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Thermodynamics of the Complexation of Imidazole with Divalent Copper, Nickel, Cadmium, Zinc, and Cobalt Ions in Aqueous Sodium Perchlorate Solutions

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The gross stability constants (β_n) of imidazole complexes with divalent copper, nickel, cadmium, zinc, and cobalt ions were determined potentiometrically in aqueous sodium perchlorate solutions in ionic strengths of about 0.25, 0.50, 1.00, 2.00, and 4.00 at 25 °C. At the lowest ionic strength the temperatures 15 and 35 °C were also employed. The thermodynamic constants (β_n^0) were derived by extrapolation to zero ionic strength. From these the thermodynamic quantities, free energies, enthalpies, and entropies of the complex formation equilibria were calculated.

Particularly, the results for copper complexes refer to the formation of polynuclear complexes. The stability of the complexes was found to follow the order: copper > nickel > cadmium > zinc > cobalt.

In most cases the enthalpy effect was found to be the dominant factor determining the stability of the imidazole complexes studied.

In a recent paper [1] the thermodynamics of the protonation of imidazole in aqueous sodium perchlorate solutions was considered by us. These studies were extended to concern thermodynamics of the complex formation of imidazole with the divalent metal ions of the first transition metal series and cadmium in the present paper. The effect of temperature and of a neutral salt on the stabilities of the complexes was studied, and used as the basis for evaluating the thermodynamic constants.

EXPERIMENTAL

Reagents and solutions. The metal perchlorates were products of the G. F. Smith Chemical Co., and the other reagents used were guaranteed reagents of E. Merck AG. The water used was of conductivity quality.

For each ionic strength a carbonate-free sodium hydroxide solution was prepared in a nitrogen atmosphere in a gas-tight burette system of Pyrex glass. The ionic strengths of the solutions were adjusted with sodium perchlorate. The alkali concentrations of the solutions were checked potentiometrically against weighed amounts of potassium biphthalate.[1]

A dilute perchloric acid solution was prepared from conc. perchloric acid, and its acidity was determined potentiometrically with the known sodium hydroxide solution. The acid concentrations were 0.1120 and 0.4213 mol l^{-1} (20 °C). By potentiometric titration with perchloric acid the purity of imidazole was found to be 99.89 %. Its melting point was 89 – 90 °C.

The stock solution of sodium perchlorate was prepared by dissolving the salt in conductivity water, adjusting the pH of the solution to about 8, allowing to stand over night, filtering through a tight glass-sinter, making the filtrate weakly acid with perchloric acid, boiling the solution and adjusting the pH to about 5.5 with sodium hydroxide.[1] The concentration of sodium perchlorate was determined by the evaporation and ion exchange methods.[2,3] The later method was also used for the other metal perchlorate solutions to check their contents. The solutions were found to be 4.3354 and 6.353 M in sodium perchlorate (20 °C).

The metal perchlorate solutions were prepared by dissolving the commercial products in water and allowing the solutions to stand from one to two weeks before filtering and analysing for the metal perchlorate and perchloric acid contents. The copper and cadmium contents were determined electroanalytically; in the former case in a solution containing sulfuric and nitric acid and about one gram of urea, and in the latter case from a slightly alkaline solution containing potassium cyanide. The nickel concentration was determined gravimetrically with dimethylgly-

Tables 1–5. Potentiometric titrations of metal(II) imidazole solutions at different ionic strengths at 25 °C. Concentrations and volumes given at 20 °C.

Table 1. Copper(II) imidazole. 100 ml of 0.003951 M $Cu(ClO_4)_2$ and 0.01 M imidazole (20 °C).

$\underline{I}$	0.25	0.50	1.00	2.00	4.00
Titrant					
M NaOH	0.1001(8)	0.1004(6)	0.1000(3)	0.09962	0.09952
ml			pH		
3.00	5.096	5.170	5.245	5.414	5.641
3.50	5.236	5.309	5.387	5.556	5.786
3.75	5.305	5.380	5.456	5.628	5.856
4.00	5.371	5.447	5.522	5.696	5.925
4.25	5.439	5.515	5.591	5.762	5.989
4.50	5.507	5.581	5.659	5.828	6.055
4.75	5.572	5.647	5.725	5.892	6.118
5.00	5.637	5.713	5.791	5.960	6.182
5.25	5.704	5.779	5.857	6.027	6.248
5.50	5.770	5.843	5.924	6.092	6.310
5.75	5.838	5.911	5.992	6.156	6.371
6.00	5.905	5.977	6.056	6.223	6.436
6.25	5.975	6.046	6.126	-	6.501
6.50	-	-	6.196	-	6.564
7.00	-	-	6.338	-	6.694

Table 2. Nickel(II) imidazole. 100 ml of 0.003880 M $Ni(ClO_4)_2$ and 0.01 M imidazole (20 °C).

$\underline{I}$	0.25	0.50	1.00	2.00	4.00
Titrant					
M NaOH	0.1008	0.1004(6)	0.1001(9)	0.09962	0.09952
ml			pH		
3.00	6.081	6.163	6.279	6.506	6.864
3.50	6.201	6.284	6.401	6.631	6.991
3.75	6.257	6.338	6.457	6.690	7.050
4.00	6.313	6.398	6.511	6.736	7.113
4.25	6.369	6.452	6.565	6.803	7.170
4.50	6.423	6.502	6.621	6.856	7.224
4.75	6.477	6.553	6.675	6.911	7.280
5.00	6.529	6.607	6.729	6.967	7.336
5.25	6.578	6.663	6.780	7.020	7.393
5.50	6.631	6.715	6.832	7.069	7.447
5.75	6.683	6.766	6.883	7.124	7.503
6.00	6.736	6.820	6.937	7.177	7.559
6.25	6.788	6.876	6.991	7.228	7.615
6.50	6.844	-	7.043	7.290	7.670
7.00	6.952	-	7.157	7.403	7.785

Table 3. Cadmium(II) imidazole. 100 ml of 0.004664 M $Cd(ClO_4)_2$ and 0.01 M imidazole (20 °C).

