrodes (Inman, 1962, 1965; Braunstein *et al.*, 1966; and Gupta & Gaur, 1981 *a, b*) reversible to M^{2+} have been used. In this study, association constants of cadmium-chloro complexes in molten KNO_3 - $\text{Ba}(\text{NO}_3)_2$ (87.6 : 12.4 mol per cent in the temperature range 568.2 - 628.2 K using Pd-PdO-CdO indicator electrode are reported. An objective is to examine the applicability of the quasi-lattice theory (Blander & Braunstein 1960; Blander, 1961; and Hill *et al.*, 1960) for predicting activity coefficients and also the temperature coefficients of the association constants.

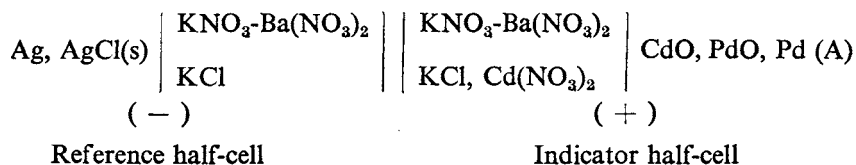
MATERIALS AND METHODS

The cell, electrodes, temperature control and measurements, solvent preparation and other experimental techniques have been described elsewhere (Gaur & Behl, 1963; and

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Gupta & Gaur, 1981 *a, b*). The chemicals used were AnalaR (BDH) grade or of equivalent purity. Anhydrous cadmium nitrate was prepared (Braunstein *et al.*, 1966) from the tetrahydrate sample by vacuum desiccation at 385 K. Palladium oxide was kept at *c* 675 K in a furnace until needed since it is reported to adsorb moisture at room temperature, even in a desiccator. CdO was desiccated at 385 K.

Emf measurements were made using the concentration cell :



Concentrations have been expressed in terms of mol ratios (R_i , mols of solute/mol of solvent) and also in ionic fractions (N_i) to enable comparison of results obtained in this study with those from calculations based on quasi-lattice model. The ionic fractions for Cd^{2+} and Cl^- , in terms of number of mols (n_i) and mol ratios (R_i) are defined by

$$N_{\text{Cd}^{2+}} = \frac{n_{\text{Cd}^{2+}}}{\sum n_{\text{cations}}} = \frac{R_{\text{Cd(NO}_3)_2}}{1 + R_{\text{KCl}}/p + R_{\text{Cd(NO}_3)_2}} \quad \dots(1)$$

$$N_{\text{Cl}^-} = \frac{n_{\text{Cl}^-}}{\sum n_{\text{anions}}} = \frac{R_{\text{KCl}}}{1 + 2p R_{\text{Cd(NO}_3)_2} + R_{\text{KCl}}} \quad \dots(2)$$

where
$$p = \frac{y + 1}{y + 2} = \frac{\text{Number of solvent cations}}{\text{Number of solvent anions}}$$

and

$$y = \frac{n_{\text{KNO}_3}}{n_{\text{Ba(NO}_3)_2}} = 7.06 \quad \dots(3)$$

RESULTS AND DISCUSSION

In the absence of any competing electrode reaction, and at solute concentrations low enough that the current is carried across the junction almost exclusively by the solvent cations, the emf of the cell (A), would be given by (Braunstein *et al.*, 1966),

$$E_{\text{cell}} = \text{Constant} + \frac{2.303 RT}{2F} \log R_{\text{Cd(NO}_3)_2} \quad \dots(4)$$

where R , T and F have their usual significance and constant is determined by the reference electrode, and the nature and composition of the solvent. Liquid junction potential has been minimised by using same solvent in both the half-cells. Plots of E_{cell} vs. $\log R_{\text{Cd(NO}_3)_2}$ (not shown) for the two-electron electrode process were always straight lines, in the concentration range in which activity coefficients were to be determined, with slopes 60.0, 61.8, 63.0 and 65.6 mV compared to the theoretical values 56.4, 58.3, 60.3 and 62.3 mV at 568.2, 588.2, 608.2 and 628.2 K respectively. This behaviour, also observed in nitrate melts in other studies (Inman, 1962, 1965;

