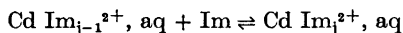


Determination of Consecutive Complexity Constants of Cadmium Imidazole in Aqueous Solutions from Polarographic and Potentiometric Data

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Complex-formation in the cadmium-imidazole system in aqueous solutions has been studied. The measurements were performed at 25°C at ionic strength 1.0 using sodium perchlorate and potassium chloride, respectively, as ionic medium. The activity coefficients of imidazole were determined by the freezing-point and the vapour pressure method. The complexity constants of the stepwise reactions



were evaluated. The maximum value of j was found to be 6, and the following complexity constants were obtained:

$j = 1, K_1 = 500 \pm 50 \text{ l/mol}$	$j = 2, K_2 = 250 \pm 50 \text{ l/mol}$
$j = 3, K_3 = 40 \pm 10 \text{ l/mol}$	$j = 4, K_4 = 9.0 \pm 2 \text{ l/mol}$
$j = 5, K_5 = 4.0 \pm 2 \text{ l/mol}$	$j = 6, K_6 = 7.0 \pm 3 \text{ l/mol}$

The mathematic treatment of step equilibria of complex compounds examined by polarographic methods has been given by several authors.¹⁻⁴ According to this treatment the shift in half-wave potential is related to the consecutive stability constants of the various complex ions by the Bodländer-Bjerrum equation⁵ converted to polarographic conditions:

$$\begin{aligned} \text{Antilog} \left(\frac{0.4343 nF}{RT} \Delta E_{\frac{1}{2}} + \log \frac{I_M}{I_C} \right) &= \gamma_M \sum_{j=0}^N \beta_j \frac{X^j \gamma_X^j}{\gamma_{MX_j}} \\ &= \beta_0 + \beta_1 X \frac{\gamma_M \gamma_X}{\gamma_{MX}} + \beta_2 X^2 \frac{\gamma_M \gamma_X^2}{\gamma_{MX_2}} \dots \end{aligned} \quad (1)$$

where $\Delta E_{\frac{1}{2}}$ is the difference in half-wave potential between free and complexed metal-ions, I_M is the diffusion current constant of the free, hydrated metal-ions, I_C is the experimental mean value of the diffusion current constant for the mixture of complexes, β_j is the over-all stability constant as defined by

Bjerrum,^{5,6} X is the concentration of the uncomplexed ligand, and γ indicates the activity coefficients. By definition β_0 equals 1. (All the terms are related to the surface of the dropping mercury electrode as will be discussed below.)

The terms on the left-hand side of eqn. (1) are known or experimentally determinable. The polarographic measurements permit the evaluation of the expression on the right-hand side of the equation. However, very often the calculations are based on the assumptions that all the activity coefficients in (1) are unity and I_M equals I_C .

The present paper presents an attempt to determine the complexity constants of the cadmium-imidazole system in aqueous solutions without these approximations. The necessity of taking the magnitude of activity coefficients into account on the calculations will be illustrated. Although the influence from the other correction term turns out to be small, it may as well be included since the necessary data are readily available in the ordinary course of experiments.

Following well known procedures^{10,11} the cadmium-imidazole system has been investigated titrimetrically and the results have been compared with those obtained by polarographic measurements.

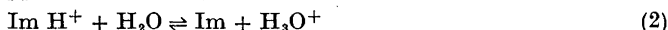
EXPERIMENTAL

Materials. All chemicals were of reagent grade and were used without further purification. All solutions were kept at a constant ionic strength at 1.0 and the measurements were carried out in both sodium perchlorate and potassium chloride solutions. Only the measurements on sodium perchlorate solutions are described here in detail. The results from potassium chloride solutions were obtained in a similar way, and in the following the total compositions of the potassium chloride solutions are given in parantheses.

Titration curves were obtained from imidazole solutions with and without cadmium ions.

The pH was initially adjusted to 3.00 using HNO_3 (HCl), and titrations were performed by addition of 0.2 M NaOH + 1.0 M NaClO_4 (0.2 M KOH + 1.0 M KCl) using an automatic titrator (SBR2, PHM26, TTT11, ABU1, TTA3, Radiometer, Copenhagen, Denmark). The temperature was kept constant at $25^\circ\text{C} \pm 0.1^\circ$ by a water-bath in which also the reference electrode was placed. This was a Hg/Hg₂SO₄, Na₂SO₄(sat.) electrode (in KCl: saturated calomel electrode). The imidazole was found to have a pK of 7.35 at an ionic strength of 1.0. Fig. 1 gives a typical differences titration curve, *i.e.* in this case the difference between the titration curves for 0.01 M imidazole + 5×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ and 0.01 M imidazole.