$\underline{I}$	0.25	0.50	1.00	2.00	4.00
Titrant					
M NaOH	0.1001(8)	0.1004(6)	0.1000(3)	0.09962	0.09952
ml			pH		
3.00	6.245	6.319	6.441	6.666	7.048
3.50	6.354	6.434	6.555	6.783	7.170
3.75	6.409	6.490	6.611	6.847	7.226
4.00	6.460	6.540	6.661	6.898	7.283
4.25	6.512	6.589	6.714	6.954	7.342
4.50	6.563	6.642	6.764	7.006	7.393
4.75	6.612	6.693	6.817	7.060	7.451
5.00	6.663	6.743	6.864	7.111	7.501
5.25	6.714	6.792	6.916	7.163	7.555
5.50	6.763	6.846	6.965	7.212	7.610
5.75	6.813	6.899	7.016	7.263	7.662
6.00	6.864	6.949	7.067	7.315	7.716
6.25	6.916	6.998	7.119	7.368	7.768
6.50	6.967	7.054	7.170	7.424	7.823
7.00	7.075	7.161	7.282	7.537	7.941

Table 4. Zinc(II) imidazole. 100 ml of 0.003936 M $Zn(ClO_4)_2$ and 0.01 M imidazole (20 °C).

$\underline{I}$	0.25	0.50	1.00	2.00	4.00
Titrant					
M NaOH	0.1001(8)	0.1004(6)	0.1000(3)	0.09962	0.09952
ml			pH		
3.00	6.325	6.397	6.511	6.713	6.954
3.50	6.416	6.488	6.600	6.799	7.031
3.75	6.463	6.532	6.643	6.838	7.068
4.00	6.506	6.572	6.685	6.878	7.103
4.25	6.550	6.615	6.725	6.917	7.140
4.50	6.590	6.654	6.764	6.954	7.176
4.75	6.631	6.694	6.805	6.992	7.210
5.00	6.671	6.735	6.844	7.029	7.245
5.25	6.712	6.777	6.883	7.066	7.279
5.50	6.752	6.816	6.922	7.103	7.315
5.75	6.793	6.858	6.962	7.142	7.348
6.00	6.834	6.897	7.001	7.183	7.384
6.25	6.876	6.941	-	-	7.418

Table 5. Cobalt(II) imidazole. 100 ml of 0.004243 M $Co(ClO_4)_2$ and 0.01 M imidazole (20 °C).

$\underline{I}$	0.25	0.50	1.00	2.00	4.00
Titrant					
M NaOH	0.1008	0.1004(6)	0.1001(9)	0.09962	0.09952
ml			pH		
3.00	6.408	6.634	6.631	6.955	7.290
3.50	6.512	6.737	6.737	7.055	7.407
3.75	6.563	6.790	6.788	7.104	7.459
4.00	6.612	6.840	6.837	7.155	7.512
4.25	6.658	6.886	6.888	7.200	7.561
4.50	6.703	6.935	6.933	7.250	7.611
4.75	6.751	6.982	6.982	7.295	7.662
5.00	6.796	7.028	7.026	7.342	7.711
5.25	6.842	7.075	7.072	7.388	7.758
5.50	6.886	7.119	7.119	7.435	7.806
5.75	6.932	7.167	7.168	7.484	7.853
6.00	6.979	7.214	7.214	7.532	7.900
6.25	7.026	7.258	7.261	7.579	7.949
6.50	7.075	-	7.309	7.635	7.998
7.00	7.175	-	7.408	7.743	8.096

oxime. The EDTA-titration with Erio T as an indicator at a pH of about 10 was used for zinc analyses. The concentrations of the metal perchlorate solutions (at 20 °C) were the following:
0.3161 M $Cu(ClO_4)_2$, 0.9700 M $Ni(ClO_4)_2$, 0.2331 M $Cd(ClO_4)_2$, 0.3149 M $Zn(ClO_4)_2$ and 0.943 M $Co(ClO_4)_2$. The excess or lack of perchloric acid in the metal perchlorate solutions was determined by adding known amounts of perchloric acid to the samples and titrating potentiometrically with a known alkali solution.

Apparatus and methods. All measuring flasks were checked by weighing their water contents at 20 °C. A water thermostat with an accuracy ± 0.01 °C was used for potentiometric titrations at 15, 25, and 35 °C. These were performed with a potentiometer Radiometer PHM 4 using a Beckman No. 41263 glass electrode and an immersion type calomel electrode in a cell of the following type (20 °C):

Glass electrode	100 ml 0.01 M Imidazole 0.01 M $HClO_4$ 0.003 – 0.03 M $M(ClO_4)_2$ $(I - 0.01 - 3(0.003 - 0.03))$ M $NaClO_4$	0.01 M NaCl $(I - 0.01)$ M $NaClO_4$	Hg_2Cl_2,Hg

The effect of temperature on the concentrations was taken into account in the calculations.[1–3] The experimental results of the titrations are given in Tables 1 – 10.

RESULTS AND DISCUSSION

Assuming the complex formation between imidazole (HL) and divalent metal ions to happen stepwise and to be mononuclear, the overall complexation equilibria may be presented as follows:

$$M^{2+} + n\ HL \rightleftharpoons M(HL)_n{}^{2+} \tag{1}$$

The corresponding cumulative (gross) stability constants are then

$$\beta_n = [M(HL)_n{}^{2+}]/[M^{2+}][HL]^n \tag{2}$$

The electroneutrality principle gives in the experimental conditions used that

$$[H_2L^+] = C_{HL} - C_B - [H^+] \tag{3}$$

where H_2L^+ is the protonated form of imidazole[1] and C_B is the total concentration of the added sodium hydroxide in the studied solution. The protolysis constant of imidazole

$$K_1 = [H^+][HL]/[H_2L^+] \tag{4}$$

was determined in the previous paper.[1] The total concentrations of imidazole (C_{HL}) and of the metal ions (C_M) in the studied solutions are

$$C_{HL} = [HL] + [H_2L^+] + \sum n[M(HL)_n{}^{2+}] \tag{5}$$

$$C_M = [M^{2+}] + \sum[M(HL)_n{}^{2+}] \tag{6}$$

From the expressions (2), (5), and (6) we obtain

$$G/[HL](C_M - G) = \beta_1 + [(2C_M - G)[HL]/(C_M - G)]\beta_2 + [(3C_m - G][HL]^2/(C_M - G)]\beta_3 + \cdots\cdots \tag{7}$$

where $G = C_{HL} - [HL] - [H_2L^+]$ and $[H_2L^+]$ is calculated from eqn. (3) and [HL] from eqn. (4) on the basis of the measured values of pH of the solutions.

