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Phthalic Acid as a Reagent in Inorganic Qualitative Analysis of Metal Ions. Part IV. Thermodynamics of the Complexation of Phthalate Ion with Divalent Copper, Nickel, and Cobalt Ions in Aqueous Sodium Perchlorate Solutions

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The complex formation of the phthalate ion with divalent copper, nickel, and cobalt ions was studied potentiometrically. The stability constants β_1 were evaluated for the three complexes as functions of the ionic strength at 25 °C. At a lower ionic strength the measurements were performed at 15 and 35 °C also. The second stability constant β_2 was derived for the copper complex only. The thermodynamic values of the stability constants were obtained by fitting the experimental data to semitheoretical equations and the thermodynamic quantities, the free energies, enthalpies, and entropies were calculated from these values.

The different precipitation behaviour of the copper(II) phthalate and benzoate complexes in the course of the qualitative analysis of metal ions is discussed.

In the previous parts of this series [1-3] we have discussed the application of phthalic acid in the inorganic qualitative analysis of metal ions,[1] the composition and structure of certain basic metal complexes [2] and the protonation equilibria of the phthalate ion.[3] To obtain a more comprehensive picture of the complex formation ability of the phthalate ion with metal ions we report in the present paper the results of our potentiometric studies on the complexation tendency of the phthalate ion with divalent copper, nickel and cobalt ions in aqueous sodium perchlorate solutions.

EXPERIMENTAL

Reagents and solutions. In addition to the reagents mentioned in the previous paper [3] the following reagents were used: copper(II) carbonate (Analyzed reagent, J. T. Baker), nickel(II) perchlorate, and cobalt(II) perchlorate (G. Frederick Smith Chemical Co.).

The copper(II) perchlorate solution was prepared by dropping conc. perchloric acid into a copper(II) carbonate water mixture and stirring well. The addition of the acid was ceased before all the carbonate had reacted. The solution was filtered through a glass-sinter (G4), made slightly acid (pH ~ 3) with a dilute perchloric acid and warmed to release the carbon dioxide. The solution was diluted with carbon dioxide-free water, and analyzed for copper electroanalytically in acidified conditions and for perchlorate by cation exchange.

The nickel(II) perchlorate solution was prepared by dissolving the salt in water, allowing the solution to stand for several days and filtering. The nickel concentration was determined gravimetrically with dimethylglyoxime and the perchlorate concentration as above.

The cobalt(II) perchlorate solution was made as the nickel(II) salt solution and analyzed for cobalt electroanalytically and for perchlorate as mentioned.

The preparation, rinsing and analyses of the other stock solutions were described in the previous part.[3] The concentrations of the stock solutions used were (20 °C): 5.440 M $NaClO_4$, 0.1738 M $Cu(ClO_4)_2$, 0.3716 M $Ni(ClO_4)_2$, 0.3897 M $Co(ClO_4)_2$, 0.1003 M $HClO_4$ and 0.09994—0.1004 M NaOH. The compositions of the solutions used in connection with the titrations are presented in Table 1.

The titrated solutions were prepared in a water thermostat at 20 °C. Sodium chloride and phthalic acid were weighed into the measuring flasks and allowed to dissolve into a small quantity of water. Sodium and metal perchlorate were then added as stock solutions, and the flask was filled with water to the mark.

Table 1. The composition of the solutions used in connection with the potentiometric titrations (20 °C). All studied solutions contained 0.01 M phthalic acid. The figures, except those for the ionic strengths, give the concentrations of $NaClO_4$ in mol/l (M).

Titrant	I	References		Studied solutions		
0.1 M NaOH		Electrode 0.01 M NaCl	Buffer 0.005 M $HClO_4$	0.005 M $Cu(ClO_4)_2$	0.01 M $Ni(ClO_4)_2$	0.01 M $Co(ClO_4)_2$
0.250	0.250	0.240	0.245	0.235	0.220	0.220
0.500	0.500	0.490	0.495	0.485	0.470	0.470
1.000	1.000	0.990	0.995	0.985	0.970	0.970
2.000	2.000	1.990	1.995	1.985	1.970	1.970

The temperature expansion of the solutions was assumed to be the same as that of pure water.[3]

Apparatus. These were described in the preceding part of this series.[3]

Measurements. To find the optimum conditions of the complex formations and the metal—ligand relations, several titrations were performed varying the metal ion concentrations and keeping the ligand concentration constant, and *vice versa*. The obtained titration curves were compared with that of phthalic acid alone at the same ionic strength.

Corresponding metal perchlorate solutions, containing no phthalic acid, were titrated at an ionic strength of 0.5 M to correct for the excess perchlorate anion concentration observed in the metal perchlorate solutions. The amount of sodium hydroxide needed to neutralize the solution was deduced from the sodium hydroxide consumption at the ordinary titration. The excesses of perchlorate anion found were the same as those obtained by cation exchange analyses of the stock solutions. The amounts of sodium perchlorate formed by the neutralization of the perchlorate anion excesses were in all cases, however, so small that they did not affect the ionic strengths of the titration solutions.

