

Thermodynamic Association Constants for CdCl⁺, CdCl₂, CdBr⁺, and CdBr₂ in Molten Ca(NO₃)₂·4H₂O

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Summary E.m.f. measurements with Ag–AgCl and with Ag–AgBr electrodes yield association constants for the formation of CdX⁺ and CdX₂ in molten Ca(NO₃)₂·4H₂O; the bromide results confirm previous measurements with Cd–Hg electrodes and with dropping Hg electrodes, and the chloride results yield ratios of second to first association constants similar to those in anhydrous molten salts, revealing no structural anomalies caused by the presence of water.

ASSOCIATION constants for dilute solute species in concentrated aqueous electrolytic solvents and their comparison with association constants in anhydrous molten salts are important sources of information on electrolyte solutions.¹ We have reported association constants in several aqueous and hydrate melts,^{2–4} obtained pairwise association constants, and deduced that the ratio of first to second association constants ($K_{\text{CdX}^+}/K_{\text{CdX}_2}$) is, as in anhydrous melts, generally about 3. Since an anomalous structural effect has been suggested⁵ for CdBr₂ in molten Ca(NO₃)₂·4H₂O, based on the supposed absence of the species CdBr₂ in solution, an accurate redetermination of association constants in this system, and determination of association constants in related systems is needed to resolve the discrepancies.

We report here new potentiometric measurements of the association constants of CdCl⁺, CdCl₂, CdBr⁺, and CdBr₂ in molten Ca(NO₃)₂·4H₂O at 50 °C. The Ag–AgCl and Ag–AgBr electrodes were stable to ± 0.001 mV and ± 0.01 mV respectively, permitting evaluation^{1,6} of the pairwise association constants to ± 5% and of the association constants for CdX₂ to ± 10%. The use of the halide electrodes provides a more direct and accurate analysis of the first and second association constants with fewer experimental measurements than is possible polarographically or with amalgam electrodes.

Nernst behaviour of the electrodes was observed over the concentration range shown in Figure 1. Electrodes were a modification of those used in previous studies^{2,4} and will be described elsewhere. Care is required in the preparation of electrodes and selection of chemicals in order to obtain results of the high precision required by the small e.m.f. changes, especially for the chloride. Large clear crystals of Mallinckrodt Ca(NO₃)₂·4H₂O were fused at 50 °C to a clear melt that remained clear throughout the additions of

halide and of cadmium. Plots of $(1/\gamma_{\text{Ca}}) - 1$ and $(1/\gamma_{\text{Br}}) - 1$ are shown in Figure 2 along with the slopes whose extrapolation^{1,6} leads to the values of K_1 and K_2 in the Table.† The linearity of $(1/\gamma_{\text{Br}}) - 1$ makes evaluation

TABLE

Association constants of Cd^{II} with Cl⁻ or Br⁻ in molten Ca(NO₃)₂·4H₂O at 40 °C (mol/mol Ca)⁻¹

$K_1(\text{CdCl}^+)$	$K_2(\text{CdCl}_2)$	$K_1(\text{CdBr}^+)$	$K_2(\text{CdBr}_2)$
1070 ± 50	340 ± 50	3900 ± 200	1400 ± 100

of the slopes required for extrapolation to zero halide concentration to evaluate K_1 and K_2 unequivocal. Since the very slight curvature of $(1/\gamma_{\text{Ca}}) - 1$ is opposite in sign

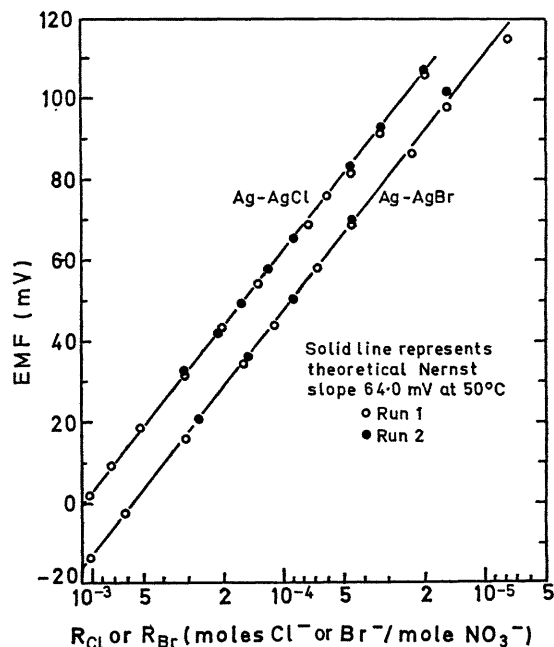


FIGURE 1. Demonstration of Nernst response of indicator electrode to Br⁻ or Cl⁻ in the absence of Cd²⁺. E.m.f. vs concentration of Br⁻ or Cl⁻.

