# Cadmium—Imidazole Complex Formation in Aqueous Solutions. Stability Constants, Changes in Standard Free Energies, Enthalpies, Entropies, and Heat Capacities Accompanying the Complex Formation at 5, 15, 25, and 40 °C

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The over-all complexity constants, changes in standard values of free energy, enthalpy, and molar heat capacity of the equilibrium:

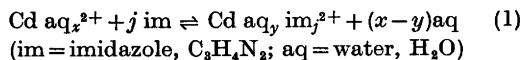$$Cd\ aq_x^{2+} + j\ im \rightleftharpoons Cd\ aq_y im_j^{2+} + (x-y)aq$$
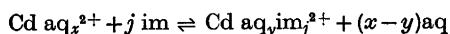
have been determined at 5, 15, 25, and 40 °C. The measurements were performed in aqueous solutions at pH 9.5 and ionic strength 1.0 established with sodium perchlorate. The complexity constants were obtained by means of the polarographic standard method, and the experimental results were fitted to a polynomium of the type:

$$\log K_{0j} = A_j + B_j/T + C_j/T^2$$

by application of a polynomium regression program. The enthalpies and entropies of the various steps show remarkable differences and it is concluded that structural changes occur, most probably, so that the cadmium ions are six-coordinated, when $j = 1$, 5, and 6, and only four-coordinated when $j = 2$, 3, and 4.

The over-all complexity constants, K_{0j}, of the complex equilibria:

$$Cd\ aq_x^{2+} + j\ im \rightleftharpoons Cd\ aq_y\ im_j^{2+} + (x-y)aq \quad (1)$$
(im = imidazole, $C_3H_4N_2$; aq = water, H_2O)

are related to thermodynamic quantities by the equations:

$$-RT \ln K_{0j} = \Delta^\circ_{0j}G = \Delta^\circ_{0j}H - T\Delta^\circ_{0j}S \quad (2)$$

$$\partial \ln K_{0j}/\partial(1/T) = -\Delta^\circ_{0j}H/R \quad (3)$$

where $\Delta^\circ_{0j}G$, $\Delta^\circ_{0j}H$ and $\Delta^\circ_{0j}S$ indicate changes in standard free energy, enthalpy and entropy,

respectively, accompanying reaction (1). From a knowledge of values of $\Delta^\circ_{0j}H$ the corresponding changes in standard molar heat capacity, $\Delta^\circ_{0j}C_p$, can be found:

$$\partial \Delta^\circ_{0j}H/\partial T = \Delta^\circ_{0j}C_p \quad (4)$$

In our previous studies [1,2] on cadmium-imidazole complex formation carried out at 25 °C, the complexity constants of reaction (1) were determined. The maximum value of j was found to be 6. In the present paper we shall report the measurements of the complexity constants at four different temperatures covering the range from 5 to 40 °C. The determinations were performed at constant ionic strength by a polarographic procedure described earlier,[1] and the values of the activity coefficients at 37 °C and at the freezing points of the imidazole solutions reported in the same paper will be utilized. Having determined the enthalpy and entropy changes connected to the complex formation we have some background to discuss whether structural changes may occur at various steps of the complex formation.[3-6]

EXPERIMENTAL

Chemicals. The cadmium perchlorate was prepared as described earlier.[1] All other chemicals were of analytical grade and were used without further purification.

Polarographic measurements. The equipment and experimental procedure in the polarographic measurements were the same as described

earlier.[1] In order to avoid precipitations of cadmium-imidazole complex compounds [2] the half wave potentials were determined with a total concentration of cadmium not exceeding 5×10^{-4} mol/kg but in no experiments it was necessary to go below 5×10^{-5} mol/kg. The concentration of imidazole was varied from 0.01 to 1.0 mol/kg in 15 steps. To ensure that the imidazole was present as unprotonated molecule, pH was kept constant at 9.5 and the ionic strength at 1.0 by addition of sodium perchlorate.