The ionic strength is kept constant at 1.0 by means of NaClO_4 (curve A) and KCl (curve B). From Fig. 1 it appears that the equilibrium



is shifted to the right by addition of cadmium ions. This indicates a complex formation between the unprotonated imidazole molecule and the cadmium ion.

In solutions with a concentration of Cd-ions of 5×10^{-4} M and with an ionic strength of 1.0 the precipitation of $\text{Cd}(\text{OH})_2$ takes place at pH = 9.7. This corresponds to a solubility product of $\text{Cd}(\text{OH})_2 = 1.5 \times 10^{-12}$ mol³/l³ which is in good agreement with data from literature.⁸

Polarographic measurements. The polarograms were obtained using a Radiometer model PO₄ Polarograph in connexion with a three-electrode system consisting of a dropping mercury electrode, a counter electrode, and a reference electrode. The electrodes together with a glass electrode and a thermistor were immersed into a water jacketed electrolysis cell in which the temperature was continuously registered and kept constant

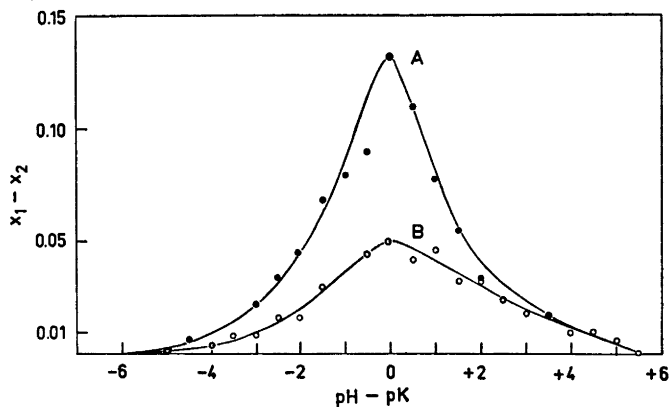


Fig. 1. Difference in the acid mol fraction of imidazole in the absence and presence of cadmium ions at ionic strength 1.0. Curve A, with sodium perchlorate. Curve B, with potassium chloride. pK relates to the value of pure imidazole in the respective ionic medium.

at $25^\circ\text{C} \pm 0.05$. Besides imidazole the solutions contained cadmium ions, 5×10^{-4} M, and a supporting electrolyte, 1 M. The concentration of imidazole was varied from 0.01 to 1.0 M. Purified oxygenfree nitrogen was used to exclude air from the polarographic cell. According to the results from the titration curves, pH was kept constant at 9.5 through the experiments by means of a pH-stat arrangement made up of the same components as utilized for the titrations. The drop time of the dropping mercury electrode was kept constant at $3.0 \text{ sec} \pm 0.1$ at an applied voltage of -600 mV vs. SCE (SCE = Saturated Calomel Electrode). At this potential the value of the capillary constant $m^{2/3}t^{1/6}$ was 2.64. The potentials of the dropping mercury *vs.* the reference electrode were measured continuously with a Radiometer model 26 pH-meter and recorded together with the polarograms on an external recorder. All the polarograms were started from an initial voltage of -100 mV vs. SCE .

The applied voltages *vs.* SCE were measured with an accuracy of about 0.1 mV and duplicate experiments showed that it was possible to estimate the halfwave potential with a reproducibility of the order of 0.5 mV. The reversibility of the electrode reactions was controlled by means of a Kalousek Commutator with a chopper frequency of 6.25 Hz. In all measurements the reversibility of the electrode was found to be well established.

In order to test the experimental set-up some investigations about complex formation with cadmium- and chloride-ions were carried out. The concentration of Cd-ions (as $\text{Cd}(\text{NO}_3)_2$) was 5×10^{-4} M and the concentration of Cl^- -ions (as NaCl) was varied from

Table 1. Complexity constants for the cadmium-chloride system.

