# Thermochemical Studies on Metal Complexes

VIII. Free Energy, Enthalpy, and Entropy Changes for Stepwise Formation of Cadmium(II) Thiocyanate and Acetate Complexes at Different Ionic Strengths

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The enthalpy changes for the stepwise reactions:

$$CdA_{j-1}^{3-j} + A^- \longrightarrow CdA_j^{2-j}$$
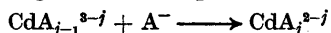
where A^- is the thiocyanate or acetate ion, have been determined at different ionic strengths by a calorimetric titration procedure. From these enthalpy changes and the changes of free energy, computed from the stability constants, the entropy changes have been calculated from the relation:

$$T\Delta S_j^\circ = \Delta H_j^\circ - \Delta G_j^\circ$$

The measurements were performed at 25.00°C in aqueous sodium perchlorate media, the total equivalent concentration of all ions being constant, $I'=0.25$, 0.50, 1.00, and 2.00 (M).

No general systematic trend was found for the enthalpy and entropy terms of the investigated systems when the ionic strength was varied. It seems, however, that for the first two steps the variation of these two terms with the ionic strength depends on the degree of entropy stabilization of the complex species.

In two previous papers [1,2] the influence of ionic strength on complex formation and the splitting up of the free energy change for this formation into one enthalpy and one entropy term according to the relation:

$$\Delta G_j^\circ = \Delta H_j^\circ - T\Delta S_j^\circ \tag{1}$$

have been reported. The present investigation is an extension of this study and describes the calorimetric determination of the enthalpy changes for the formation of cadmium(II) thiocyanate and acetate complex species. The stability constants used have been determined previously.[1] From these constants, the concentrations of the various complex species and the changes in free energy have been computed. The calorimetric determinations of the reaction heats were made using a reaction calorimeter and a titration pro-

cedure described earlier.[3] The measurements were carried out at 25.00°C and in aqueous sodium perchlorate media, the total equivalent concentration of all ions being constant (see Ref. 1), $I'=0.25$, 0.50, 1.00, and 2.00 (M). The values obtained were combined with the results at $I=3.00$ (M) from previous measurements.[4,5]

The calculations of the enthalpy values from the titration data and a list of most of the symbols and equations used were described earlier.[6] A least squares program developed by Sillén *et al.*[7,8] and the high speed computer IBM 7090 at NEUCC in Copenhagen were used. The results obtained in this way were checked with special experiments at high ligand concentrations, which gave better enthalpy values for the third step, using the eqns.:

$$\varDelta h_v = \sum_{j=1}^{N} \sum_{k=1}^{j} \alpha_j \cdot \varDelta H_k^\circ \qquad (2)$$

α_j was calculated from the equilibrium constants and $\varDelta H_1^\circ$ and $\varDelta H_2^\circ$ taken from the values determined by the high speed computer.

EXPERIMENTAL

Chemicals. Cadmium(II) perchlorate, sodium perchlorate, and *ligand solutions* were prepared and analysed as previously [4,5] and the pH of all cadmium solutions was maintained at 4. At higher pH values the cadmium ion is hydrolysed [9] and at lower values the heat effect from the reaction
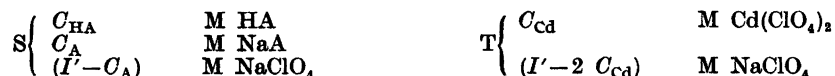
$$H^+ + Ac^- \longrightarrow HAc$$
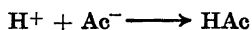
cannot be neglected. All chemicals were of analytical grade and for the preparations of solutions and the performance of titrations only calibrated volumetric flasks, burettes, and pipettes were used.

Procedure. The calorimeter and the titration procedure used were the same as described in a previous paper.[3] This calorimeter was equipped with a device for the successive addition of known amounts, here 5 ml portions up to a total of 30 ml, of a solution, T, into a calorimeter solution, S, initial volume 100.0 ml. The compositions of the solutions S and T were:

$$S\begin{cases} C_{Cd} & \text{M Cd(ClO}_4)_2 \\ \\ (I'-2\,C_{Cd}) & \text{M NaClO}_4 \end{cases} \qquad T\begin{cases} C_{HA} & \text{M HA} \\ C_A & \text{M NaA} \\ (I'-C_A) & \text{M NaClO}_4 \end{cases}$$

$$A^- = SCN^- \text{ or } Ac^-$$

or, for the measurements at high ligand concentrations:

$$S\begin{cases} C_{HA} & \text{M HA} \\ C_A & \text{M NaA} \\ (I'-C_A) & \text{M NaClO}_4 \end{cases} \qquad T\begin{cases} C_{Cd} & \text{M Cd(ClO}_4)_2 \\ \\ (I'-2\,C_{Cd}) & \text{M NaClO}_4 \end{cases}$$

Each titration series was repeated at least once.