The temperature control. The temperature was continuously recorded and kept constant within ± 0.05 °C. All solutions were pre-cooled (preheated) before being added to the cell. In order to obtain better thermal stability at 5 °C and to avoid condensation, the experimental equipment was placed in a cold-storage room with a temperature a little below 5 °C. By means of a water bath the temperature in the cell was then kept at 5 ± 0.05 °C.

RESULTS

By application of the results from the polarographic measurements the over-all complexity constants, K_{0j} at ionic strength 1.0, were determined at 5, 15, 25, and 40 °C. The results are shown in Table 1. In order to obtain

Fig. 1. Dependence of $(1/j) \log K_{0j}$ for the Cd(II)-imidazole system *versus* the reciprocal absolute temperature for $j = 1, 2, 3, 4, 5,$ and 6. Ionic strength 1.0 by means of sodium perchlorate, pH 9.5.

Table 1. Logarithm of the over-all stability constants for the cadmium-imidazole system at four different temperatures. Ionic strength 1.0 by means of sodium perchlorate, pH 9.5. Standard deviations $= \pm 0.05$.

j	5 °C	15 °C	25 °C	40 °C
1	3.08	2.95	2.70	2.48
2	5.48	5.26	5.10	4.85
3	7.30	7.00	6.63	6.30
4	8.35	8.11	7.60	6.70
5	8.30	8.30	8.18	7.74
6	9.90	9.48	8.95	7.92

a correspondence in dimensions of the consecutive complexity constants the mean over-all complexity constants, $K_{0j}^{1/j}$ are compared, and for similar reasons the mean standard thermodynamic quantities: $\Delta^\circ_{0j}G/j$, $\Delta^\circ_{0j}H/j$, $\Delta^\circ_{0j}S/j$ and $\Delta^\circ_{0j}C_p/j$ are considered. The thermodynamic functions are then compared per mol of coordinated imidazole. In Fig. 1 the logarithm of the estimated values of the mean over-all complexity constants together with the standard deviations are plotted *versus* the reciprocal absolute temperature. The curves combining the estimated values have been determined by fitting a function of the type:

$$\log K_{0j} = A_j + B_j/T + C_j/T^2 \ (j = 1,2,3,4,5,6) \qquad (5)$$

The parameters A_j, B_j, and C_j were determined by application of a subroutine polynomium POLRG in the FORTRAN series. Knowing the values of these parameters the mean standard enthalpy and the mean standard molar heat capacity at 25 °C can be determined:

$$0.4343 \ \Delta^\circ_{0j}H/R = -B_j - 2C_j/298 \qquad (6)$$

$$0.4343 \ \Delta^\circ_{0j}C_p/R = 2C_j/298^2 \qquad (7)$$

When the standard enthalpy is independent of temperature within the temperature range covered here, the best curve describing the experimental results must be a straight line and $\Delta^\circ_{0j}C_p$ must be zero. Fig. 1 shows that this is the case for the first three steps whereas the last three steps are accompanied by a remarkable change in standard molar heat capacity. The results obtained for $\Delta^\circ_{0j}C_p$ together with other thermodynamic data are shown in Table 2. But although it must not be forgotten, that
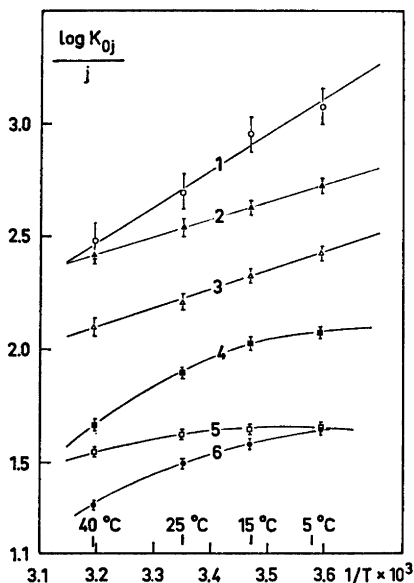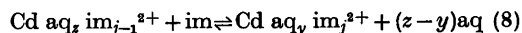
Table 2. Calculated values of changes in the over-all thermodynamic functions $\Delta^\circ_{0j}G$, $\Delta^\circ_{0j}H$, $\Delta^\circ_{0j}S$, and $\Delta^\circ_{0j}C_p$ at 25 °C for the cadmium-imidazole system. Ionic strength 1.0 by means of sodium perchlorate, pH 9.5.

