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Note

STUDIES ON ION ASSOCIATION. CALORIMETRIC STUDY OF THE FORMATION OF MONOAZIDO COMPLEXES OF Ni(II), Zn(II) and Cd(II)

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The thermodynamics of formation of monothiocyanato and monoselenocyanato complexes of some divalent metal ions have been studied previously [1,2]. It was thought useful to extend the study to another pseudo halide ion, N_3^-. The present paper reports the calorimetric determination of the heat of reaction of

$$\begin{array}{ccc} M^{2+}_{(aq.)} & + N^-_{3(aq.)} & \rightleftharpoons MN^+_{3(aq.)} \\ (C_1 - x) & (C_2 - x) & x \end{array} \qquad (1)$$

at 298.16 K, where M = Ni(II), Zn(II) and Cd(II).

EXPERIMENTAL

Chemicals and reagents

All chemicals were of analytical grade. Solutions were prepared in triply distilled water. Solutions of metal perchlorates were prepared from the respective carbonates by adding excess of carbonate in perchloric acid and digesting in a water bath, with subsequent estimation by standard gravimetric methods.

Determination of enthalpies

The enthalpy change of association was obtained by direct calorimetry. The calorimetric set-up and the experimental details have been described previously [3]. The performance of the equipment was checked from time to time by determining the heat of neutralization of $HClO_4$ acid with NaOH · $-\Delta H^0$ of this reaction was found to be 56.03 ± 0.17 kJ mole^{-1}; the best literature value is 55.86 kJ mole^{-1}.

To determine ΔH, $(250 - V)$ cm^3 of metal(II) perchlorate were placed in

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the reaction vessel and V cm^3 (between 3 and 6 cm^3) of sodium azide solution of appropriate concentration were added instantaneously by breaking a thin glass bulb in which it was equilibrated in contact with the perchlorate solution. The heat change was measured within a few seconds of mixing and then at intervals of 30 s for 3 min. The readings were plotted against time, and the extrapolated value to zero time was taken for the following calculation.

The heat liberated in the calorimeter on mixing sodium azide and metal(II) perchlorate is related to the enthalpy change, ΔH, of reaction (1) by

$$-q = x\,\Delta H V \tag{2}$$

where q, x and V represent the heat liberated, concentration of the complex formed, and the volume of solution (0.25 dm^3), respectively. Values of x can be obtained from the previously determined thermodynamic equilibrium constants [4] of reaction (1)

$$K = \frac{a_{\mathrm{MN}_3^+}}{a_{\mathrm{M}^{2+}}a_{\mathrm{N}_3^-}} = \frac{x}{(C_1 - x)(C_2 - x)} \times \frac{1}{f_{\mathrm{M}^{2+}}} \tag{3}$$

where f is the activity coefficient (assuming $f_{\mathrm{N}_3^-} = f_{\mathrm{MN}_3^+}$). In the working concentrations of the reactants, higher complexes are formed in negligible quantity [4].

The simultaneous determination of x and $f_{\mathrm{M}^{2+}}$ was carried out in the following way by a series of approximations and refinements. As a first approximation, $f_{\mathrm{M}^{2+}}$ was taken as 1 and a value of x calculated from eqn. (3). Using this value of x and known values of C_1 and C_2, the approximate ionic strength of the solution, I, and hence $f_{\mathrm{M}^{2+}}$ were calculated. The new value of $f_{\mathrm{M}^{2+}}$ was substituted in eqn. (3) to obtain a refined value of x. This was repeated until constant values of x and $f_{\mathrm{M}^{2+}}$ were obtained.

For the calculation of $f_{\mathrm{M}^{2+}}$, the semi-empirical equation of Davies [5], with $C = 0.2$, was used

$$-\log f_i = AZ_i^2\left(\frac{I^{1/2}}{1 + I^{1/2}} - CI\right) \tag{4}$$

where I is the ionic strength of the solution, Z is the valency of the ion, A and C are constants; $A = 0.511$ at 298.16 K in water. Although there is some controversy concerning the value of C to be used, it does not seriously affect the calculation of equilibrium constant [6].

RESULTS AND DISCUSSION

The results of the calorimetric measurements are given in Table 1. The ΔH values reported are for the experimental range of ionic strength (generally 0.1—0.2). Preliminary observations have shown that in this region of ionic strength, variation of ΔH with ionic strength lies within experimental error, and hence our experimental results may be taken to be approximately equal

TABLE 1

Thermodynamic functions of monoazido complexes

Reaction	$-\Delta G^0$ * (kJ mole^{-1})	ΔH^0 ** (kJ mole^{-1})	ΔS^0 J K^{-1} mole^{-1})
$Ni^{2+} + N_3^- \rightleftharpoons NiN_3^+$	9.64 ± 0.39	6.32 ± 0.53	53.6 ± 3
$Cd^{2+} + N_3^- \rightleftharpoons CdN_3^+$	13.43 ± 0.30	0.34 ± 0.13	46.2 ± 1.4
$Zn^{2+} + N_3^- \rightleftharpoons ZnN_3^+$	8.21 ± 0.25	15.39 ± 0.65	79.2 ± 3

* ΔG^0 values taken from our previous determination (ref. 4).