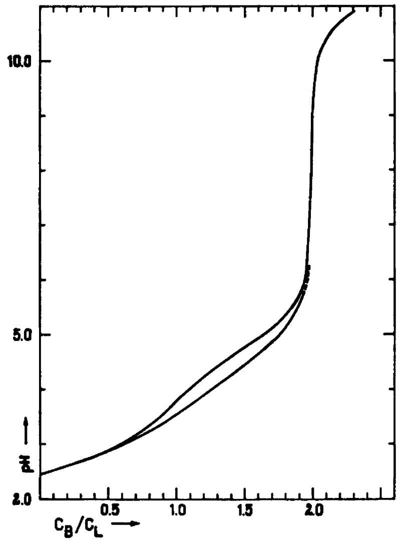

Fig. 1. The potentiometric titration curve of a solution 0.01 M in phthalic acid and 0.005 M in $Cu(ClO_4)_2$ at the ionic strength 0.5 and at 25 °C (the lower curve). The upper curve represents the titration of a solution 0.01 M in phthalic acid under the same conditions.

The ordinary complex titrations were performed at four ionic strengths at 25 °C. Titrations were also made at 15 and 35 °C to find the effect of the temperature variation, but only at the ionic strength of 0.5 M. The added increments of the sodium hydroxide solutions were 0.2 ml. The emf of the titrated solution was generally stabilized in 2 min. The titration was continued until the formation of metal hydroxide began. At the beginning and end of every titration, reference measurements were made with the reference buffer solution. If a difference greater than the potential reading accuracy (±0.2 mV) was observed a new titration was performed.

The type of titration cell was the following:

Glass electrode	100 ml 0.01 M $C_8H_6O_4$ X M $M(ClO_4)_2$ $(I-3X)$ M $NaClO_4$	‖

0.01 M NaCl $(I-0.01)$ M $NaClO_4$	Hg_2Cl_2, Hg

With this arrangement we attempted to minimize the diffusion potentials.

RESULTS AND DISCUSSION

Several titrations were done at ionic strength 0.5 M by varying the metal—ligand relation from tenfold excess of the metal ions to tenfold excess of the ligand ions in respect of each others to find the optimum complex formation conditions and the corresponding metal—ligand relations. According to the calculations the best results for copper(II) complexes were obtained when the solution was 0.01 M in phthalic acid and 0.005 M in copper(II) perchlorate. Both β_1 and β_2 could be calculated from the measurements. In the first case a complex containing one and in the latter case two seven membered chelate rings are formed. A typical titration curve is presented in Fig. 1. In the case of a dicarboxylic ligand, the formation of dinuclear metal complexes may be suspected. However, the formation of the complexes of the form $(M_2L)^{2+}$ was found to be negligible, although a tenfold excess of the metal ion with respect to the ligand concentration was used. A complex of the type M_2L_2 is yet more unlikely at low conc. of copper(II) ions.

The complex formation tendency of nickel(II) and cobalt(II) ions with the phthalate ion is still weaker than that of copper(II) ion. No positive value of β_2 was obtained for these metals. However, comparable values for β_1 were obtained using 0.01 M solutions at the metal—ligand ratio 1:1. From Fig. 1 it is also seen that the formation of complexes of the form $(MHL)^+$ is slight, because the difference between the titration curves in Fig. 1 is not generally observed until the vicinity of the first equivalent point of phthalic acid is reached.

The assumed complex formation equilibria of phthalate ion ($C_8H_4O_4^{2-}=L^{2-}$) with divalent metal ions prevailing in aqueous solutions may therefore be presented as follows:

$$M^{2+}+L^{2-}\rightleftharpoons ML \qquad (1)$$

$$ML+L^{2-}\rightleftharpoons ML_2^{2-} \qquad (2)$$

The corresponding consecutive complex formation constants are

$$k_1=[ML]/[M^{2+}][L^{2-}] \qquad (3)$$

$$k_2=[ML_2^{2-}]/[ML][L^{2-}] \qquad (4)$$

and the gross stability constants

$$\beta_1=k_1 \qquad (5)$$

$$\beta_2=[ML_2^{2-}]/[M^{2+}][L^{2-}]^2=\beta_1 k_2 \qquad (6)$$

On the basis of the total concentrations of the phthalate ion (C_L), the metal ion (C_M), and the hydrogen ion (C_H) of the solution, and the equations (5) and (6) the concentration of the free ligand and the constants β_n may be calculated from the equations:

$$[L^{2-}]=(2C_L-C_B-[H^+])/P \qquad (7)$$

$$\sum_{n=1}^{2}\{\beta_n[L^{2-}]^{n-1}(C_L-nC_M-Q[L^{2-}])\}+ + (C_L/[L^{2-}])-Q=0 \qquad (8)$$

where C_B is the total concentration of the added sodium hydroxide in the titrated solution and
$P=K_1[H^+]+2\,K_1K_2[H^+]^2$
$Q=1+K_1[H^+]+K_1K_2[H^+]^2$
and in which K_1 and K_2 are the first and second protonation constants of the phthalate ion determined in the previous part of this series.[3] Because of the low values of pH the hydroxyl ion concentration was neglected in the equations. The values of β_n were calculated by the method of least squares from eqn. (8).