j	$(\Delta^\circ_{0j}G/R) \times 10^{-3}$	$(\Delta^\circ_{0j}H/R) \times 10^{-3}$	$\Delta^\circ_{0j}S/R$	$\Delta^\circ_{0j}C_p/R$
1	-1.85 ± 0.03	-3.5 ± 0.3	-5.5 ± 0.2	0
2	-3.50 ± 0.03	-3.5 ± 0.3	0.0 ± 0.2	0
3	-4.55 ± 0.03	-5.7 ± 0.3	-3.8 ± 0.2	0
4	-5.22 ± 0.03	-11.0 ± 0.5	-19.4 ± 0.3	-380 ± 50
5	-5.62 ± 0.03	-4.4 ± 0.5	$+4.2 \pm 0.3$	-275 ± 50
6	-6.15 ± 0.03	-12.6 ± 0.5	-21.6 ± 0.3	-350 ± 50

$\Delta^\circ_{0j}C_p$-data obtained in this way may be defective to some extent due to accumulation of errors when first and second derivatives are calculated from experimental free energy data, the actual values agree reasonably well with those found for similar compounds, *i.e.* silver-imidazole complex compounds,[7] tetraamyl-ammonium bromide [8,9] and tetrabutylphosphonium bromide,[10] all compounds containing organic nitrogen. Similar observations as described here for the last three complex compounds have been made for rare earth complexes,[11-13] a lot of weak organic acids,[14] and water.[15] Furthermore, when regarding Fig. 1 it is seen, that the temperature coefficients of $\log K_{0j}$ — and consequently the changes in standard enthalpies, $\Delta^\circ_{0j}H$ — are of the right order of magnitude and with the right sign as

Fig. 2. Changes of the mean thermodynamic quantities, $-\Delta^\circ_{0j}G/jR$, $-\Delta^\circ_{0j}H/jR$ (upper part) and $-\Delta^\circ_{0j}S/jR$ (lower part) at 25 °C *versus* step number, j, in the Cd(II)-imidazole system.

would be expected for a complex formation of the type investigated in this paper.[3,4,5] This suggests, that no serious experimental and systematic errors affect the results. The changes in free energies and entropies are calculated by application of eqn. (2). Fig. 2 summarizes the results. The values of $\Delta^\circ_{0j}G$, $\Delta^\circ_{0j}H$, and $\Delta^\circ_{0j}S$ were calculated at 25 °C and plotted *versus* j, where j indicates the step of reaction (1). The vertical lines indicate standard deviations. From the values shown in Table 2, the thermodynamic quantities $\Delta^\circ_{1-j,j}$ (G,H,S,C_p) corresponding to the step equilibria:

$$\text{Cd aq}_z \text{ im}_{j-1}{}^{2+} + \text{im} \rightleftharpoons \text{Cd aq}_y \text{ im}_j{}^{2+} + (z-y)\text{aq} \quad (8)$$

can be calculated by the equations:

$$\Delta^\circ_{j-1,j}(G,H,S,C_p) = \Delta^\circ_{0j}(G,H,S,C_p) - \Delta^\circ_{0,j-1}(G,H,S,C_p) \quad (9)$$