Eqn. (7) is of the form $y = b_0 + x_1b_1 + x_2b_2 + \cdots\cdot$ and its constants β_n were therefore calculated with a library regression program[4] on an IBM 1130 computer.

A general conception of the complexation tendency of imidazole with divalent metal ions was obtained from the titration curves of imidazole – metal ion mixtures which showed the complex formation of imidazole with copper(II) ions to be clearly stronger than that with the other metals studied. The nickel, cadmium, and cobalt solutions could be titrated with the base so long as 70 % of the protonated imidazole was neutralized. In the case of copper and zinc solutions, only 62.5 % of the protonated imidazole could be neutralized before turbidity occurred. The precipitate formation order followed the precipitation order of the corresponding metal hydroxides.

The values of the gross stability constants β_n were calculated from eqn. (7) on the basis of the data in Tables 1 – 10 as described above, and their logarithms are presented in Tables 11 – 18.

As eqn. (1) shows, imidazole is coordinated to the central metal ion without any change of its charge. Therefore the dependence of the values of log β_n on the ionic strength might be represented by the equation:

$$\log \beta_n = \log \beta_n{}^0 + BI \tag{8}$$

where $\beta_n{}^0$ is the thermodynamic value in zero ionic strength and B a constant. The values of

Tables 6–10. Potentiometric titrations of metal(II) imidazole solutions at 15, 25, and 35 °C. Volumes and concentrations at 20 °C. Ionic strength 0.25.

Table 6. 100 ml of (3.951 – 31.61) × 10^{-3} M $Cu(ClO_4)_2$ and 0.01 M imidazole. Titrant 0.1001(8) M NaOH.

M $Cu(ClO_4)_2$	0.003951	0.009483	0.03161	0.009483	0.03161	0.003951	0.009483	0.03161
Temp.		15°		25°			35°	
Titrant ml		pH		pH			pH	
3.00	5.139	4.622	4.021	4.590	3.985	5.037	4.528	3.933
3.50	5.286	4.735	4.124	4.705	4.087	5.178	4.639	4.036
3.75	5.356	4.793	4.175	4.765	4.137	5.245	4.696	4.082
4.00	5.407	4.847	4.220	4.817	4.181	5.310	4.747	4.129
4.25	5.495	4.902	4.268	4.871	4.229	5.376	4.799	4.177
4.50	5.563	4.954	4.313	4.923	4.274	5.440	4.850	4.221
4.75	5.631	5.007	4.362	4.978	4.322	5.505	4.902	4.264
5.00	5.699	5.059	4.404	5.028	4.366	5.570	4.953	4.308
5.25	5.767	5.111	4.451	5.081	4.411	5.634	5.005	4.353
5.50	5.836	5.166	4.498	5.135	4.457	5.698	5.056	4.396
5.75	5.904	5.220	4.546	5.187	4.504	5.763	5.107	4.442
6.00	5.972	5.272	4.591	5.240	4.550	5.827	5.157	4.488
6.25	6.042	5.327	4.640	5.294	4.597	5.893	5.210	4.532

Table 7. 100 ml of (3.88 – 29.73) × 10^{-3} M $Ni(ClO_4)_2$ and 0.01 M imidazole. Titrant 0.1001(8) M or 0.1008 M NaOH.

M $Ni(ClO_4)_2$	0.003680	0.00970	0.02973	0.00970	0.003680	0.00970	M $Ni(ClO_4)_2$	0.02973	0.02973 •	0.02973
Temp.		15°		25°	35°		Temp.	15°	25°	35°
Titrant		0.1001(8)	0.1008	0.1001(8)	0.1001(8)	0.1008	Titrant	0.1008	0.1008	0.1008
ml		pH		pH	pH		ml	pH	pH	pH
3.00	6.199	5.773	5.309	5.669	5.902	5.598	2.87	5.246	5.152	5.078
3.50	6.324	5.893	5.407	5.779	6.016	5.711	3.37	5.341	5.253	5.181
3.75	6.383	5.942	5.454	5.835	6.072	5.765	3.87	5.454	5.353	5.282
4.00	6.441	5.993	5.503	5.889	6.126	5.817	4.12	5.502	5.407	5.328
4.25	6.497	6.046	5.549	5.939	6.180	5.866	4.37	5.545	5.451	5.377
4.50	6.553	6.096	5.596	5.990	6.229	5.917	4.62	5.594	5.500	5.423
4.75	6.605	6.150	5.641	6.041	6.279	5.968	4.87	5.640	5.546	5.471
5.00	6.659	6.201	5.689	6.088	6.328	6.014	5.12	5.683	5.593	5.513
5.25	6.712	6.250	5.734	6.139	6.379	6.063	5.37	5.729	5.638	5.559
5.50	6.766	6.301	5.781	6.188	6.428	6.112	5.62	5.773	5.686	5.606
5.75	6.820	6.350	5.829	6.240	6.479	6.161	5.87	5.811	5.730	5.654
6.00	6.876	6.402	5.878	6.289	6.526	6.210	6.12	5.857	5.777	5.701
6.25	6.934	6.453	5.932	6.340	6.592	6.261	6.37	5.911	5.828	5.749
6.50	-	6.506	-	6.391	6.628	6.313	6.62	5.960	5.882	5.796
7.00	-	6.614	-	6.499	6.734	6.419	6.87	6.011	5.934	5.845
							7.37	6.112	6.041	5.955

Table 8. 100 ml of (4.664 – 34.98) × 10^{-3} M $Cd(ClO_4)_2$ and 0.01 M imidazole. Titrant 0.1001(8) M NaOH.