The experimental results of the complex titrations and values of β_n calculated from eqn. (8) are given in Tables 2—7.

The values of the stability constants determined could be expressed as functions of the ionic strength by the semitheoretical equation:

$$\log\beta_n=\log\beta^\circ_n-\frac{8A\sqrt{I}}{1+\alpha\sqrt{I}}+BI \qquad (9)$$

The values of log β_1 in Tables 2—7 were fitted by the method of least squares with eqn. (9). The results for the three complexes studied are given at 25 °C in Table 8. Rough values of β_2 could be calculated only for the copper(II) phthalate complex. On the basis of the obtained values it can merely be said that log β°_2 of the copper(II) phthalate complex is of the order of 5.3 ± 0.3 at 25 °C, showing a weak tendency to form the complex CuL_2^{2-}. A corresponding tendency was not found for nickel(II) and cobalt(II) ions. The log β_1 values showed the stability of the first complexes to decrease in the order: Cu > Ni > Co. The approximate thermodynamic values at 15 and 35 °C were extrapolated on the basis of eqn. (9) of the first complexes and are presented with the values of log β°_1 of the complexes at 25 °C in Table 9.

The values of log β_1 of the first complexes are presented as functions of the square root of the ionic strength at 25 °C in Fig. 2.

Table 2. Potentiometric determination of the gross stability constants β_1 and β_2 of copper(II) phthalate complexes at 25 °C. Mean values of the constants are represented.

$C_{\mathrm{M}} \times 10^3$	$C_{\mathrm{L}} \times 10^3$	$[\mathrm{H}^+] \times 10^5$	$[\mathrm{L}^{2-}] \times 10^3$	$C_{\mathrm{M}} \times 10^3$	$C_{\mathrm{L}} \times 10^3$	$[\mathrm{H}^+] \times 10^5$	$[\mathrm{L}^{2-}] \times 10^3$
$I=0.2507$				$I=1.0018$			
4.358	8.716	4.906	1.468	4.358	8.716	4.646	1.991
4.350	8.701	4.486	1.550	4.350	8.701	4.298	2.075
4.343	8.686	4.102	1.634	4.343	8.686	3.945	2.177
4.335	8.670	3.721	1.733	4.335	8.670	3.635	2.270
4.328	8.655	3.389	1.827	4.328	8.655	3.324	2.381
4.320	8.640	3.075	1.929	4.320	8.640	3.051	2.482
4.313	8.626	2.801	2.025	4.313	8.626	2.790	2.592
4.305	8.611	2.551	2.119	4.305	8.611	2.541	2.710
4.298	8.596	2.314	2.221	4.298	8.596	2.324	2.814
4.291	8.581	2.100	2.321	4.291	8.581	2.116	2.926
4.283	8.566	1.890	2.437	4.283	8.566	1.920	3.043
				4.276	8.552	1.728	3.178
				4.269	8.537	1.556	3.305
log $\beta_1=2.976\pm0.005$				log $\beta_1=2.698\pm0.008$			
log $\beta_2=4.448\pm0.018$				log $\beta_2=3.731\pm0.071$			
$I=0.5024$				$I=2.0017$			
4.373	8.746	5.471	1.675	4.381	8.762	5.241	1.728
4.366	8.731	5.041	1.759	4.373	8.746	4.849	1.811
4.358	8.716	4.628	1.852	4.366	8.731	4.486	1.896
4.350	8.701	4.248	1.947	4.358	8.716	4.150	1.981
4.343	8.686	3.899	2.042	4.350	8.701	3.839	2.067
4.335	8.670	3.565	2.147	4.343	8.686	3.538	2.161
4.328	8.655	3.260	2.253	4.335	8.670	3.273	2.247
4.320	8.640	2.969	2.369	4.328	8.655	3.016	2.340
4.313	8.626	2.715	2.474	4.320	8.640	2.779	2.433
4.305	8.611	2.473	2.589	4.313	8.626	2.551	2.533
4.298	8.596	2.244	2.711	4.305	8.611	2.324	2.652
4.291	8.581	2.035	2.832	4.298	8.596	2.125	2.758
4.283	8.566	1.840	2.959	4.291	8.581	1.928	2.882
4.276	8.552	1.656	3.093	4.283	8.566	1.756	2.990
4.269	8.537	1.485	3.232	4.276	8.552	1.580	3.128
log $\beta_1=2.795\pm0.007$				log $\beta_1=2.633\pm0.014$			
				log $\beta_2=4.144\pm0.050$			

The complex formation of phthalate ions with transition metal ions has been studied intensively as seen from Table 10, where a part of the results obtainable from the literature is represented for comparison. Systematic studies on the effects of the ionic strength and temperature are, however, fewer.