Ref.	Method	Ionic strength	$\beta_1 = K_1$	β_2	K_2	β_3	K_3	β_4	K_4
King ¹⁴	Solubility $t = 25^\circ\text{C}$	Adjusted to 3.0 with sodium perchlorate	25	154	—	250	—	—	—
Eriksson ⁹	Polarography $t = 25^\circ\text{C}$	Adjusted to 3.0 with sodium perchlorate	35	115	—	290	—	—	—
This paper	Polarography $t = 25^\circ\text{C}$	Adjusted to 1.0 with sodium perchlorate	38	141	4.0	120	0.9	—	—

0.01 to 1.0 M. Sodium perchlorate was added to maintain constant ionic strength of 1.0. As a reference electrode was used a $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{Na}_2\text{SO}_4(\text{sat.})$ electrode. The various stability constants were evaluated by using the graphical method reported by De Ford and Hume.¹ Table 1 summarizes the results compared with data from literature.

Determination of the activity coefficient. The activity coefficients were calculated from freezing point and vapour pressure determinations. The freezing point measurements were carried out on a Fiske osmometer (Fiske Associates, Uxbridge, Mass.) in which the freezing points can be measured with an accuracy of 0.001°C. The vapour pressure measurements were carried out on a Knauer osmometer (H. Knauer & Co., Berlin, BDR), in which the temperature difference can be measured with an accuracy of 0.0001°C. The temperature was kept at 37°C with a stability of $\pm 0.001^\circ\text{C}$ per hour.

The instrument were calibrated by using solutions with known osmotic coefficients. The calculated activity coefficients were adjusted to 25°C by interpolation.

RESULTS AND DISCUSSION

When determining *the activity coefficients* it must be noted that the total concentration of cadmium is in the order of 5×10^{-4} M and since the experiments were carried out in aqueous solutions at constant ionic strength 1.0, it must be assumed that the activity coefficients of all the cadmium compounds – *i.e.* simple ions and complex ions – are determined by the ionic strength in the solution and in such a way that $\gamma_{\text{M}} = \gamma_{\text{MJ}}$ for all J in equn. (1). The concentration of imidazole was varied during the experiments from 0.01 M to 1.0 M. Thus the activity coefficient for imidazole would be expected to be neither constant nor close to unity. Actual determination of the electrolyte activity obtained by the use of ion-specific electrodes – *i.e.* a silver/silver chloride electrode and a sodium electrode – showed that the activity of the electrolyte remained constant when the concentration of imidazole was varied within the range used in the experiments. Further, vapour pressure measurements on imidazole dissolved partly in pure water and partly in 1.0 M NaClO_4 showed that the osmotic coefficients – and so consequently the activity coefficients – of imidazole were identical at corresponding concentrations of imidazole. These informations, along with the approximation $\gamma_{\text{M}} = \gamma_{\text{MJ}}$, denote that the system is – in principle – reduced to a two-component system as regards to variations in activity coefficients. On this system the Gibbs-Duhem relation may be applied:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0; n_1 = \text{water}, n_2 = \text{imidazole}$$

Regarding n_1 as constant the activity coefficient of imidazole in the mixtures can be determined, *e.g.* by freezing point and vapour pressure methods. The results are shown in Fig. 2, from which it appears that in the vapour pressure experiments at 37°C (curve A) the logarithm of the activity coefficients of imidazole varies linearly with the concentration of imidazole within the concentration range used in these experiments, while in the freezing point experiments (curve B) the linear dependence stops at a concentration of imidazole of approximately 0.15 M where the dependence becomes non-linear.

Concerning a molecule like imidazole it can be shown that when the logarithm of the activity coefficients turns out to be linearly dependent of the concentration the same must be the case with the osmotic coefficients, and furthermore the slope from the logarithm plot must be twice the slope from the

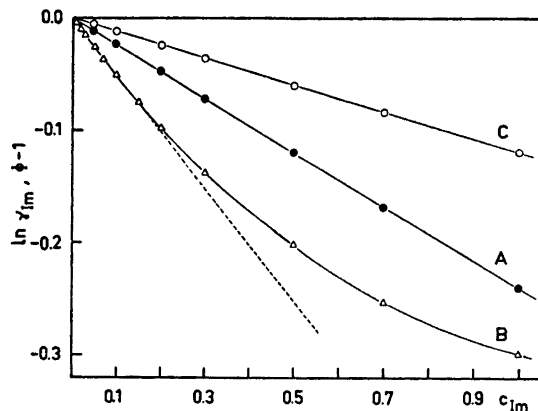


Fig. 2. Dependence of log of the activity coefficient of imidazole on the concentration of imidazole. Curve A, at 37°C. Curve B, at the freezing-points of the imidazole solutions. The dotted line indicates the limiting value of the slope at infinite dilution of imidazole. Curve C, dependence of the osmotic coefficient of imidazole on the concentration of imidazole at 37°C. Note: The slope of curve A is twice that of curve C.