M $Cd(ClO_4)_2$	0.004664	0.01166	0.03498	0.01166	0.03498	0.004664	0.01166	0.03498
Temp.		15°		25°			35°	
Titrant ml		pH		pH			pH	
3.00	6.385	5.983	5.509	5.889	5.407	6.130	5.806	5.335
3.50	6.499	6.096	5.616	6.000	5.510	6.244	5.915	5.440
3.75	6.555	6.147	5.663	6.049	5.561	6.297	5.969	5.487
4.00	6.612	6.198	5.711	6.100	5.608	6.346	6.017	5.533
4.25	6.665	6.250	5.760	6.151	5.658	6.395	6.066	5.579
4.50	6.715	6.299	5.805	6.200	5.703	6.444	6.117	5.626
4.75	6.763	6.348	5.854	6.249	5.748	6.493	6.164	5.672
5.00	6.812	6.399	5.901	6.299	5.796	6.540	6.212	5.716
5.25	6.862	6.448	5.947	6.348	5.841	6.588	6.261	5.760
5.50	6.915	6.497	5.994	6.396	5.887	6.635	6.308	5.808
5.75	6.967	6.546	6.041	6.445	5.934	6.683	6.355	5.855
6.00	7.018	6.595	6.090	6.494	5.982	6.733	6.406	5.902
6.25	7.069	6.647	6.137	6.546	6.031	6.786	6.457	5.953
6.50	7.123	6.698	6.186	6.599	6.078	6.838	6.508	6.004
7.00	7.235	6.805	6.295	6.709	6.186	6.946	6.620	6.105

Table 9. 100 ml of (3.936 – 31.49) × 10^{-3} M $Zn(ClO_4)_2$ and 0.01 M imidazole. Titrant 0.1001(8) M NaOH.

M $Zn(ClO_4)_2$	0.003936	0.009447	0.03149	0.009447	0.03149	0.003936	0.009447	0.03149
Temp.		15°		25°			35°	
Titrant ml		pH		pH			pH	
3.00	6.479	6.217	5.748	6.075	5.622	6.164	5.934	5.494
3.50	6.570	6.315	5.848	6.171	5.725	6.256	6.032	5.596
3.75	6.616	6.360	5.897	6.218	5.769	6.301	6.078	5.642
4.00	6.659	6.404	5.942	6.261	5.816	6.344	6.121	5.687
4.25	6.703	6.450	5.990	6.305	5.862	6.387	6.167	5.733
4.50	6.743	6.492	6.032	6.348	5.907	6.426	6.206	5.776
4.75	6.784	6.535	6.075	6.391	5.953	6.467	6.248	5.821
5.00	6.824	6.575	6.121	6.431	5.997	6.508	6.289	5.864
5.25	6.866	6.617	6.164	6.474	6.037	6.548	6.330	5.905
5.50	6.904	6.659	6.208	6.512	6.078	6.589	6.373	5.949
5.75	6.946	6.701	6.254	6.553	6.124	6.630	6.414	5.990
6.00	6.990	6.743	6.299	6.595	6.168	6.671	6.454	6.032
6.25	7.032	6.787	6.343	6.638	6.213	6.712	6.495	6.078

Table 10. 100 ml of (4.24 – 31.21) × 10^{-3} M $Co(ClO_4)_2$ and 0.01 M imidazole. Titrant 0.1008 M NaOH.

M $Co(ClO_4)_2$	0.00424	0.00943	0.03121	0.00943	0.03121	0.00424	0.00943	0.03121
Temp.		15°		25°			35°	
Titrant ml		pH		pH			pH	
3.00	6.566	6.296	5.818	6.162	5.709	6.243	6.035	5.598
3.50	6.671	6.402	5.916	6.268	5.811	6.346	6.138	5.701
3.75	6.723	6.455	5.969	6.319	5.862	6.396	6.189	5.749
4.00	6.772	6.504	6.014	6.368	5.907	6.441	6.236	5.796
4.25	6.820	6.549	6.060	6.415	5.955	6.486	6.282	5.844
4.50	6.867	6.596	6.107	6.463	6.000	6.534	6.326	5.889
4.75	6.914	6.644	6.154	6.508	6.048	6.580	6.372	5.935
5.00	6.959	6.694	6.199	6.554	6.092	6.622	6.418	5.979
5.25	7.007	6.742	6.245	6.589	6.139	6.668	6.462	6.025
5.50	7.054	6.784	6.294	6.647	6.181	6.710	6.506	6.069
5.75	7.103	6.833	6.338	6.693	6.228	6.755	6.552	6.113
6.00	7.150	6.880	6.387	6.738	6.274	6.799	6.598	6.159
6.25	7.199	6.927	6.432	6.785	6.321	6.846	6.643	6.205
6.50	7.246	6.978	6.479	6.835	6.369	6.894	6.691	6.251
7.00	7.351	7.078	6.579	6.936	6.470	6.988	6.789	6.351

log β_n at 25 °C in Tables 11 – 15 for the lowest metal ion concentrations were fitted by the method of least squares to eqn. (8). The values of log β_n^0 and B of the different complexes are given in Table 19. The values of log β_n calculated from eqn. (8) are also given in Tables 11 – 15. The values of the constant B obtained at 25 °C were also used to calculate the values of log β_n^0 from eqn. (8) at the ionic strength 0.25 at 15 and 35 °C on the basis of the data for the lowest metal ion concentrations in Tables 16 – 18. The errors due to this approximation in the values of log β_n^0 are negligible. The results of these calculations are also given in Table 19.

The values of log β_1 calculated from eqn. (7) are represented as functions of the ionic strength in Fig. 1. The log β_1 values satisfy eqn. (8) well,

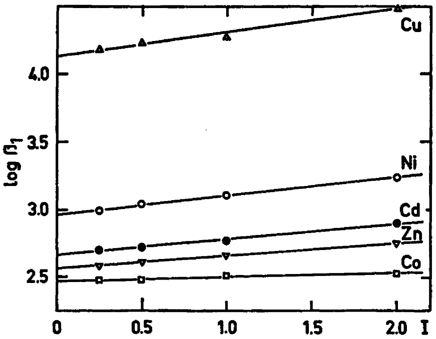

Fig. 1. The values of log β_1 of the first copper(II), nickel(II), cadmium(II), zinc(II), and cobalt(II) imidazole complexes calculated from eqns. (7) and (8) as functions of the ionic strength at 25 °C.