When inspecting the results in Table 10 the diversity of the stability constant values is observed to be rather high. For the copper(II) phthalate complexes our values of log β_1 are in best agreement with those of Yamasaki *et al.*[7] The difference between our values and those reported by Ghosh and Nair[9] is obviously at least partly due to the fact that these authors have taken into consideration the formation of CuHL^+ complexes which was disregarded in the present case as described above. A log β_1 value of about 0.97 at 25 °C was found[9] for the complex CuHL^+, which shows its weak stability and low tendency of formation.

By assuming the difference between the titration curves (Fig. 1) to be wholly due to the formation of MHL^+ complexes at the $C_{\mathrm{B}}/C_{\mathrm{L}}$ values from zero to one we calculated from the titration curves at 25 °C the following maximum values of log β_1 for the MHL^+ complexes: 1.2 ± 0.4 (Cu), $I=0.473$; 0.72 ± 0.1 (Ni), $I=0.494$; 1.28 ± 0.04 (Co), $I=0.493$. Their effect in the pH ranges used in Tables 2—7 is negligible.

Table 3. Potentiometric determination of the gross stability constants β_1 and β_2 of copper(II) phthalate complexes at 15 and 35 °C. Mean values of the constants are represented.

$I=0.5034$, 15 °C				$I=0.5014$, 35° C			
C_M $\times 10^3$	C_L $\times 10^3$	[H+] $\times 10^5$	[L^{2-}] $\times 10^3$	C_M $\times 10^3$	C_L $\times 10^3$	[H+] $\times 10^5$	[L^{2-}] $\times 10^3$
4.367	8.734	4.461	1.903	4.349	8.699	4.887	1.748
4.359	8.719	4.083	2.006	4.342	8.684	4.482	1.840
4.352	8.704	3.736	2.111	4.334	8.669	4.110	1.933
4.344	8.688	3.433	2.208	4.327	8.654	3.755	2.035
4.337	8.673	3.130	2.324	4.319	8.639	3.443	2.129
4.329	8.658	2.876	2.420	4.312	8.624	3.122	2.249
4.322	8.643	2.632	2.526	4.304	8.609	2.863	2.343
4.314	8.629	2.380	2.662	4.297	8.594	2.596	2.463
4.307	8.614	2.161	2.786	4.290	8.579	2.380	2.552
4.299	8.599	1.977	2.883	4.282	8.565	2.142	2.688
4.292	8.584	1.781	3.024	4.275	8.550	1.942	2.800
4.285	8.569	1.604	3.159	4.267	8.535	1.741	2.939
				4.260	8.521	1.567	3.061
log $\beta_1=2.764\pm0.007$				log $\beta_1=2.849\pm0.008$ log $\beta_2=3.569\pm0.136$			

Table 4. Potentiometric determination of the constant β_1 of nickel(II) phthalate complex at 25 °C. $C_M=C_L$. C_M was the same in all series.

$I=0.2492$			$I=0.5009$		$I=1.002$		$I=2.002$	
C_M $\times 10^3$	[H+] $\times 10^5$	[L^{2-}] $\times 10^3$	[H+] $\times 10^5$	[L^{2-}] $\times 10^3$	[H+] $\times 10^5$	[L^{2-}] $\times 10^3$	[H+] $\times 10^5$	[L^{2-}] $\times 10^3$
8.689	2.332	2.957	2.323	3.518	2.305	3.830	2.133	3.689
8.674	2.166	3.058	2.149	3.652	2.125	3.989	1.958	3.861
8.658	1.988	3.194	1.988	3.783	1.958	4.147	1.811	4.002
8.643	1.832	3.317	1.832	3.927	1.804	4.303	1.656	4.190
8.629	1.688	3.437	1.695	4.051	1.656	4.472	1.538	4.307
8.614	1.556	3.553	1.562	4.186	1.520	4.637	1.417	4.453
8.599	1.428	3.679	1.434	4.331	1.401	4.776	1.306	4.592
8.584	1.311	3.798	1.316	4.469	1.286	4.924	1.194	4.759
8.569	1.199	3.924	1.190	4.670	1.171	5.100	1.096	4.898
8.555	1.096	4.040	1.088	4.805	1.063	5.285	0.998	5.063
8.540	0.998	4.160	0.987	4.963	0.968	5.431	0.902	5.254
8.525	0.902	4.299	0.859	5.104	0.868	5.645	0.806	5.492
8.511	0.809	4.454	0.806	5.263	0.778	5.835	0.734	5.601
8.496	0.726	4.589	0.717	5.458	0.698	5.995	0.656	5.791
8.482	0.646	4.733	0.636	5.644	0.614	6.235	0.572	6.089
8.468	0.568	4.900	0.542	6.019	0.546	6.353	0.507	6.251
log $\beta_1=1.892\pm0.009$			1.719 ± 0.023		1.560 ± 0.011		1.631 ± 0.020	

The formation of the complex CuL_2^{2-} is so weak and highly dependent on the metal—ligand ratio in the experiments that the deviations between the log β_2 values are not surprising (Table 10).