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‡ $\frac{1}{2}K_1 = \lim_{R_X \rightarrow 0} S_0 = \lim_{R_X \rightarrow 0} F$ $K_1 K_2 = \frac{1}{2}K_1^2 + \lim_{R_X \rightarrow 0} \left(\frac{\partial S_0}{\partial R_X} \right) = \lim_{R_X \rightarrow 0} \left(\frac{\partial F}{\partial R_X} \right)$ where $S_0 = \lim_{R_{\text{Ca}} \rightarrow 0} \left(\frac{\partial(1/\gamma_X - 1)}{\partial R_{\text{Ca}}} \right)_{R_X}$;
 $F = (1 + K_1 R_X) S_0$ and $X = \text{Cl}$ or Br .

to the curvature of $\ln 1/\gamma_{\text{Cl}}$, upper and lower bounds may be placed on the slopes.^{1,6} The bromide results are in excellent agreement with our previous results obtained polarographically and with Cd amalgam electrodes, with the same or lower uncertainty as estimated conservatively from the range of calculated values.

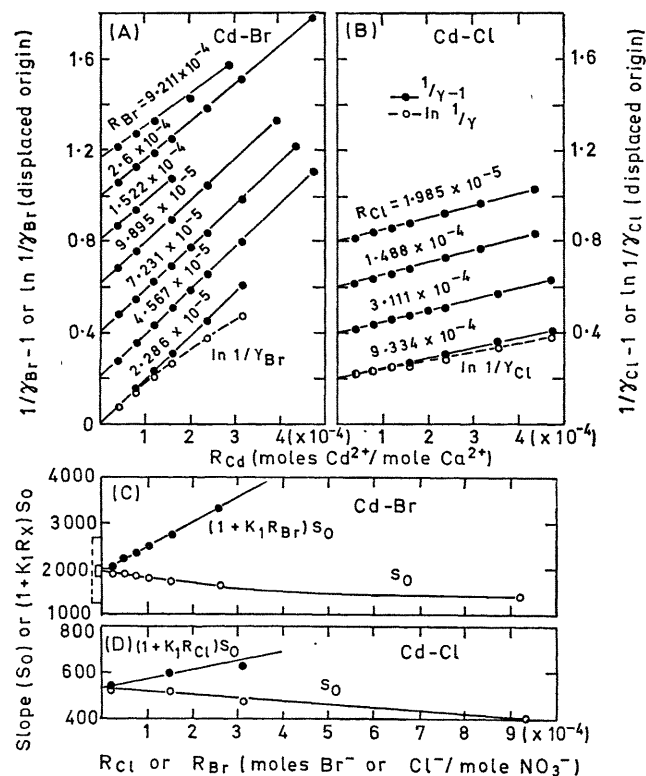


FIGURE 2. (A) Determination of limiting slopes to obtain K_1 and K_2 for formation of CdBr^+ and CdBr_2 : —●— $1/\gamma_{\text{Br}} - 1$ vs stoichiometric concentration of Cd^{2+} at constant Br^- ; ---○--- $\ln 1/\gamma_{\text{Br}}$ vs stoichiometric concentration of Cd^{2+} at constant Br^- .

(B) Determination of limiting slopes to determine K_1 and K_2 for formation of CdCl^+ and CdCl_2 : —●— $1/\gamma_{\text{Cl}} - 1$ vs stoichiometric concentration of Cd^{2+} at constant Cl^- ; ---○--- $\ln 1/\gamma_{\text{Cl}}$ vs stoichiometric concentration of Cd^{2+} at constant Cl^- .