Tables 11–15. The gross stability constants of metal(II) imidazole complexes calculated from eqns. (7) and (8) at 25°C.

Table 11. Copper(II) imidazole complex. $C_{Cu(ClO_4)_2} = 0.003946$ M, $C_{HL} = 0.009988$ M (25 °C).

	log β_1		log β_2		log β_3		log β_4	
I	(7)	(8)	(7)	(8)	(7)	(8)	(7)	(8)
0	–	4.127	–	7.747	–	10.408	–	13.947
0.2497	4.176	4.170	7.827	7.793	10.558	10.562	14.039	13.983
0.4994	4.228	4.213	7.778	7.838	10.721	10.716	13.936	14.019
0.9988	4.267	4.299	7.958	7.929	–	–	14.119	14.091
1.9977	4.483	4.471	8.106	8.110	11.639	11.640	–	–

Table 12. Nickel(II) imidazole complex. $C_{Ni(ClO_4)_2} = 0.003876$ M, $C_{HL} = 0.009988$ M (25 °C).

	log β_1		log β_2		log β_3	log β_4	log β_5
I	(7)	(8)	(7)	(8)	(7)	(7)	(7)
0	–	2.962	–	5.515	–	–	–
0.2497	2.993	2.997	5.565	5.529	–	–	12.265
0.4994	3.034	3.032	5.517	5.543	–	–	12.328
0.9988	3.105	3.101	5.548	5.571	7.709	10.042	–
1.9977	3.238	3.240	5.641	5.627	8.054	10.482	–
3.9954	3.454	–	–	–	–	–	–

Table 13. Cadmium(II) imidazole complex. $C_{Cd(ClO_4)_2} = 0.004659$ M, $C_{HL} = 0.009988$ M (25 °C).

	log β_1		log β_2		log β_3	log β_4
I	(7)	(8)	(7)	(8)	(7)	(7)
0	–	2.665	–	4.647	–	–
0.2497	2.699	2.693	4.735	4.693	–	–
0.4994	2.718	2.721	4.740	4.739	–	–
0.9988	2.768	2.777	4.757	4.831	–	8.415
1.9977	2.892	2.888	5.047	5.015	6.996	–
3.9964	3.090	–	–	–	–	–

Table 14. Zinc(II) imidazole complex. $C_{Zn(ClO_4)_2} = 0.003931$ M, $C_{HL} = 0.009988$ M (25 °C).

	log β_1		log β_2	log β_3	log β_4	
I	(7)	(8)	(7)	(7)	(7)	(8)
0	–	2.570	–	–	–	9.785
0.2497	2.588	2.592	4.424	–	9.970	9.924
0.4994	2.618	2.614	–	7.596	10.041	10.062
0.9988	2.663	2.659	4.451	–	10.292	10.340
1.9977	2.745	2.747	–	8.253	10.919	10.895
3.9954	3.441	–	–	–	–	–

Table 15. Cobalt(II) imidazole complex. $C_{Co(ClO_4)_2} = 0.004238$ M, $C_{HL} = 0.009988$ M (25 °C).

	log β_1		log β_3		log β_4
I	(7)	(8)	(7)	(8)	(7)
0	–	2.473	–	6.484	–
0.2497	2.476	2.480	6.657	6.569	–
0.4994	2.484	2.487	6.523	6.655	–
0.9988	2.511	2.501	6.870	6.826	–
1.9977	2.525	2.529	–	–	8.688

Tables 16–18. The gross stability constants of copper(II), nickel(II), cadmium(II), zinc(II), and cobalt(II) imidazole complexes calculated from eqn. (7) at various temperatures.

Table 16. Temp. 15 °C. $I = 0.2502$. $C_{\mathrm{HL}} = 0.0100$ M.

$C_{\mathrm{M}} \times 10^3$	$M(ClO_4)_2$	log β_1	log β_2	log β_3	log β_4
3.955	$Cu(ClO_4)_2$	4.395	8.180	11.770	14.400
9.492		4.416	8.182	–	–
31.64		4.467	–	–	–
3.883	$Ni(ClO_4)_2$	3.181	5.781	7.815	–
9.709		3.228	5.593	8.612	–
29.76		3.213	5.932	9.456	13.359
4.668	$Cd(ClO_4)_2$	2.845	5.024	–	–
11.67		2.897	4.868	–	–
35.01		2.874	–	8.362	–
3.931	$Zn(ClO_4)_2$	2.655	4.647	7.846	–
9.456		2.677	–	7.951	–
31.52		2.658	5.119	8.189	–
4.247	$Co(ClO_4)_2$	2.618	4.188	6.868	–
9.438		2.616	–	7.259	–
31.24		2.606	–	7.703	

Table 17. Temp. 25 °C. $I = 0.2497$. $C_{\mathrm{HL}} = 0.009988$ M.

$C_{\mathrm{M}} \times 10^3$	$M(ClO_4)_2$	log β_1	log β_2	log β_3	log β_4	log β_5
3.946	$Cu(ClO_4)_2$	4.176	7.827	10.558	14.039	–
9.472		4.230	7.762	10.558	–	–
31.57		4.281	–	–	–	–
3.876	$Ni(ClO_4)_2$	2.993	5.565	–	–	12.265
9.689		3.068	5.639	8.467	11.245	–
29.70		3.064	–	–	–	–
4.659	$Cd(ClO_4)_2$	2.699	4.735	–	–	–
11.65		2.690	4.802	–	–	–
34.94		2.725	4.800	–	–	–
3.931	$Zn(ClO_4)_2$	2.588	4.424	–	9.970	–
9.436		2.582	4.396	7.623	–	–
31.45		2.560	–	7.918	–	–
4.238	$Co(ClO_4)_2$	2.476	–	6.657	–	11.612
9.419		2.477	–	6.855	–	–
31.17		2.484	–	7.404	–	–

Table 18. Temp. 35 °C. $I = 0.2492$. $C_{\mathrm{HL}} = 0.009969$ M.