The dilution heats of the ligands were determined by similar titration series without cadmium perchlorate in the solutions. For the central ion no effect was found upon diluting from $C_{Cd}=0.050$ (M) to $C_{Cd}=0.001$ (M) and it was assumed that the dilution heats of the central ion and of the various complexes could be neglected at all ionic strengths.

The thermodynamic standard state for the solute species M, A, and MA_j, where M is the central ion and A the ligand, is in this study a temperature of 25.00°C and a hypothetically ideal one molar solution having neutral salt such that the total equivalent concentration of all ions is constant and equal to I'.[5] The zero superscript, when used with ΔG, ΔH, and ΔS, refers to the standard changes in these quantities with reference to this standard state.

MEASUREMENTS AND RESULTS

The electrical calibrations [3] gave a linear dependence of the heat equivalent of the calorimetric system upon the total volume of titrant, v (ml), added. By use of a least squares method, the results were described by the relation

$$-\varepsilon_v = l + kv \tag{3}$$

where the constants l and k are given in Table 1. l depends on the ionic strength while k is constant within the accuracy of the measurements. The accuracy of the ε_v-function is better than $\pm 5 \times 10^{-3}$ cal·ohm^{-1} in the range $0 < v < 30$ (ml). No differences were observed between the two systems with different ligands.

The cadmium(II) thiocyanate system. In the potentiometric investigation [1] four mononuclear complex species were found to describe the experimental data at all ionic strengths and concentration ranges used (except for $I'=0.25$ (M) where only three mononuclear species were found). The stabilities of the complex species are so low that the ligand concentration range must be extended as high as possible. For that reason the titration series were performed in two ways. In titrations of type I the central ion was supplied by solution S and the ligand by solution T. The concentrations were at $I'=0.25$ (M): $C_{Cd}=0.0250$ (M) and $C_{SCN}=0.250$ (M); at $I'=0.50$ (M): $C_{Cd}=0.0500$ (M) and $C_{SCN}=0.500$ (M); at $I'=1.00$ and 2.00 (M): $C_{Cd}=0.0500$ (M) and $C_{CSN}=1.000$ (M). For this system $C_{HA}=0$ in all measurements.

The dilution heats of the ligand were determined as described above and corresponding values of v and $Q_{dil.}$ are collected in Table 2. The measured values, Q_X, are corrected for the dilution heats according to the equation

$$Q_X - Q_{dil.} = Q_{corr.} \tag{4}$$

Table 1. The different values of the constants l and k in the relation $-\varepsilon_v = l + kv$.

I' (M)	Pipette volume (ml)	k	l
0.25	5	0.0207	2.213
0.5	5	0.0207	2.191
1	5	0.0204	2.166
2	5	0.0204	2.136

Table 2. The dilution heats, $Q_{dil.}$, for portions of 5.02 ml of the different thiocyanate solutions, T, added to 100.0 ml I' M $NaClO_4$ solutions.

v (ml)	$Q_{dil.}$ (cal)							
	$I'=0.25$ (M)		$I'=0.5$ (M)		$I'=1$ (M)		$I'=2$ (M)	
5.02	−0.007	−0.008	−0.016	−0.039	−0.127	−0.111	−0.085	−0.132
10.05	−0.007	−0.005	−0.029	−0.036	−0.078	−0.107	−0.110	−0.105
15.07	−0.008	−0.007	−0.018	−0.040	−0.091	−0.111	−0.083	−0.088
20.09	−0.006	−0.007	−0.010	−0.021	−0.100	−0.103	−0.087	−0.087
25.11	−0.004	−0.005	0.003	−0.019	−0.102	−0.080	−0.074	−0.069
30.14			−0.039	−0.031	−0.081	−0.097	−0.066	−0.063

Table 3. The total reaction heats corrected for dilution, $\sum Q_{corr.}$, obtained in the titrations of the thiocyanate system at different ionic strengths.