Bobtelsky and Bar-Gadda [13] determined spectrophotometrically, using Job's method, the value 3.55 of log k_2 for the second stepwise stability constant of the complex CuL_2^{2-} at the ionic strength about 0.4 and 18—25 °C. From our values of log β_2—log β_1 we obtain an approximate value of 1.2 for log k_2. The value of 3.55 must be too high.

For the nickel(II) phthalate complex the

Table 5. Potentiometric determination of the stability constant β_1 of nickel(II) phthalate complex at 15 and 35 °C. $C_M = C_L$.

$I=0.5020$, 15 °C			$I=0.500$, 35 °C		
C_M $\times 10^3$	$[H^+]$ $\times 10^5$	$[L^{2-}]$ $\times 10^3$	C_M $\times 10^3$	$[H^+]$ $\times 10^5$	$[L^{2-}]$ $\times 10^3$
8.707	2.134	3.794	8.672	2.301	3.555
8.691	1.953	3.981	8.657	2.126	3.694
8.676	1.824	4.084	8.642	1.972	3.817
8.661	1.710	4.165	8.627	1.822	3.951
8.646	1.565	4.343	8.612	1.683	4.082
8.632	1.438	4.501	8.597	1.544	4.239
8.617	1.316	4.670	8.582	1.416	4.390
8.602	1.200	4.853	8.567	1.298	4.535
8.587	1.094	5.026	8.553	1.186	4.686
8.572	0.993	5.209	8.538	1.079	4.845
8.558	0.905	5.355	8.524	0.989	4.951
8.543	0.819	5.525	8.509	1.055	4.323
8.529	0.731	5.740	8.494	0.802	5.295
8.514	0.661	5.857	8.480	0.721	5.429
8.499	0.591	6.008	8.466	0.637	5.634
8.485	0.517	6.237	8.451	0.563	5.799
$\log \beta_1 = 1.550 \pm 0.023$			$\log \beta_1 = 1.650 \pm 0.125$		

Table 6. Potentiometric determination of the stability constant β_1 of cobalt(II) phthalate complex at 25 °C. $C_M = C_L$. C_M was the same in all series.

	$I=0.2505$		$I=0.5028$		$I=1.003$		$I=2.0012$	
C_M $\times 10^3$	$[H^+]$ $\times 10^5$	$[L^{2-}]$ $\times 10^3$	$[H^+]$ $\times 10^5$	$[L^{2-}]$ $\times 10^3$	$[H^+]$ $\times 10^5$	$[L^{2-}]$ $\times 10^3$	$[H^+]$ $\times 10^5$	$[L^{2-}]$ $\times 10^3$
8.709	2.397	3.040	2.369	3.648	2.444	3.817	2.270	3.658
8.694	2.217	3.163	2.183	3.809	2.261	3.969	2.084	3.838
8.679	2.043	3.299	2.035	3.924	2.100	4.104	1.935	3.972
8.664	1.883	3.435	1.876	4.084	1.935	4.269	1.790	4.119
8.649	1.742	3.555	1.742	4.208	1.790	4.415	1.650	4.281
8.634	1.612	3.671	1.605	4.362	1.643	4.592	1.538	4.387
8.619	1.485	3.798	1.468	4.547	1.514	4.747	1.412	4.557
8.604	1.368	3.920	1.342	4.727	1.390	4.913	1.291	4.741
8.589	1.256	4.051	1.242	4.844	1.271	5.091	1.190	4.880
8.575	1.148	4.190	1.144	4.968	1.158	5.280	1.088	5.048
8.560	1.050	4.320	1.034	5.180	1.058	5.435	0.998	5.184
8.546	0.957	4.455	0.942	5.337	0.960	5.617	0.895	5.430
8.531	0.865	4.611	0.851	5.519	0.868	5.802	0.815	5.575
8.516	0.778	4.768	0.760	5.747	0.778	6.010	0.728	5.810
8.502	0.698	4.923	0.687	5.881	0.693	6.238	0.653	5.997
8.487	0.626	5.050	0.607	6.121	0.614	6.456	0.584	6.175
$\log \beta_1 = 1.754 \pm 0.011$			1.492 ± 0.023		1.449 ± 0.020		1.498 ± 0.023	

agreement between the log β_1 values is on the other hand better (Table 10). In the case of the cobalt(II) phthalate complex our value of log β_1 agrees best with the previously reported value[10] at 35 °C.