$C_{\mathrm{M}} \times 10^3$	$M(ClO_4)_2$	log β_1	log β_2	log β_3	log β_4
3.939	$Cu(ClO_4)_2$	4.055	7.432	10.295	13.368
9.454		4.063	7.461	11.077	–
31.51		4.136	–	–	–
3.868	$Ni(ClO_4)_2$	2.843	5.362	7.338	–
9.670		2.926	4.927	7.832	10.805
29.64		2.921	5.232	8.596	–
4.650	$Cd(ClO_4)_2$	2.531	4.335	6.088	–
11.62		2.559	4.372	6.098	–
34.87		2.591	4.717	–	–
3.924	$Zn(ClO_4)_2$	2.506	4.329	–	9.792
9.418		2.475	4.113	7.379	9.944
31.39		2.468	–	7.767	–
4.230	$Co(ClO_4)_2$	2.376	–	–	8.806
9.401		2.361	–	6.702	–
31.11		2.376	–	–	9.930

Table 19. The values of the constants log $\beta_n{}^0$ and B of eqn. (8) for copper(II), nickel(II), cadmium(II), zinc(II), and cobalt(II) imidazole complexes at 15, 25, and 35 °C.

	Copper(II) complexes							
°C	log $\beta_1{}^0$	B	log $\beta_2{}^0$	B	log $\beta_3{}^0$	B	log $\beta_4{}^0$	B
15	4.352	0.1723	8.135	0.1817	11.615	0.6164	14.364	0.1438
25	4.127	0.1723	7.747	0.1817	10.408	0.6164	13.947	0.1438
35	4.012	0.1723	7.387	0.1817	10.141	0.6164	13.332	0.1438
	Nickel(II) complexes				Cadmium(II) complexes			
	log $\beta_1{}^0$	B	log $\beta_2{}^0$	B	log $\beta_1{}^0$	B	log $\beta_2{}^0$	B
15	3.146	0.1390	5.767	0.0559	2.817	0.1118	4.978	0.1842
25	2.962	0.1390	5.515	0.0559	2.665	0.1118	4.647	0.1842
35	2.808	0.1390	5.348	0.0559	2.503	0.1118	4.289	0.1842
	Zinc(II) complex				Cobalt(II) complex			
	log $\beta_1{}^0$	B			log $\beta_1{}^0$	B		
15	2.633	0.0887			2.611	0.0279		
25	2.570	0.0887			2.473	0.0279		
35	2.484	0.0887			2.369	0.0279		

the log β_2 values less well and for the higher complexes the lines could only be said to be direction giving. In Fig. 1 the dependence of the stability of the first complexes on the ionic strength is seen to be the higher the stronger the complex.

At the lowest ionic strength ($I = 0.25$) the measurements were made using three different concentrations of the central metal ions, and at the temperatures 15, 25, and 35 °C. At the lowest, the central metal ion concentrations were about 0.003 – 0.004 M, while in the second cases the metal ion and imidazole concentrations were almost equal, *i.e.* about 0.01 M; and the highest metal ion concentrations used were about three times higher than the ligand concentrations. The results of the calculations on the bases of these measurements are given in Tables 16 – 18.

From Tables 16 – 18 it can be seen that the increasing of the central metal ion concentration causes a change in the complexation equilibria such that the first complex becomes dominant and its stability constant increases. This effect is observed especially in respect of copper(II) complexes and, more weakly, for nickel(II) and cadmium(II) complexes. On the stability of the weaker zinc(II) and cobalt(II) complexes the central ion concentration seems to have a smaller effect.

As an addition to the log $\beta_n{}^0$ values in Table 19 we obtain from graphs like those in Fig. 1 by extrapolation to zero ionic strength at 25 °C, for nickel(II) complexes: log $\beta_3{}^0 = 7.37$, log $\beta_4{}^0 = 9.63$, log $\beta_5{}^0 = 12.20$; and for zinc(II) complexes: log $\beta_2{}^0 = 4.42$, log $\beta_3{}^0 = 7.38$.

In Table 20 we have collected the gross stability constant values of metal(II) imidazole complexes, all, with one exception,[8] found or calculated from the stepwise stability constants given in the literature of the last years.[5–7,9–16,21] The previously determined values of different constants are found in the stability constant tables compiled by Sillén and Martell.[18,19] Generally, the present log β_n values are of the same order of magnitude as the earlier ones [18,19] and those given in Table 20. However, it should be remembered that only results in the same neutral salt solutions and ionic strengths and at the temperatures are fully comparable.

The values of log β_n in Tables 16 – 18 give some idea of the reproducibility of the results obtained in the present study and their dependence on the experimental conditions. It should be noted that an error of about ±0.01 unit in pH in working with a glass electrode is easily made, which means at least a similar error in the log β_1 values; the error increases rapidly with n. On the other hand the data of Sjöberg [5–7] in Table 20 give an idea of the effect of different

Table 20. Values of the gross stability constants of metal(II) imidazole complexes collected for comparison from the literature of last years.