osmotic coefficient plot. From Fig. 2, curves A and C, it appears that this theory is very well confirmed. Regarding the activity coefficients of imidazole at 25°C the experiments indicate a variation from 0.99 to 0.77 in the solutions used in

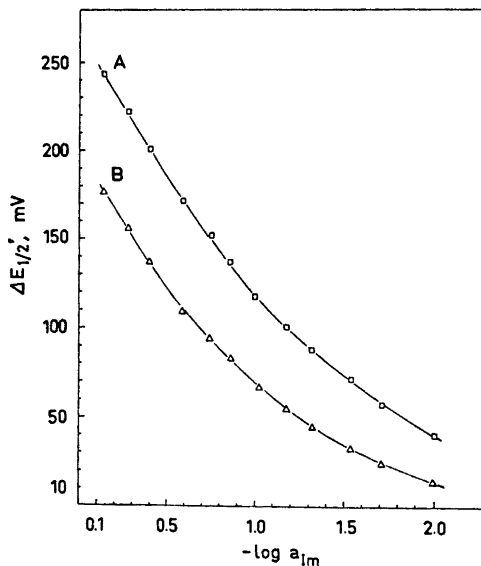


Fig. 3. Dependence of $\Delta E_{1/2}'$ on log of imidazole activity. Curve A, in 1.0 M NaClO_4 . Curve B, in 1.0 M KCl . The term $\Delta E_{1/2}'$ is defined as $\Delta E_{1/2} + \log I_M/I_C$ where $\Delta E_{1/2}$ is the observed half-wave potential and I_M and I_C are the diffusion currents of the free cadmium aquo ions and the complexed cadmium ions, respectively.

the present experiments. This emphasize the necessity of taking into account the magnitude of the activity coefficients.

The *polarographic data* are shown graphically in Fig. 3. The activity of imidazole is calculated from the concentration of the free uncomplexed imidazole molecule at the surface of the dropping mercury electrode. Actually, this is not known but can be found by an approximate technique as described by Irving.⁷ Fig. 3 shows the plot of $\Delta E_{\frac{1}{2}}'$ against $\log a_{\text{im}}$ from measurements in two different supporting electrolytes. It should be noted that the term $\Delta E_{\frac{1}{2}}'$ is the same as $RT/zF \log F_0$, where F_0 is the normal function as defined by De Ford and Hume.¹ The slope at any point of these curves will give the value of the average ligand number in the solution corresponding to the particular value of a_{im} and it seems to be likely that this maximum number is 6 in the range of imidazole concentrations used in these experiments. Due to complex formation between Cd-ions and Cl-ions the shift in half-wave potential will obviously be smaller in KCl solutions than in NaClO₄ solutions. In the latter case it is well established¹⁵ that the complex formation between supporting electrolyte and Cd-ions is of minor importance. Consequently Fig. 3 must consist of two curves. The agreement between the corresponding slope values in Fig. 3 is satisfactory when the imidazole is present in high concentrations. When present in low concentrations some deviation is observed because conditions with high concentration of KCl and low concentration of imidazole will favour complex formation between Cd-ions and Cl-ions. However, since the stability constants of cadmium-imidazole complexes are much greater than those related to cadmium-chloride complexes almost all the chloride-ions will be replaced by imidazole molecules when the activities of the two species are comparable.

This effect is more clearly shown in Fig. 4. Curve B — representing experiments from potassium chloride solutions — starts with lower values and finishes with higher values than curve A — representing experiments from sodium perchlorate solutions. Curve B raises continuously from zero to its upper limit

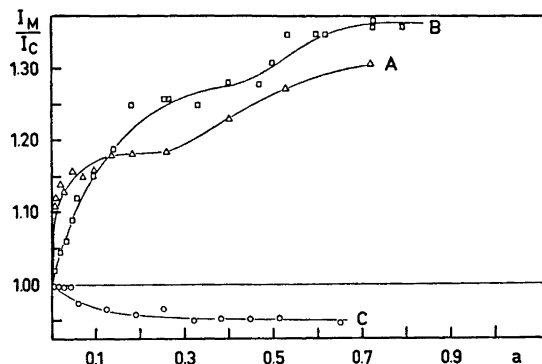
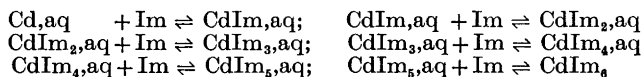