Braunstein *et al.*, 1966; and Gupta & Gaur, 1981 *a, b*) has been ascribed (Inman, 1962) to conjugate equilibrium of the type $2O^{2-} \rightleftharpoons O_2 + 4e^-$ which may lead to mixed potential involving oxygen at the palladium electrode. By extrapolating the E_{cell} vs $R_{\text{Cd}^{2+}}$ plot to $R_{\text{Cd}^{2+}} = 0$ prior to any $\text{Cd}(\text{NO}_3)_2$ additions, it was estimated that $R_{\text{Cd}^{2+}}$ due to dissolution of CdO was $c 10^{-5}$; uncertainty of this order in the initial $R_{\text{Cd}(\text{NO}_3)_2}$ would have negligible effect on the result. Activity coefficients of cadmium nitrate have been determined from the relation

$$\log \gamma_{\text{Cd}(\text{NO}_3)_2} = \frac{\Delta E_{\text{cell}}}{S_{\text{expt}}} \quad \dots(5)$$

where ΔE_{cell} is the change of emf on the addition of KCl and S_{expt} is the experimental Nernst slope which has used (Inman, 1965; Braunstein *et al.*, 1966; and Gupta & Gaur, 1981 *a, b*) instead of theoretical value $\frac{2.303 RT}{2F}$, in the evaluation of activity coefficients. Typical data of variation of $-\ln \gamma_{\text{Cd}(\text{NO}_3)_2}$ as a function of R_{KCl} were obtained, part of these plotted in Fig. 1(a)*.

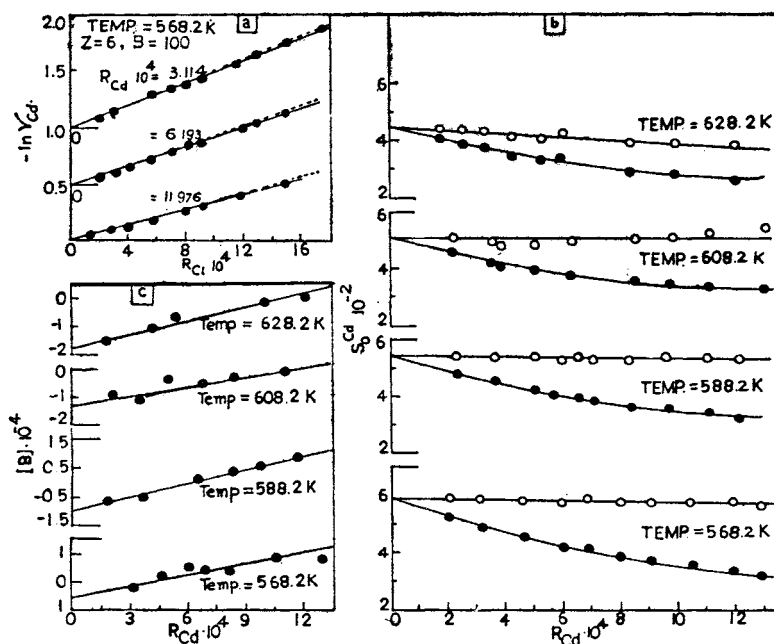


FIG. 1. (a) Variation γ_{Cd} as a function of R_{Cl} at different initial R_{Cd} (—●—) experimental, (.....) from quasi-lattice model.

(b) Graphical extrapolation of S_0^{Cd} , (—●—) eqn. (8), (—○—) eqn. (9).

(c) Extrapolation of the coefficient B (eqn. (12)).

*Detailed data at 38 initial $R_{\text{Cd}(\text{NO}_3)_2}$ and four temperatures with 502 data points may be requested from HCG.

The graphical method of analysis (Braunstein *et al.*, 1962) has been used for data analysis for association between Cd^{2+} and Cl^- in the charge unsymmetric solvent mixture $\text{KNO}_3\text{-Ba}(\text{NO}_3)_2$, as employed in this study. Essential details, as needed in presentation, are given below.