v (ml)	$\sum Q_{corr.}$ (cal)							
	$I'=0.25$ (M)		$I'=0.5$ (M)		$I'=1$ (M)		$I'=2$ (M)	
5.02	1.010	1.017	2.695	2.729	4.877	4.875	4.891	4.882
10.05	1.854	1.861	4.974	4.495	8.238	8.255	8.303	8.282
15.07	2.527	2.527	6.762	6.758	10.603	10.650	10.727	10.669
20.09	3.096	3.074	8.255	8.236	12.382	12.424	12.528	12.465
25.11	3.554	3.531	9.466	9.434	13.740	13.785	13.895	13.835
30.14			10.499	10.447	14.837	14.865	14.987	14.894

Table 4. The heats of dilution, $Q_{dil.}$, and reaction corrected for dilution, $Q_{corr.}$, obtained in the titrations of thiocyanate solutions, S, by I' M $NaClO_4$ solutions and central ion solutions, T, respectively.

I' (M)	v (ml)	$Q_{dil.}$ (cal)	$Q_{corr.}$ (cal)
0.5	5.02	0.012	0.856
	10.05	−0.005	0.771
	15.07	−0.015	0.739
1	5.02	−0.029	1.101
	10.05	−0.019	1.054
	15.07	−0.022	1.010
2	5.02	−0.013	1.085
	10.05	−0.019	1.043
	15.07	−0.027	1.028

where $Q_{\text{dil.}}$ is taken from the corresponding addition in the dilution series. The effect of complex formation on the dilution heat in measurements of Q_{X} could be neglected. The corresponding values of v and $Q_{\text{corr.}}$ are given in Table 3.

In titrations of type II the ligand was supplied by solution S and the central ion by solution T, which, allows a much higher final concentration of the ligand. The concentrations were at $I'=0.50$: $C_{\text{Cd}}=0.0500$ (M) and $C_{\text{SCN}}=0.250$ (M); at $I'=1.00$ and 2.00 (M); $C_{\text{Cd}}=0.0500$ (M) and $C_{\text{SCN}}=0.500$ (M). The dilution heats of the ligand were determined and the corrections performed as above. The corresponding values of v, $Q_{\text{dil.}}$ and $Q_{\text{corr.}}$ are collected in Table 4. The values of β_j used and $-\varDelta G_j^\circ$, $-\varDelta H_j^\circ$, and $\varDelta S_j^\circ$ obtained at the various I' are given in Table 8. Not even the titrations of type II could give any reliable values for the enthalpy changes of the fourth step, and at 0.25 and 0.50 M the values for the third step are also very uncertain.

The cadmium(II) acetate system. In the potentiometric investigation [5] three mononuclear complex species were found to describe the experimental data at all ionic strengths and concentration ranges used. For this system too the stabilities are so low that the ligand concentration must be extended as high as possible. In titrations of type I the concentrations were at $I'=0.25$ (M): $C_{\text{Cd}}=0.025$ (M) and $C_{\text{Ac}}=0.250$ (M); at $I'=0.50$ (M): $C_{\text{Cd}}=0.0500$ (M) and $C_{\text{Ac}}=0.500$ (M); at $I'=1.00$ and 2.00 (M): $C_{\text{Cd}}=0.0500$ (M) and $C_{\text{Ac}}=1.000$ (M). For this system $2\cdot C_{\text{HA}}=C_{\text{A}}$ in all measurements.

The dilution heats were determined and the corrections performed as above. Corresponding values of v and $Q_{\text{dil.}}$ are collected in Table 5 and of v and $Q_{\text{corr.}}$, in Table 6.

In titrations of type II the concentrations were at $I'=0.50$ (M): $C_{\text{Cd}}=0.0500$ (M) and $C_{\text{Ac}}=0.500$ (M); at $I'=1.00$ and 2.00 (M): $C_{\text{Cd}}=0.0500$ (M) and $C_{\text{Ac}}=1.000$ (M).

The dilution heats were determined and the corrections performed as above. The corresponding values of v, $Q_{\text{dil.}}$, and $Q_{\text{corr.}}$ are collected in Table 7. The values of β_j used and $-\varDelta G_j^\circ$, $-\varDelta H_j^\circ$, and $\varDelta S_j^\circ$ obtained at the various I' are given in Table 8. At $I'=0.25$ (M) it was not possible to determine the enthalpy changes for the second and the third step and at 0.50 (M) that of the third step could not be determined even with the titrations of type II.