** The ΔH^0 values presented here are the means of eight to ten readings. The concentration ranges in the experiments are: $[Ni^{2+}]$, 4—8 × 10^{-2}; $[Cd^{2+}]$, 4—8 × 10^{-2}; $[Zn^{2+}]$, 4—8 × 10^{-2}; and $[N_3^-]$, 2—5 × 10^{-2} mole dm^{-3}.

to ΔH^0. The endothermicity of the reactions indicate hard—hard interaction [7]. It can be seen that the positive ΔH^0 value is the least for Cd(II) which is a soft acceptor of electrons. Table 1 also summarises the results of our previous determination [4] of equilibrium constants (ΔG^0) by potentiometry.

SCN^-, $SeCN^-$ and N_3^- can be arranged in the following increasing order of "softness" on the basis of Pearson's classification [8,9]: $N_3^- < SCN^- < SeCN^-$. Among the metal ions studied, Cd(II) is a "soft" acceptor of electrons [10], and hence the following order of stabilities is expected [11]: $CdN_3^+ < CdSCN^+ < CdSeCN^+$.

Table 2 shows the ΔG^0, ΔH^0 and ΔS^0 values of the respective reactions. Comparison of results recorded in Table 2 is made because the results have been obtained by identical methods, viz. ΔG^0 by potentiometry using concentration cells of the type

$$\text{Ag, AgX} \left| \begin{array}{l} \text{NaX or KX } (C_1) \\ \\ \text{M (ClO}_4)_2\ (C_2) \end{array} \right\| \begin{array}{l} \text{Satd.} \\ \text{NH}_4\text{NO}_3 \\ \text{bridge} \end{array} \left\| \ \text{NaX or KX } (C_1) \ \right| \text{AgX, Ag}$$

($X^- = N_3^-$, SCN^- or $SeCN^-$)

and ΔH^0 by calorimetry. A perusal of Table 2 shows that while the standard enthalpy change ($-\Delta H^0$) follows the same sequence as predicted above, the standard free energy change ($-\Delta G^0$) shows the reverse of the expected

TABLE 2

Thermodynamic functions of Cd(II) systems

$Cd^{2+}_{aq.} + X^-_{aq.} \rightleftharpoons CdX^+_{aq.}$ ($X^- = SCN^-, SeCN^-, N_3^-$)

ΔG^0 (kJ mole^{-1})			ΔH^0 (kJ mole^{-1})			ΔS^0 (J K^{-1} mole^{-1})		
$SeCN^-$	SCN^-	N_3^-	$SeCN^-$	SCN^-	N_3^-	$SeCN^-$	SCN^-	N_3^-
−11.3	−12.3	−13.4	−11.1	−2.93	+0.34	0.75	31.3	46.2
±0.2	±0.1	±0.30	±0.40	±0.42	±0.13	±2.2	±0.8	±1.4

sequence. This is perhaps caused by the standard entropy change of the reaction (ΔS^0). The sequence for ΔS^0, which is the same as for $-\Delta G^0$, may be at least partly due to the following sequence of hydration of the anions: $SeCN^- < SCN^- < N_3^-$.

The difference in hydration between SCN^- and $SeCN^-$ ions may be due to their relative sizes. The charge distribution in the ion N_3^-, which is best represented as $^-N{=}\overset{+}{N}{=}N^-$, may be responsible for its relatively greater hydration. The higher value of ΔS^0 for $CdSCN^+$ compared to that for $CdSeCN^+$ has been explained as due to the existence of mixed species of $CdSCN^+$ (both N- and S-bonded species) and the predominance of single species (N-bonded) for $CdSeCN^+$ in solution [2]. The higher hydration of the N_3^- ion may be mainly responsible for the high ΔS^0 of CdN_3^+ which can only have one type of species.

Comparison of our results can be made with the data reported in the literature. Gerding [12] has reported the ΔH of reaction (1) for Cd(II) in 3 M sodium perchlorate solutions at 298.16 K by calorimetry to be —4.81 kJ mole^{-1}, which is different from our value of 0.338 kJ mole^{-1} corresponding to zero ionic strength. Ahrland and Avsar [13,14] have also determined ΔH for azido complexes of Ni(II) and Zn(II) calorimetrically in 3 M sodium perchlorate solutions at 298.16 K. Their reported values for NiN_3^+ and ZnN_3^+ are —0.96 and 2.57 kJ mole^{-1}, respectively. It may be seen that ΔH corresponding to $I = 0$ (ΔH^0) has an invariably higher algebraic value than for $I = 3.0$. A similar difference is also observed with respect to $CdSCN^+$ species. Nancollas and Torrance [15] have reported a value of —2.93 kJ mole^{-1} for ΔH^0 ($I \rightarrow 0$) at 298.16 K which is algebraically higher than the value of —8.11 kJ mole^{-1} in 3 M sodium perchlorate solution at the same temperature reported by Gerding [12]; both the determinations have been made calorimetrically. It may be because sodium perchlorate does not act as an indifferent electrolyte when it is present in large excess. The inert character of sodium perchlorate at high concentrations has been very seriously questioned [6,16].

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