Considering the deviations of $\gamma_{\text{Cd}(\text{NO}_3)_2}$ from unity are due to the formation of the associated species of the type CdCl^+ , CdCl_2 , $\text{Cd}_2\text{Cl}^{3+}$ *etc.*, the equation† for activity coefficient is given by (Braunstein *et al.*, 1973)

$$-\ln \gamma_{\text{Cd}} = K_{11}R_{\text{Cl}} + K_{11}(2K_{21} - pK_{11}) R_{\text{Cl}}R_{\text{Cd}} + K_{11}(K_{12} - \frac{1}{2} K_{11}) R_{\text{Cl}}^2 + \dots \quad \dots(6)$$

where association constants K_{11} , K_{12} and K_{21} defined by

$$\begin{aligned} K_{11} &= R_{\text{CdCl}^+}/R_{\text{Cd}^{2+}} \cdot R_{\text{Cl}^-} \\ K_{12} &= R_{\text{CdCl}_2}/R_{\text{CdCl}^+} \cdot R_{\text{Cl}^-} \\ K_{21} &= R_{\text{Cd}_2\text{Cl}^{3+}}/R_{\text{CdCl}^+} \cdot R_{\text{Cd}^{2+}} \end{aligned} \quad \dots(7)$$

were evaluated from the relations

$$K_{11} = S_{0,0}^{\text{Cd}} = \lim_{R_{\text{Cd}} \rightarrow 0} [S_0^{\text{Cd}}] = \lim_{\substack{R_{\text{Cl}} \rightarrow 0 \\ R_{\text{Cd}} \rightarrow 0}} \left[\frac{\partial \ln (1/\gamma_{\text{Cd}})}{\partial R_{\text{Cl}}} \right]_{R_{\text{Cd}}} \quad \dots(8)$$

$$2K_{11} K_{21} = \lim_{\substack{R_{\text{Cd}} \rightarrow 0 \\ R_{\text{Cl}} \rightarrow 0}} \left[\frac{\partial (1 + K_{11}R_{\text{Cd}}) S_0^{\text{Cd}}}{\partial R_{\text{Cd}}} \right] \quad \dots(9)$$

where S_0^{Cd} is defined by

$$S_0^{\text{Cd}} = \lim_{R_{\text{Cl}} \rightarrow 0} \left[\frac{\partial \ln (1/\gamma_{\text{Cd}})}{\partial R_{\text{Cl}}} \right]_{R_{\text{Cd}}} = K_{11} + K_{11}(2K_{21} - pK_{11}) R_{\text{Cd}} \dots(10)$$

+ higher terms in R_{Cd}

The extrapolated plots [Fig. 1 (b)] yield the thermodynamic association constants. The plots corresponding to equation (9) had either zero or negative slopes [(Fig. 1(b)) of small magnitudes, indicating the absence of dinuclear species of the type $\text{Cd}_2\text{Cl}^{3+}$ under the experimental conditions employed in the present investigation. To evaluate K_{12} , equation (6) was rewritten in the form (Braunstein *et al.*, 1962)

$$-\ln \gamma_{\text{Cd}} = A R_{\text{Cl}} + B R_{\text{Cl}}^2 + \dots \quad \dots(11)$$

†Subscripts Cd and Cl refer to the components $\text{Cd}(\text{NO}_3)_2$ and KCl respectively.

Values of B were obtained by least-squares fitting the data to equation (11) at several fixed concentration of $\text{Cd}(\text{NO}_3)_2$. Extrapolated value of B at $R_{\text{Cd}} = 0$, $[B_0]$, (Fig. 1(c)), gave K_{12} from the equation

$$\lim_{R_{\text{Cl}} \rightarrow 0} [B] = [B_0] = K_{11}(K_{12} - \frac{1}{2} K_{11}) \quad \dots(12)$$

Values of the association constants K_{11} along with the ratio K_{12}/K_{11} are given in Table I. The ratio K_{12}/K_{11} is in the range 0.4–0.5 which may be compared with statistically expected ratio (Blander, 1961, 1964) $Z - 1/2Z = 0.40$ or 0.42 for $Z = 5$ or 6 where Z is the quasi-lattice coordination number.

TABLE I

Association constants K_{11} and K_{12} , and, specific Helmholtz free energies $-\Delta A_{11}$ and $-\Delta A_{12}$ for association of Cd^{2+} and Cl^- in molten $\text{KNO}_3 - \text{Ba}(\text{NO}_3)_2$ eutectic.