Fig. 4. Variation of the ratio I_M/I_C against the activity of the complex-forming agent. [Curve A: Cadmium-imidazole system in 1.0 M NaClO₄. Curve B: Cadmium-imidazole system in 1.0 M KCl. Curve C: Cadmium-chloride system where ionic strength was kept constant by adding sodium perchlorate.

caused by the complex-formation of Cd-ions and Cl-ions. On the other hand the sudden jump in curve A from zero to approximately 1.1 at lower concentrations of imidazole shows that the complex-formation with Cd-ions and water (ClO_4^- -ions) has no influence in the present experiments. Regarding curve C (showing the results from experiments with Cd-Cl complex-formation at ionic strength 1.0) together with curve A and B the additional conclusion can be drawn that the mobilities of cadmium-chloride complexes are greater than the mobilities of cadmium-water (perchlorate) complexes.

Fig. 3 shows that the function F_0 is a polynomial in ascending powers of a_{Im} , and the results make it possible that the highest number of stability constants to be determined is 6. It is therefore possible, in principle, to calculate the 6 stability constants from 6 values of the function F_0 corresponding to a range of a_{Im} values. Owing to inevitable experimental errors the resulting 6 simultaneous equations available for the determination of the desired constants will probably be inconsistent and so it is necessary to use more values of a_{Im} than 6.

In this paper a computing program based on the graphical method is used. The graphical method is described in detail elsewhere,¹⁻⁴ and will not be repeated here. Only the final results involving the derived complexity constants will be quoted. Application of the modified graphical procedure to the results showed that under the conditions employed the following equilibria exist (ionic charges omitted):



i.e. the maximum coordination number of the Cd-ions against imidazole is found to be 6. The values of the various stability constants belonging to the equilibria shown above are listed in Table 2, where conventionally the letter β is used for the over-all stability constants and the letter K for the consecutive stability constants. This table also contains the computed standard derivations of the various complexity constants. The results are compared with data from literature. The agreement between previous values for β_1 , β_2 , β_3 , and β_4 and those here reported appears quite acceptable. To our knowledge values for β_5 and β_6 are reported here for the first time.

In Fig. 5 the function

$$\alpha = \frac{\sum_{j=0}^n \text{CdIm}_j \gamma_{\text{CdIm}_j}}{a_{\text{Cd}^{2+}, \text{ tot}}}$$

is used to show the contributions of the individual complexes to the complete system. The distances between the curves give a direct measure of the percentage of the various complex compounds. The dotted lines indicate the various $\text{p}K$ -values. It is remarkable that the normal sequence of $\text{p}K$ -values in equilibria of this kind is broken here when coming to $\text{p}K_4$ - *i.e.* $\text{p}K_5$ is greater than $\text{p}K_6$. This indicates that the fifth complex compound is more unstable as compared with the fourth and the sixth ones probably caused by symmetrical

Table 2. Complexity constants for the cadmium-imidazole system.

Ref.	Method	1	2	Ligand No. 3	4	5	6
Tandford and Wagner ¹²	EMK-measurements with glass-electrode $\mu=0.15$ $t=25^\circ\text{C}$	β 630	—	—	—	—	—
		K	125	35	14	—	—
Li, White and Doody ¹³	Polarography $\mu=0.15$ with KNO_3 $t=25^\circ\text{C}$	β	1.2×10^5	—	—	—	—
		K	—	25	11	—	—
This paper	Polarography $\mu=1.0$ with NaClO_4 $t=25^\circ\text{C}$	β	500 ± 50	$(1.2 \pm 0.1) \times 10^5$	$(4.5 \pm 0.5) \times 10^6$	$(4.0 \pm 0.5) \times 10^7$	$(1.5 \pm 0.5) \times 10^8$ (9 ± 1) $\times 10^8$
		K	—	250 ± 50	40 ± 10	9 ± 2	4 ± 2 7 ± 3