In this context it is interesting to notice that Evans and Monk[14] in connection with their studies on association constants of zinc dicarboxylates in water have pointed out that owing to the formation of metal chloride com-

Table 7. Potentiometric determination of the stability constant β_1 of cobalt(II) phthalate complex at 15 and 35 °C. $C_M=C_L$.

$I=0.5039$, 15 °C			$I=0.5018$, 35 °C		
C_M $\times 10^3$	$[H^+]$ $\times 10^5$	$[L^{2-}]$ $\times 10^3$	C_M $\times 10^3$	$[H^+]$ $\times 10^5$	$[L^{2-}]$ $\times 10^3$
8.727	2.370	3.604	8.693	2.417	3.575
8.712	2.196	3.744	8.677	2.233	3.724
8.697	2.042	3.866	8.662	2.063	3.872
8.682	1.876	4.036	8.647	1.913	4.003
8.667	1.731	4.186	8.632	1.768	4.147
8.652	1.584	4.370	8.617	1.633	4.287
8.637	1.456	4.532	8.603	1.509	4.422
8.622	1.343	4.669	8.588	1.389	4.567
8.607	1.229	4.837	8.573	1.274	4.721
8.593	1.121	5.016	8.558	1.164	4.885
8.578	1.026	5.163	8.544	1.063	5.038
8.563	0.935	5.316	8.529	0.971	5.175
8.548	0.852	5.449	8.514	0.877	5.355
8.534	0.767	5.628	8.500	0.793	5.513
8.519	0.686	5.826	8.485	0.713	5.666
8.505	0.613	5.993	8.471	0.640	5.807
$\log \beta_1=1.505\pm0.011$			$\log \beta_1=1.434\pm0.014$		

Table 8. The values of $\log \beta_1$ of the copper(II), nickel(II) and cobalt(II) phthalate complexes calculated from eqns. (8) and (9) at different ionic strengths and at 25 °C. The constants α and B of eqn. (9) are also given.

Copper			Nickel			Cobalt		
I	$\log \beta_1$ eqn. (8)	$\log \beta_1$ eqn. (9)	I	$\log \beta_1$ eqn. (8)	$\log \beta_1$ eqn. (9)	I	$\log \beta_1$ eqn. (8)	$\log \beta_1$ eqn. (9)
0.2507	2.976	2.971	0.2492	1.892	1.901	0.2505	1.754	1.735
0.5024	2.795	2.810	0.5009	1.719	1.699	0.5028	1.492	1.533
1.0018	2.698	2.687	1.0020	1.560	1.574	1.0029	1.449	1.419
2.0017	2.633	2.636	2.0002	1.631	1.627	2.0012	1.498	1.504
$\alpha=1.879$, $B=0.1096$			$\alpha=1.204$, $B=0.3375$			$\alpha=1.144$, $B=0.3869$		

plexes in solutions there is obviously no preference in precision to use the $H_2,Pt-Ag,AgCl$ electrode system (without liquid junction potentials) with emf measurement readings to ±0.01 mV compared with the glass electrode—saturated calomel electrode system (with liquid junction potentials) with emf read to ±0.1 mV when doing the stability constant determinations of metal complexes. The chloride complex formation tendency of copper(II), nickel(II), and cobalt(II) ions is likewise of about the same order as that of the zinc(II) ions.[15]

The thermodynamic values of the stability constants were assumed to depend on the absolute temperature according to the equation:

$$\log \beta^\circ_n=a+b/T \qquad (10)$$

where a and b are parameters obtained by fitting the data from Table 9 to the equation. The values of the constants are:

Complex	a	$-b\times10^2$
Copper	5.9199	5.7279
Nickel	5.3695	6.9761
Cobalt	2.6967	−0.6037

The dependence of the experimental values of $\log \beta^\circ_1$ of the copper(II) phthalate complex on $1/T$ seems to be almost linear (Fig. 3). For

Table 9. The thermodynamic values of the stability constants of the first copper(II), nickel(II), and cobalt(II) phthalate complexes calculated from eqn. (9) at different temperatures. The values[4] of the constant A of eqn. (9) are also represented.

°C	A	Cu $\log \beta^\circ_1$	Ni $\log \beta^\circ_1$	Co $\log \beta^\circ_1$
15	0.5028	3.932	2.918	2.886
25	0.5115	3.999	3.093	2.941
35	0.5211	4.061	3.073	2.871