Temp.	568.2 K	588.2 K	608.2 K	628.2 K	
K_{11}	600_{-15}^{+20} (594)	550 ± 15 (546)	515_{-15}^{+10} (534)	450_{-20}^{+15} (444)	
K_{12}	291_{-8}^{+10}	243 ± 8	236_{-8}^{+8}	185_{-12}^{+9}	
K_{11}/K_{12}	0.49	0.44	0.46	0.41	
$Z = 6$	$-\Delta A_{11}$	$21.81_{-0.12}^{+0.15}$ (21.76)	$22.15_{-0.14}^{+0.18}$ (22.12)	$22.58_{-0.10}^{+0.14}$ (22.76)	$22.62_{-0.24}^{+0.17}$ (22.55)
	$-\Delta A_{12}$	$22.51_{-0.13}^{+0.16}$	22.43 ± 0.16	$22.05_{-0.11}^{+0.16}$	$22.56_{-0.35}^{+0.34}$
β^*	100	92	90	75	

K_{ij} 's are in (mols/mol of solvent) $^{-1}$

A_{ij} 's are in kJ mol^{-1} (values have been given for $Z = 6$ only).

*Value of β is one giving the best fit.

Values given in parentheses have been evaluated from quasi-lattice model, taking the value of β giving the best fit.

Computed values of K_{11} and K_{12} were used to evaluate the "specific bond free energies" $\Delta \epsilon_{ij}$ i.e., the energy required for the formation of the association species $\text{Cd}_i\text{Cl}_j^{(2i-j)+}$

$$K_{11} = Z(\beta_{11} - 1) \quad \dots(13)$$

$$K_{12} = \frac{Z-1}{2} \left[\beta_{12} - 1 + \frac{\beta_{12} - \beta_{11}}{\beta_{11} - 1} \right] \quad \dots(14)$$

where $\beta_{ij} = \exp(-\Delta \epsilon_{ij}/RT)$

Since the value of Z is not known *a priori*, $\Delta \epsilon_{11}$ and $\Delta \epsilon_{12}$ were calculated for $Z = 4, 5, 6$ which cover a reasonable range of values of this parameter (Blander, 1964). The calculated values of $\Delta \epsilon_{11}$ and $\Delta \epsilon_{12}$ were found to be constant (Table I) in the temperature range 568.2–628.2 K for different values of Z , indicating that the specific entropy of association (Blander, 1961) given by $\Delta S_{ij} = d(-\Delta A_{ij})/dT$ may be considered negligible so that $\Delta \epsilon_{ij}$ could also be considered (Alvarez Funes *et al.*, 1962; Braunstein *et al.*, 1966; and White *et al.*, 1968) as the specific Helmholtz free energy ΔA_{ij} for the formation of ij th bond in $Cd_iCl_j^{(2i-j)+}$.

The specific Helmholtz free energy (23.17 kJ mol⁻¹ for $Z = 5$) for the association of cadmium ion with that of chloride has been found to be comparable with those reported earlier (Braunstein *et al.*, 1964; Bombi *et al.*, 1966; and Inman 1965).

Applicability of the quasi-lattice model in calculating activity coefficients using asymmetric approximation was also examined. For the system $K^+/Ba^{2+}, Cd^{2+}, Cl^-, NO_3^-$ dilute in Cd^{2+} and Cl^- , equation (Hess, 1961) based on asymmetric approximation is

$$\gamma_{Cd(NO_3)_2} = \frac{(1 - Y)^Z \left[1 + \frac{Y}{(1 - Y)\beta} \right]^{Z-2}}{(1 - N_{Cl})^2} \quad \dots(15)$$

where
$$\frac{Y}{1 - Y} = \left[\frac{N_{Cl} - YZ N_{Cd}}{1 - N_{Cl} - ZN_{Cd}(1 - Y)} \right] \beta \quad \dots(16)$$

in which Y is the fraction of Z sites adjacent to Cd^{2+} ion that are occupied by Cl^- ions. Calculations were made for $Z = 6$, and the quasi-lattice parameter β was estimated from the experimental association constants. From the best fit of the value of β , activity coefficients (Fig. 1(a)) and hence K_{11} and ΔA_{11} were evaluated from quasi-lattice equations; these when compared (Table I) with those from the extrapolation method used, indicate the limit of applicability of quasi-lattice theory in calculating the activity coefficients. Nevertheless, the quasi-lattice equations derived for ions of same size and charge, are still useful in the present case where the size and charge of ions are different, for predicting activity coefficient and also the temperature coefficients of the association constants.

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