Polarographic Study of the Anomalous Behaviour of Bromocadmium(II) Complexes in Molten Calcium Nitrate Tetrahydrate

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Summary New evidence from polarographic data suggests that desolvation of the neutral species, formally written $Cd^{II}Br_2$, may occur in aqueous melts.

BRAUNSTEIN *et al.*[1] have reported association constants for bromo-cadmium(II) complexes in the aqueous melt, $Ca(NO_3)_2,4H_2O$. They used a graphical technique[2] to analyse their polarographic and potentiometric titration data and recorded no unusual behaviour in this system. Stability constants were given as:

$$K_1 = 460 \pm 25;\ K_2 = 180 \pm 25 \text{ (molal units).}$$

We describe new polarographic data obtained for the same system. Some anomalies in the system are also reported. The computer technique of Inman[3,4] has been used to gain adequate precision and meaningful error parameters for the derived stability constants. The d.c. manual polarographic method was used to determine half-wave potential shifts from plots according to the Heyrovsky–Ilkovic equation.[5,6] A dropping mercury electrode, mercury pool anode, and a silver–silver(I) reference electrode with an asbestos wick junction,[1,7] have been used. Cd^{II} ions, added as $Cd^{II}(NO_3)_2$, $4H_2O$, were titrated with solid KBr, in a filtered $Ca(NO_3)_2,4H_2O$ melt at 50°. It was necessary to use metal-ion concentrations $\leqslant 10^{-4}$ m to avoid polarographic maxima,[7] (*cf.* ref. 8).

The derived half-wave potential shifts showed smooth, curvilinear dependence on ligand concentration, indicating that bromocadmium complexes should be formed in a stepwise fashion, without the predominance of any single entity. However, analysis of the data, using the standard program,[3,4] always resulted in a 4-degree best fit with values of β_2 spanning zero, as exemplified in the Table. Similar results from other sets of data had β_2-values of both positive and negative signs.

In view of these factors, and the problem of analysing the data in terms of a "$CdBr_2$" species, the data were recomputed omitting the second-degree terms in the relevant polynomials. In all cases, considerably improved data fits were obtained when only the first-, third-, and fourth-degree terms were included. No complications due to the presence of dinuclear complexes were apparent. The Table shows a comparison of the data fits obtained for a typical set of results when β_2 was initially included and then excluded in the computation.

TABLE

	Stability constants (molal units)	
	With β_2	Without β_2
β_0	$1{\cdot}05 \pm 0{\cdot}09$	$1{\cdot}07 \pm 0{\cdot}04$
β_1	586 ± 111	555 ± 30
β_2	$(-1{\cdot}09 \pm 3{\cdot}62) \times 10^4$	—
β_3	$(2{\cdot}80 \pm 0{\cdot}36) \times 10^7$	$(2{\cdot}69 \pm 0{\cdot}09) \times 10^7$
β_4	$(7{\cdot}34 \pm 0{\cdot}94) \times 10^8$	$(7{\cdot}59 \pm 0{\cdot}43) \times 10^8$

	Statistical error parameters	
	With β_2	Without β_2
$S_{\min}$	0·13	0·14
σ (e.e.)	11·2	9·6
σ ($\Delta E_{\frac{1}{2}}$)	0·30	0·26

Most probable values for the successive stability constants, obtained from a large number of sets of data, were found to be: $\beta_1 = 450 \pm 150$; $\beta_3 = (2{\cdot}1 \pm 0{\cdot}9) \times 10^7$; $\beta_4 = (5{\cdot}8 \pm 1{\cdot}6) \times 10^8$ (in molal units). The value of β_1 agrees well with that of Braunstein,[1] but makes a more realistic assessment of the precision.[3,4] The cadmium(II)–bromide bond-energy term,[9] ϵ_C was calculated to be $-6{\cdot}7$ kcal. mole^{-1}, corresponding to its Helmholtz free-energy of association in the hypothetical anhydrous melt, assuming[9] that the cadmium(II)–aquo bond-energy, ϵ_H is taken as $-1{\cdot}41$ kcal. mole^{-1}.

Braunstein *et al.* did not report complexes higher than the di-substituted species. The apparent absence of "$CdBr_2$" *in solution* appears to conflict with their results.

The very low value of the stability constant for the species formally written as $Cd^{II}Br_2$ (conveniently assumed as zero in this case), indicates that a structural change occurs at the second bromide-ion substitution. The resulting species may be wholly or partially desolvated at this stage; evidence of the formation of a colloidal precipitate was obtained at higher Cd^{II} concentrations $\geqslant 5 \times 10^{-4}$ m in the presence of Br^- ions. A future publication will describe additional results and consider a substitution mechanism.

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[1] J. Braunstein, A. R. Alvarez-Funes, and H. Braunstein, *J. Phys. Chem.*, 1966, **70**, 2734.
[2] J. Braunstein, M. Blander, and R. M. Lindgren, *J. Amer. Chem. Soc.*, 1962, **84**, 1529.
[3] D. Inman, I. Regan, and B. Girling, *J. Chem. Soc.*, 1964, 348.
[4] D. Inman, D. G. Lovering, and R. Narayan, *Trans. Faraday Soc.*, 1968, **64**, 2476.
[5] D. R. Crow and J. V. Westwood, *Quart. Rev.*, 1965, **19**, 57.
[6] D. G. Lovering, M.Phil. Thesis, University of London, 1966.
[7] D. G. Lovering, Ph.D. Thesis, City University, London, 1969.
[8] D. Inman, D. G. Lovering, and R. Narayan, *Trans. Faraday Soc.*, 1968, **64**, 2487.
[9] J. Braunstein, *J. Phys. Chem.*, 1967, **71**, 3402.