$$\log K_{j-1,j} = \log K_{0j} - \log K_{0,j-1} \quad (10)$$

DISCUSSION

Cadmium ions in aqueous solutions are generally suggested to be coordinated with six water molecules,[4] and likewise it seems reasonable to assume, that complexes with five and six imidazole ligands in aqueous solutions will have a similar, octahedral configuration.[16] The simplest reaction scheme of complex formation would be, that a water molecule from step to step was replaced by an imidazole molecule as visualized in (8) when $z-y = 1$. From Fig. 2 it is seen that for $j = 1$, 3, 4, and 6 the reduction in free energy is mainly governed by the enthalpy term and so the results in these three cases agree well with the simple reaction scheme. If, however, a sudden change in $\Delta^\circ_{0j}H$
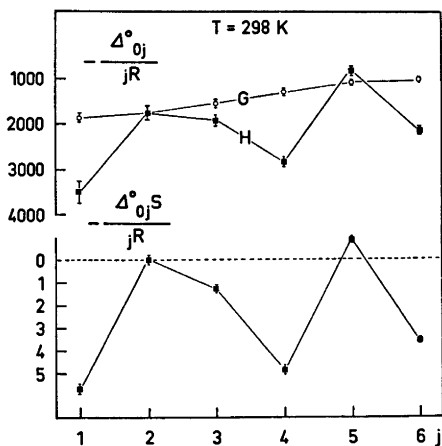
towards positive values is observed, this may be caused by a sudden change in the coordination geometry.[4,5,17,18] The necessary increase in entropy can be explained by a change in the hydration shell belonging to the metal ions.[5,18,19] So, when structural changes occur, the contribution to the $-\Delta^\circ_{0j}G$ is mainly coming from a large gain in entropy, and the enthalpy change contributes only slightly. An example of such a case — given by Ahrland [4] is the complex formation between cadmium and halide ions. Similar effects in the cadmium-imidazole system are observed at the second and fifth step (Fig. 2). In the second step, $\Delta^\circ_{1,2}H$ was found $\cong 0$, i.e. the reduction in free energy is due to contribution from the entropy term. We therefore assume, that the coordination at this step changes from six to four, and the consecutive complex-equilibrium can be written:

$$\text{Cd aq}_5 \text{ im}^{2+} + \text{im} \rightleftharpoons \text{Cd aq}_2 \text{ im}_2^{2+} + 3\text{aq} \qquad (11)$$
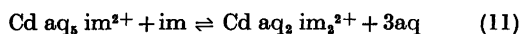
As seen from Fig. 2 the fourth coordinated cadmium-imidazole complex compound is characterized by very small values in both enthalpy and entropy indicating a relatively stable compound. This is in good agreement with the results observed by Bjerrum [20] in the case of cadmium-ammine complex formation. Based on these observations Bjerrum introduced the term "characteristic coordination number" besides the maximum coordination number, and he found these values to be 4 and 6, respectively, for the cadmium ion. The thermodynamic data shown in Fig. 2 seem to confirm the presence of such "characteristic" complex compounds also in the cadmium-imidazole system. Most likely the imidazole molecules are strongly bound in this characteristic form involving a change in the hydration shell. This effect might explain the contribution to the change in heat capacity observed at this step of the complex formation.

According to the above mentioned it is assumed, that the complex components at the fourth step exist in a four-coordinated form. In order to be able to end up as six-coordinated compounds a new coordination change must occur. The results shown in fig. 2 suggest this coordination change to occur at the fifth step in the complex formation, and therefore we propose the fifth complex equilibrium:
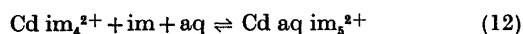
$$\text{Cd im}_4^{2+} + \text{im} + \text{aq} \rightleftharpoons \text{Cd aq im}_5^{2+} \qquad (12)$$

Most likely the coordination change at the fifth step is accompanied by a formation of a new coordination geometry, which at this step is characterized by a lack of symmetry. The influence on the hydration shell is therefore weaker than that at the fourth step. This involves $\Delta^\circ_{45}C_p > 0$ in good agreement with the experimental results. In this six-coordinated form the high symmetry is re-established. From Table 1 it is seen that $\Delta^\circ_{56}C_p < 0$, in good agreement with the expected value.

Conclusions. Based on values of enthalpy changes, estimated from free energy data, we have tried to suggest a model by means of which we were able to describe the consecutive complex formation between Cd(II)-ions and uncharged imidazole molecules. According to this model it is assumed, that during the complex formation the Cd(II)-ions change their coordination number twice: at the second step from six to four and at the fifth step from four to six.

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