Table 5. The dilution heats, $Q_{\text{dil.}}$, for portions of 5.02 ml of the different acetate solutions, T, added to 100.0 ml I' M $NaClO_4$ solutions.

v (ml)	$Q_{\text{dil.}}$ (cal)							
	$I'=0.25$ (M)		$I'=0.5$ (M)		$I'=1$ (M)		$I'=2$ (M)	
5.02	0.030	0.024	0.016	0.011	0.018	0.002	0.094	0.087
10.05	0.027	0.033	0.010	0.017	0.007	0.000	0.070	0.072
15.07	0.033	0.027	0.003	0.023	0.020	0.007	0.049	0.061
20.09	0.021	0.027	0.016	0.016	0.015	0.008	0.071	0.061
25.11	0.014	0.009	0.016	0.014	0.013	0.011	0.071	0.056
30.14	0.011	0.016	0.014	0.014	0.019	0.008	0.060	0.063

Table 6. The total reaction heats corrected for dilution, $\sum Q_{corr.}$, obtained in the titrations of the acetate system at different ionic strengths.

v (ml)	$\sum Q_{corr.}$ (cal)							
	$I'=0.25$ (M)		$I'=0.5$ (M)		$I'=1$ (M)		$I'=2$ (M)	
5.02	−0.604	−0.611	−1.767	−1.770	−2.992	−2.967	−2.960	−2.949
10.05	−1.121	−1.150	−3.251	−3.256	−5.129	−5.094	−5.064	−5.063
15.07	−1.548	−1.623	−4.476	−4.461	−6.618	−6.608	−6.524	−6.535
20.09	−1.921	−2.020	−5.470	−5.439	−7.667	−7.680	−7.530	−7.541
25.11	−2.235	−2.317	−6.280	−6.228	−8.446	−8.496	−8.279	−8.280
30.14	−2.493	−2.555	−6.938	−6.889	−9.024	−9.085	−8.825	−8.824

DISCUSSION

No systematic investigation of enthalpy and entropy changes at different ionic strengths for the two systems studied in this work has been found in the literature. However, there are resemblances to the systems investigated previously,[2] especially comparing the thiocyanate system with the iodide and the acetate system with the chloride.

For these four systems it may consequently be possible to distinguish between two groups: (*i*) mainly enthalpy stabilized consisting of the iodide and the thiocyanate systems, and (*ii*) mainly entropy stabilized including the chloride and the acetate systems. Within the concentration range used the enthalpy changes, $-\Delta H_j°$, generally decrease with increasing ionic strength for the first group while for the second group the enthalpy changes, $-\Delta H_j°$, in most cases increase with increasing ionic strength. The differences are most obvious in the first two steps as the stabilizing term changes for both the iodide and the acetate systems at the third step (see Table 8). The proton

Table 7. The heats of dilution, $Q_{dil.}$, and reaction corrected for dilution, $Q_{corr.}$, obtained in the titrations of acetate solutions, S, by I' M NaClO$_4$ solutions and central ion solutions, T, respectively.

I' (M)	v (ml)	Q_{dil} (cal)	$Q_{corr.}$ (cal)
0.5	5.02	0.016	−0.565
	10.05	0.007	−0.542
	15.07	0.018	−0.559
1	5.02	0.052	−0.605
	10.05	0.026	−0.598
	15.07	0.030	−0.603
2	5.02	0.103	−0.611
	10.05	0.091	−0.608
	15.07	0.083	−0.601

Table 8. The stability constants used and the computed values of free energy, enthalpy, and entropy changes for the stepwise reactions of the cadmium thiocyanate and acetate complex systems at different ionic strengths. The $\Delta H_j°$-values with their computed standard deviations, the β_j, $\Delta G_j°$, and $\Delta S_j°$-values with their estimated errors. The values at ionic strength 3 M are taken from Refs. 4 and 5.