Metal ion	Method	Temp. °C	I (added salt)	log β_1	log β_2	log β_3	log β_4	log β_5	log β_6	Ref.
Cu^{2+}	gl. electrode	25	3.0 ($NaClO_4$)	4.66	8.64	11.94	14.60	—	17.46	5,6
		25	3.0 (NaCl)	4.46	8.13	11.21	13.48	—	15.95	5
		25	3.0 ($NaClO_4$)	4.66	8.65	11.95	14.61	15.61	17.31	7
		25	3.0 (NaCl)	4.40	8.06	11.06	13.38	14.30	15.36	7
		25	0.16 (KNO_3)	4.31	7.84	10.76	12.90	—	—	8
		25	5.0 (NaCl)	4.51	8.32	11.37	14.04	—	—	17
Ni^{2+}	gl. electrode	25	0.16 (KNO_3)	3.09	5.56	7.56	9.10	10.2	10.7	8
	pot.	25	0.5 (NH_4NO_3)	2.81 – 2.96	5.17 – 5.26	6.95 – 7.09	7.77 – 8.02	8.76	9.26	9
Cd^{2+}	pot.	25	0.5 (KNO_3)	2.67 – 2.72	4.83 – 4.87	6.01 – 6.22	7.0 – 7.14	—	—	10
	?	25	0.1	3.03	5.14	6.48	7.27	—	—	11
	pot.	25	0.5 (NH_4NO_3)	2.64 – 2.686	4.73	5.88 – 6.00	7.08 – 7.13	—	—	12
	pot.	25	0.1 (KNO_3)	2.71	4.71	6.06	—	—	—	13
	polarog.	25	1.0 ($NaClO_4$)	2.70	5.08	6.65	7.60	8.18	8.95	14
	»	25	?	2.79	4.45	5.96	7.03	—	—	15
Zn^{2+}	pot.	25	0.5 (NH_4NO_3)	2.29 – 2.46	4.65 – 4.72	6.87 – 7.15	9.08 – 9.11	—	—	9
Co^{2+}	pot.	25	0.5 (NH_4NO_3)	2.19 – 2.25	4.10 – 4.17	5.40 – 5.53	6.50 – 7.03	—	—	9
	gl. electrode	25	0.16 (KNO_3)	2.47	4.40	5.85	6.85	7.35	—	8
	pot.	25	0.5 (NH_4NO_3)	2.23	4.09	5.00	6.01	6.70	7.27	16

neutral salts on the values of the stability constants, showing the effect also to increase with *n*. Further, the results of Berthon *et al.*[9,10,12,13] in Table 20 show the effect of different calculation procedures (generally in use, *loc. cit.*) on the values of the stability constants; the differences increase here with *n* also. The results are interesting and show how on the whole it is difficult to obtain values of the stability constants of the higher complexes assumed to be formed stepwise in a complex series, which are compatible with each other. It is clear that the increase of the ligand (imidazole) to metal ion concentration ratio favors the formation of the higher complexes and the determination of their stability constants (*cf.* Refs. 5 – 7). On the other hand it should be taken into account that the possibility of the effect of the complex formation between the metal ions and inorganic ligands is generally increased when changing from perchlorates to other neutral salts.

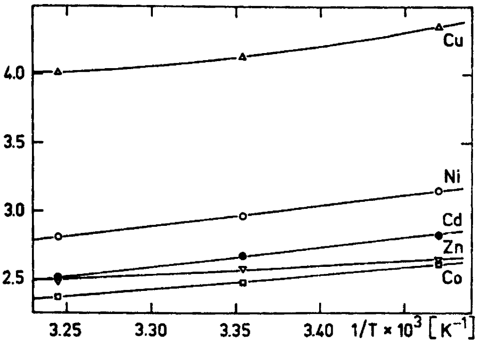

Fig. 2. The values of log β_1^0 of the first copper(II), nickel(II), cadmium(II), zinc(II), and cobalt(II) imidazole complexes represented as functions of the reciprocals of the absolute temperature.

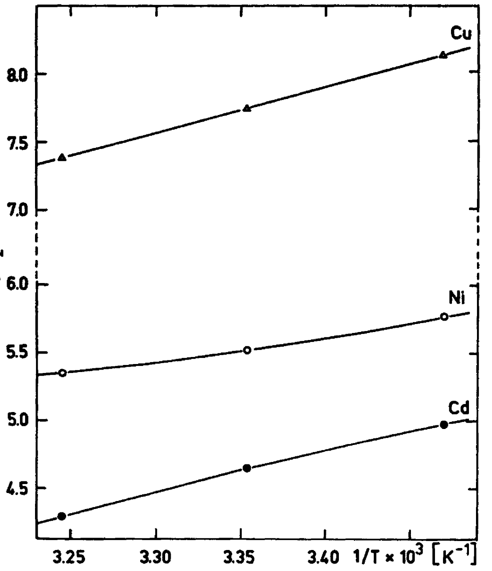

Fig. 3. The values of log β_2^0 of the second copper(II), nickel(II), and cadmium(II) imidazole complexes represented as functions of 1/*T* (K^{-1}).

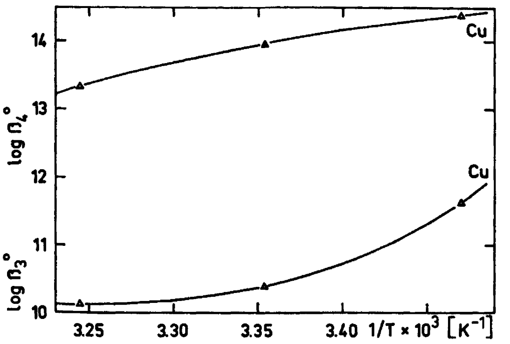

Fig. 4. The values of log β_3^0 and log β_4^0 of the third and fourth copper(II) imidazole complexes represented as functions of 1/*T* (K^{-1}).

In the works referred in Table 20 and in Refs. 18 and 19, as also in the present study, it was assumed when calculating the stability constants of the imidazole metal complexes that the complex formation was mononuclear and proceeded stepwise. However, Bridson and Walker[20] were the first to point out that on the basis of their spectrophotometric measurements at least, copper(II) ions would form with imidazole hydroxyl-bridged binuclear complexes in 10^{-3} M aqueous copper(II) perchlorate solutions when the imidazole metal ion mol-ratio was only 4. Sjöberg[5,7] also pointed to the same possibility in Ref. 17 recently. Jensen[21] on his side gave evidence for polynuclear complex formation of imidazole with cadmium(II) ions. Also our studies on the effect of the variation of the imidazole to metal ion concentration ratio pointed, at sufficiently high pH values, to possible polynuclear complex formation, specially in respect of copper(II) ions with imidazole.

Table 21. The values of the constants a, b, and c of eqn. (9) calculated by the method of least squares for copper(II), nickel(II), cadmium(II), zinc(II), and cobalt(II) complexes.