(C) Graphical evaluation of K_1 and K_2 , CdBr^+ and CdBr_2 : —○— limiting slopes, $S_0 = \lim_{R_{\text{Cd}} \rightarrow 0} \left[\partial \left(\frac{1}{\gamma_{\text{Br}}} - 1 \right) / \partial R_{\text{Cd}} \right]_{R_{\text{Br}}}$

of curves in (A); —●— Extrapolation function, $(1 + K_1 R_{\text{Br}})S_0$; solid bar at ordinate corresponds to the 5% uncertainty in K_1 reported here and in ref. 2; broken bar at ordinate corresponds to the 33% uncertainty in K_1 reported in ref. 5.

(D) Graphical evaluation of K_1 and K_2 , CdCl^+ and CdCl_2 : —○— limiting slopes $S_0 = \lim_{R_{\text{Cd}} \rightarrow 0} \left[\partial \left(\frac{1}{\gamma_{\text{Cl}}} - 1 \right) / \partial R_{\text{Cd}} \right]_{R_{\text{Cl}}}$ of curves in (B); —●— extrapolation function, $(1 + K_1 R_{\text{Cl}})S_0$.

The new chloride results and accurately confirmed bromide results give a ratio of K_1/K_2 of about 3, similar to

values found for anhydrous molten salts,^{1,6} revealing no anomalous effects resulting from the presence of water.

Lovering's and Alner's⁵ failure to find values of an association constant for CdBr_2 , on which they base their proposal of an anomalous structural effect, may result from errors in either their data or their application of Inman's computer program,⁷ the former being more likely. The computer program as used by Lovering and Alner does not fit simultaneously the data at all metal and ligand concentrations, but treats each metal concentration separately, with no provision for systematic extrapolation to zero metal concentration. Progress in programming techniques should make a complete simultaneous fit possible. The method used⁴ by Lovering and Alner must limit the number of possible modes of association (since it necessarily truncates the polynomial expansion) and such assumptions can lead to spurious values of association constants.⁸ Precise estimates of the association constants are further hampered by the statistical dependence of the reported coefficients.⁸ The graphical method avoids the above assumptions and the lower association constants are virtually independent of the higher constants.⁶ We submit that unrealistic large negative values of an association constant, as reported in the Lovering-Alner computation, cannot be interpreted as zero values, but must rather indicate incorrect assumptions about the species and their interactions, or experimental error. Zero is an allowable value for an association constant, and a chemical and statistical model that is incapable of finding a value near zero is inadequate. Although Inman *et al.* have reported agreement between computer estimated and graphically evaluated pairwise association constants,⁹ explicit consideration of the above points is needed in order to establish that the computer-evaluated higher equilibrium quotients are the thermodynamic association constants.

Recalculation of some of our earlier e.m.f. data^{2,3} with the computer program used by Lovering and Alner^{5,7} also leads to non-zero positive values of the second association constant,¹⁰ although with greater uncertainty than the graphical computation. A zero value for K_2 requires a limiting slope of zero for the extrapolation functions $(1 + K_1 R_{\text{Br}})S_0$ and $(1 + K_1 R_{\text{Cl}})S_0$ shown as the upper curves in sections (C) and (D) of Figure 2. The graphical computation not only extracts the association constants from e.m.f. data by requiring consistency of the values derived from both the slopes and the extrapolation functions, but also eliminates possible spurious values by these same consistency tests.⁶ Analysis of the data shows that the absence of the species CdBr_2 and CdCl_2 in molten $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is most unlikely.

Lovering and Alner's reported polarographic measurements^{5,10} are probably not of the accuracy attainable in our earlier polarographic measurements^{2,3} with the ORNL Q1988 polarograph,¹¹ operated both manually and automatically, which was designed for accurate measurements at low concentrations. They are certainly less accurate than our new potentiometric results.

Since our new measurements with bromide electrodes yield activity coefficients (γ) of bromide as a function of cadmium and bromide concentrations while our earlier measurements with cadmium electrodes yield activity coefficients of dissolved cadmium nitrate, direct evaluation of the activities of both solutes, without Gibbs-Duhem integration, will permit an even more direct evaluation of

the association constants without computer iteration. Analysis of the results is in progress and will be presented shortly.

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