Ligand	I (M)	j	0.25	0.5	1	2	$I=3$
SCN⁻	β_j (M⁻ʲ)	1	27.0 ± 0.5	22.6 ± 0.5	20.7 ± 0.5	22.0 ± 0.5	25.5 ± 0.4
		2	125 ± 8	109 ± 5	97 ± 5	111 ± 5	175 ± 6
		3	200 ± 100	120 ± 30	107 ± 20	177 ± 17	300 ± 30
		4	—	95 ± 50	75 ± 30	107 ± 25	300 ± 40
	$-\Delta G_j° \times 10^{-3}$ (cal·mole⁻¹)	1	1.95 ± 0.02	1.85 ± 0.02	1.80 ± 0.02	1.83 ± 0.02	1.92 ± 0.02
		2	0.91 ± 0.04	0.93 ± 0.05	0.92 ± 0.02	0.96 ± 0.04	1.14 ± 0.07
		3	0.28 ± 0.37	0.06 ± 0.14	0.06 ± 0.16	0.28 ± 0.08	0.32 ± 0.12
		4	—	−0.1 ± 0.7	−0.21 ± 0.38	−0.29 ± 0.22	0.00 ± 0.26
	$-\Delta H_j° \times 10^{-3}$ (cal·mole⁻¹)	1	2.24 ± 0.03	2.24 ± 0.03	2.29 ± 0.01	2.22 ± 0.01	1.94 ± 0.01
		2	2.67 ± 0.39	2.45 ± 0.20	1.93 ± 0.09	1.85 ± 0.11	1.73 ± 0.06
		3	—	—	2.2 ± 0.9	2.2 ± 1.0	1.57 ± 0.20
		4	—	—	—	—	1.04 ± 0.41
	$\Delta S_j°$ (cal·mole⁻¹·degree⁻¹)	1	−1.0 ± 0.1	−1.3 ± 0.1	−1.6 ± 0.1	−1.3 ± 0.1	−0.1 ± 0.1
		2	−6.0 ± 1.3	−5.0 ± 0.7	−3.4 ± 0.3	−3.0 ± 0.4	−2.0 ± 0.4
		3	—	—	−7.2 ± 3.1	−6.5 ± 3.4	−4.2 ± 0.8
		4	—	—	—	—	−3.5 ± 1.6
Ac⁻	β_j (M⁻ʲ)	1	18.5 ± 1.0	15.5 ± 0.5	15.0 ± 0.5	17.2 ± 0.5	20.0 ± 1.0
		2	100 ± 20	80 ± 6	66 ± 4	95 ± 6	190 ± 20
		3	500 ± 200	150 ± 20	110 ± 10	135 ± 10	260 ± 50
		4	—	—	—	—	100 ± 50
	$-\Delta G_j° \times 10^{-3}$ (cal·mole⁻¹)	1	1.73 ± 0.04	1.62 ± 0.02	1.60 ± 0.02	1.69 ± 0.03	1.78 ± 0.04
		2	1.00 ± 0.17	0.97 ± 0.07	0.88 ± 0.06	1.01 ± 0.06	1.33 ± 0.09
		3	0.95 ± 0.41	0.37 ± 0.13	0.30 ± 0.09	0.21 ± 0.09	0.19 ± 0.19
		4	—	—	—	—	−0.57 ± 0.51
	$-\Delta H_j° \times 10^{-3}$ (cal·mole⁻¹)	1	−1.69 ± 0.02	−1.76 ± 0.01	−1.62 ± 0.01	−1.50 ± 0.01	−1.46 ± 0.03
		2	—	−1.47 ± 0.08	−1.23 ± 0.06	−1.08 ± 0.05	−0.39 ± 0.05
		3	—	—	0.60 ± 0.34	0.07 ± 0.58	−0.95 ± 0.30
		4	—	—	—	—	—
	$\Delta S_j°$ (cal·mole⁻¹·degree⁻¹)	1	11.5 ± 0.2	11.3 ± 0.1	10.8 ± 0.1	10.7 ± 0.1	10.9 ± 0.1
		2	—	8.2 ± 0.4	7.1 ± 0.3	7.0 ± 0.3	5.8 ± 0.3
		3	—	—	−1.0 ± 1.2	0.5 ± 2.0	3.8 ± 1.2
		4	—	—	—	—	—

acetate system,[10,11] which is entropy stabilized, behaves as the systems in group (*ii*). The variations in the entropy changes with the ionic strength cannot be related to the two groups in such a simple way as the variations in the enthalpy changes. The trend is, however, that the difference between the two groups caused by the enthalpy term is opposed by the variation in the entropy term. This is the reason for the fact that the variations in the free energy changes with increasing ionic strength for these systems do not differ between the two groups. In most cases the free energy changes go through a minimum [1] when the ionic strength is varied, as may be calculated from the expected variation of the activity coefficients. The most interesting result from the measurements is, however, for all four systems investigated, the comparatively small variations of the enthalpy and the entropy terms when using different ionic strengths.

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