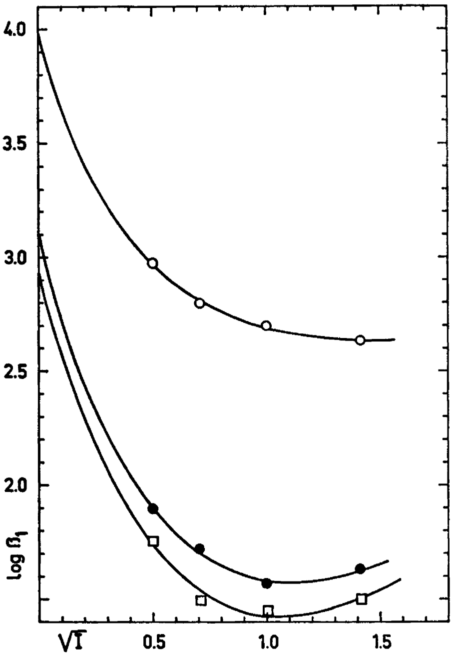

Fig. 2. The values of log β_1 of the copper(II), nickel(II), and cobalt(II) phthalate complexes represented as functions of the square root of the ionic strength at 25 °C. Curve: ○, copper; ●, nickel; □, cobalt.

nickel(II) and cobalt(II) phthalate complexes the dependence of log β°_1 on temperature is more uncertain.

The thermodynamic quantities, free energies, enthalpies, and entropies of the complex formation equilibria were calculated on the basis of the constants a and b from eqns. (11)–(13):

$$\Delta G^\circ = -2.303\ R(aT+b) \tag{11}$$

$$\Delta H^\circ = -2.303\ Rb \tag{12}$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \tag{13}$$

where R is the general gas constant 8.31433 J K^{-1} mol^{-1} and T the absolute temperature. The results are given in Table 11.

The thermodynamics of the formation of the copper(II), nickel(II), and cobalt(II) phthalate complexes has been studied by Nair *et al.*[9,10,16] only. Their values of the thermodynamic quantities at 25 °C (?) were converted to SI units[17] by assuming them to be expressed in thermochemical calories (factor 4.184). The converted values are given for comparison in Table 12.

By comparing the present results in Table 11 with those of Nair *et al.* in Table 12 they can be said to be only roughly of the same order of magnitude, except for ΔG° and the copper(II) complex. It is interesting to observe that the data (Table 12) for the copper(II) complex are from the later calorimetric studies of Parthasarathy and Nair[16] who did not take into account the formation of $CuHL^+$ (*cf.* Table 10 and above), whereas the data for the cobalt(II) and nickel(II) complexes were obtained by Desai and Nair[10] from the temperature coefficient measurements performed with a H,Pt–Ag,AgCl electrode system.

The formations of the copper(II) and nickel(II) phthalate complexes are endothermic reactions; the enthalpy changes (ΔH) are positive and unfavorable from the viewpoint of complex formation and the stability of the complex (*cf.* Table 11). The entropy effects (ΔS), however, are also positive (and dominating) which implies free release of water molecules of hydration in the complex formation and obviously makes this possible and increases the stability of the complexes. The stabilities of the complexes increase only slightly with the increasing temperature.

In the case of the cobalt(II) phthalate complex ΔH is not so unfavorable for complex formation as in the former cases, but the entropy change (ΔS) is lower and means lower liberation of water molecules of hydration and therefore also lower stability of the complex.

Hamm *et al.*[18] concluded on the basis of their kinetic measurements (at 25 °C) on the formation of chromium(III) complexes with dicar-

Table 10. Comparison of the values of log β_n of the copper(II), nickel(II), and cobalt(II) complexes of the phthalate ion determined by different workers.

Metal ion	°C	Ionic strength (added salt)	log β_1	log β_2	Method	Ref.
Cu^{2+}	18	0.01		4.51	glass el.	5
	25	→0		4.06	glass el.	6
	25	0.1 (KNO_3)	3.10		glass el.	7
	25	0.1($NaClO_4$)	3.20		glass el.	this work
	25	→0	3.98		glass el.	7
	25	→0	4.00	5.34 ± 0.3	glass el.	this work
	—	→0	3.46	4.83	spectrophotom.	8
	25	0 corr.	3.10		glass el., Ag—AgCl	9
	25	0 corr.	4.038		calorimetric	16
	25	0 corr.	3.14		solubility	9
	35	0 corr.	3.50		solubility	9
	35	→0	4.06		glass. el	this work
Ni^{2+}	15	0 corr.	2.911		H,Ag-AgCl	10
	15	→0	2.92		glass el.	this work
	25	0.1 (KNO_3)	2.14		glass el.	7
	25	0.1 ($NaClO_4$)	2.19		glass el.	this work
	25	→0	3.09		glass el.	this work
	25	0 corr.	2.95		H,Ag—AgCl	10
	35	0 corr.	2.996		H,Ag—AgCl	10
	35	→0	3.07		glass el.	this work
Co^{2+}	15	0 corr.	2.795		H,Ag—AgCl	10
	15	→0	2.89		glass el.	this work
	25	0 corr.	2.83		H,Ag—AgCl	10
	25	→0	2.94		glass el.	this work
	25	0 corr.	2.76 ± 0.06	3.66 ± 0.1	ion exchange	11
	25	0 corr.	2.86 ± 0.02		glass el.	12
	35	→0	2.87		glass el.	this work
	35	0 corr	2.885		H,Ag—AgCl	10