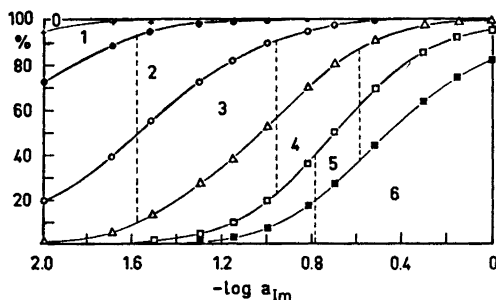


Fig. 5. Mol fraction of individual cadmium-imidazole complexes as a function of log of imidazole activity. The figures 0, 1, 2, 3, 4, 5, and 6 indicate the distribution of the different complex species: Cdaq^{2+} , CdIm, aq^{2+} , $\text{CdIm}_2, \text{aq}^{2+}$, $\text{CdIm}_3, \text{aq}^{2+}$, $\text{CdIm}_4, \text{aq}^{2+}$, $\text{CdIm}_5, \text{aq}^{2+}$, and $\text{CdIm}_6, \text{aq}^{2+}$, respectively. pK -values are shown as vertically dotted lines. Ionic strength = 1.0 with sodium perchlorate.

reasons. Also it must be noted that as long as the activity coefficients of imidazole is close to 1 very little is present of the fifth and sixth complex compounds — *i.e.* the imidazole must be present in high concentration in order to determine these complex compounds with accuracy. From Table 3 it appears that below an activity of imidazole of 0.1 M ($C_{\text{im}} = 0.104$) the fifth and sixth complex compounds are present in so small quantities that it is very likely they would not be recognized with the method used in this paper.

Table 3. Calculated distribution of the various complex compounds in the cadmium-imidazole system at specified activities of imidazole using the complexity constants evaluated by polarography. Total activity of Cd = 5×10^{-4} M; supporting electrolyte = 1.0 M NaClO_4 ; pH = 9.5.

$a_{\text{im, tot.}}$	1.0×10^{-2}	3.0×10^{-2}	5×10^{-2}	1.0×10^{-1}	3×10^{-1}	5×10^{-1}	10×10^{-1}
mol % Cd, free	5	0.4	0.1	—	—	—	—
CdIm	23.4	5.5	2.1	0.4	—	—	—
CdIm ₂	52.2	38.7	25.3	10.0	0.8	0.2	—
CdIm ₃	18.4	42.8	47.0	37.2	8.2	2.5	0.4
CdIm ₄	1.2	11.2	20.6	32.9	22.0	11.5	3.7
CdIm ₅	—	1.2	3.8	12.2	24.7	21.5	13.7
CdIm ₆	—	0.2	1.1	7.3	44.3	64.3	82.2

Titration curves. The results from titration curves are shown graphically in Fig. 1. If X_1 indicates the acid fraction in a pure imidazole solution and X_2 indicates the acid fraction in an imidazole solution containing Cd-ions obviously the magnitude of the difference $X_1 - X_2$ depends on the stability con-

stants of the complex-formation. The results shown in Fig. 1 are derived from solutions containing 0.01 M imidazole and 5×10^{-4} M Cd^{2+} . The ionic strength is kept constant at 1.0 by means of NaClO_4 (curve A) and KCl (curve B). Here again the effect from the complex-formation between Cd-ions and Cl-ions is clearly seen and is the reason why the maximum value in curve B is smaller (about 0.05) than that in curve A (about 0.13). The complexity constant of the cadmium-imidazole complex formation can be calculated from curve A using the theory described by Graae¹⁰ and Hendrickson,¹¹ but it must be noted that this constant is an average complexity constant corresponding to a certain distribution of complex species at this particular values of cadmium and imidazole. This average complexity constant is calculated to be approximately 5×10^{-3} . From Table 3 it is seen that the composition of the solution is such that about 5 % of the added Cd-ions are in the solution as free (hydrated) ions. About 23 % are in the form $\text{CdIm},\text{aq}^{2+}$, about 52 % are in the form $\text{CdIm}_2,\text{aq}^{2+}$, about 19 % are in the form $\text{CdIm}_3,\text{aq}^{2+}$ and about 1 % is in the form $\text{CdIm}_4,\text{aq}^{2+}$. By using these values obtained from polarographic data we get a mean stability constant of approximately 2×10^{-3} which is in good agreement with the value obtained from titration data.

At present, the question about the fifth and the sixth complex compounds is under investigation in this institute. The results from these experiments will be discussed elsewhere, but as an example it can be mentioned that under certain specified experimental conditions the fifth complex compound appears as a white precipitate with perchlorate as counter ion.

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