$\log \beta_n^0$	Metal	$C_M \times 10^3$ (25 °C)	$a \times 10^{-3}$	$b \times 10^{-1}$	$c \times 10^2$
$\log \beta_1^0$	Cu	3.946	−14.599	−8.8786	−14.740
	Ni	3.876	−3.9788	−1.8703	−2.7906
	Cd	4.659	1.3230	1.6226	3.0599
	Zn	3.931	3.0481	2.5249	4.1775
	Co	4.238	−4.5107	−2.4193	−3.8696
$\log \beta_2^0$	Cu	3.946	−3.7094	−0.59981	−0.43733
	Ni	3.876	−11.279	−6.3942	−10.607
	Cd	4.659	3.5792	3.8941	7.4756
$\log \beta_3^0$	Cu	3.946	−124.73	−80.476	−133.09
$\log \beta_4^0$	Cu	3.946	26.286	20.575	34.762

Table 22. The thermodynamic quantities calculated from eqns. (10) – (12) for the different metal-(II) ion imidazole complex equilibria at 15, 25, and 35 °C. The values of $\log \beta_n^0$ are included.

°C	Metal	$\log \beta_n^0$	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta S^0$ (JK^{-1} mol^{-1})
		$\log \beta_1^0$			
15	Cu	4.352	24.01	45.2	73
25		4.127	23.56	28.6	17
35		4.012	23.68	11.5	−39
15	Ni	3.146	17.36	31.8	50
25		2.962	16.91	28.7	39
35		2.808	16.57	25.4	28
15	Cd	2.817	15.54	23.3	27
25		2.665	15.22	26.8	38
35		2.503	14.77	30.3	50
15	Zn	2.633	14.53	8.1	−22
25		2.570	14.67	12.8	−6
35		2.484	14.66	17.6	9
15	Co	2.611	14.41	24.8	36
25		2.473	14.12	20.5	21
35		2.369	13.98	16.0	6
		$\log \beta_2^0$			
15	Cu	8.135	44.89	64	66
25		7.747	44.23	63	64
35		7.387	43.59	63	63
15	Ni	5.767	31.82	47	53
25		5.515	31.49	35	13
35		5.348	31.56	23	−27
15	Cd	4.978	27.47	50	79
25		4.647	26.53	58	108
35		4.289	25.31	67	137
		$\log \beta_3^0$			
15	Cu	11.615	64.07	272	722
25		10.408	59.41	123	212
35		10.141	59.83	−31	−297
		$\log \beta_4^0$			
15	Cu	14.364	79.25	49	−104
25		13.947	79.62	88	29
35		13.332	78.66	129	163

Table 23. Thermodynamic quantities of the metal(II) ion imidazole complex equilibria found in literature.

°C	Metal ion	I (added salt)	β_n	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (JK^{-1} mol^{-1})	Ref.
10 – 50	Cu^{2+}	0.16 (KNO_3)	β_1	126 ± 5	73.6	8
25		0.025	β_1	32	–	23
25		0.16 (KNO_3)	β_4	96.0	84	23
10 – 50	Ni^{2+}	0.16 (KNO_3)	β_1	91.2 ± 5.4	50.6	8
25		0.022	β_1	24	–	23
25		0.16 (KNO_3)	β_6	77.0	42	23
25 – 35	Cd^{2+}		β_4	56.1	44.8	15
25	Zn^{2+}	0.025	β_1	16	–	23
25		0.16 (KNO_3)	β_4	67.8	50	23
10 – 50	Co^{2+}	0.16 (KNO_3)	β_1	73.6 ± 5.4	45.6	8

The values of log β_n^0 of the different metal(II) ion imidazole complexes obtained are presented as functions of the reciprocals of the absolute temperature in Figs. 2 – 4. For the first complexes the curves are almost linear, but the curvature increases further the higher the complex. Therefore the equation[22]

$$\log \beta_n^0 = -a/T - cT + b \qquad (9)$$

was used to express the temperature dependence of the values of log β_n^0. The values of log β_n^0 in Table 19 were fitted to eqn. (9). The values of the constants a, b and c obtained are given in Table 21.

The thermodynamic quantities, free energies, enthalpies, and entropies of the complexation equilibria (1) were calculated on the basis of the values of the constants a, b, and c given in Table 21 from the following known equations:

$$\Delta G^0 = 2.303\ R(a - bT + cT^2) \qquad (10)$$

$$\Delta H^0 = 2.303\ R(a - cT^2) \qquad (11)$$

$$\Delta S^0 = 2.303\ R(b - 2cT) \qquad (12)$$

where $T = 273.16 + t$ °C and $R = 8.31433$ J K^{-1} mol^{-1}. The results obtained for the thermodynamic quantities are given in Table 22, where the values of log β_n^0 are also included for comparison.

The values of the enthalpies are seen to be negative with the one exception of the $Cu(HL)_3^{2+}$ complex, possibly due to inaccuracies of the measurements, (Table 22).

The values in Table 22 show generally that for the imidazole complexes studied here the enthalpy effect is the dominant factor determining the complex stability, which explains the high complex formation tendency of imidazole with the studied metal(II) ions.

As regards the accuracy of the thermodynamic data given in Table 22, we may estimate that in the case of the first complexes the errors are of about ±0.1 kJ mol^{-1} in ΔG°, ±2 – 4 kJ mol^{-1} in ΔH^0 and ±8 – 12 J K^{-1} mol^{-1} in ΔS^0, and obviously increase for the higher complexes.

In Table 23 we have collected the earlier thermodynamic data of the complex equilibria found in the literature. When these values are compared with those obtained by us and given in Table 22, it will be seen that the enthalpy values determined by Bauman and Wang[23] by calorimetric enthalpy titrations are in good agreement with the present ones, whereas the data of Sklenskaya and Karapet'yants[8] are generally not, being several times greater.

It is interesting to note that in some recent papers Powell[24,25] has paid attention to the dependence of the calorimetrically determined enthalpy values on the ionic strength of the solutions, and to the possible errors caused in the enthalpy values when correcting these for the ionic strength to obtain the ΔH^0 values using different assumed, semitheoretical activity functions. Also we have already[1] considered the ionic strength dependence of enthalpy values.

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