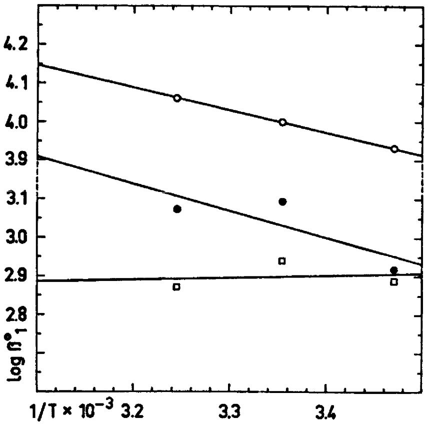

Fig. 3. The values of log β°_1 of the copper(II), nickel(II), and cobalt(II) phthalate complexes represented as functions of the reciprocal absolute temperature. Curve: ○, copper; ●, nickel; □, cobalt.

boxylic anions, among others with phthalate ion, that the escape of a hydration water molecule is the slowest and rate determining step in the complex formation. Possibly we can assume the situation to be the same with the other metal phthalate complexes and so the liberation tendency of the hydration water molecules is parallel with the complex formation tendency, the complex stability and the entropy effect.

Because we do not know exactly the hydration degree of the species in eqns. (1) or (2) and the numbers of the liberated water molecules in the complex formation reactions and the inaccuracy of the present data a further going consideration [19,20] of the thermodynamic quantities would be inappropriate.

When considering the analytical method [1] and the application of benzoic acid [21] instead of phthalic acid, the observed difficulties with

Table 11. The values of log β°_1 calculated from eqn. (10) and the values of the free energy, enthalpy, and entropy calculated from the relations (11)–(13) and for the first complexation equilibria of the phthalate ion with the divalent copper, nickel, and cobalt ions.

°C	log β°_1	$-\Delta G^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	
Copper(II) phthalate complex					
15	3.932	21.70		113	
25	3.999	22.83	11.0	113	
35	4.061	23.96		113	
Nickel(II) phthalate complex					
15	2.949	16.3		103	
25	3.030	17.3	13.4	103	
35	3.106	18.3		103	
Cobalt(II) phthalate complex					
15	2.906	16.0		52	
25	2.899	16.6	−1.2	52	
35	2.893	17.1		52	
	±0.03	±0.2	±2	±10	Mean accuracy or better

Table 12. The thermodynamic quantities of the first copper(II), nickel(II), and cobalt(II) phthalate complexes converted from the literature [9,10,16] at 25 °C (?).

Complex (ML)	$-\Delta G^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	ΔC_p° (J K^{-1} mol^{-1})
Copper	23.05	8.41	105.4	—
Nickel	16.84±0.02	7.38±0.21	81.2±1.3	285±84
Cobalt	16.15±0.02	7.82±0.21	80.3±0.8	213±63

benzoic acid as a reagent,[1] may obviously be explained now. The copper(II) benzoate complex [7] is about half as stable (log $\beta_1 = 1.6$ at 25 °C and $I = 0.1$) as the corresponding phthalate complex (*cf.* Table 10), but the enthalpy (ΔH) of the formation of the copper(II) benzoate complex is about zero [22] and the entropy change (ΔS) about one third lower [22] in the temperature range 25–35 °C.

On the other hand the solubility products (K_S) of the copper(II) bisbenzoate and copper(II) oxalate may be calculated to be 3.5×10^{-8} (20 °C) and 2.53×10^{-8} (18 °C), respectively, in the saturated water solutions of the salts on the bases of the given solubility data.[23] The solubility product of the copper(II) diphthalato compound is not known, but may be expected to be higher than the above values because the solubility product of the copper(II) tetrachlorophthalate is $< 7.5 \times 10^{-6}$ and those of the copper(II) salts of the *ortho*-derivatives of benzoic acid are in general considerably higher at 25 °C (Ref. 23, p. 917). Therefore the higher complexation tendency of the phthalate ions with the copper(II) ions (*cf.* Table 10, although in general the formation tendency of the lower complexes increases the insolubility of the solid higher complexes [24]), the higher solubility and the property of the copper(II) diphthalato complex to form highly supersaturated solutions [5] (broken with a strong alkali [1] when precipitating the copper(II) ions as $Cu(OH)_2$ (p$K^\circ_S = 19.66$ (25 °C), Refs 15 and 23, p. 959) in the fourth cation group [1]) are obviously due to the fact that the copper(II) diphthalato complex does not separate as a precipitate in the course of the qualitative analysis of metal ions [1] in the second and further in the fifth group (the phthalate ions obviously have a greater ability than the benzoate ions to prevent copper(II) hydroxide to go as colloidal (soluble hydroxy complexes) into the fifth group [1]) depending still on the salt composition and pH of the solution, as does the copper(II) benzoate. For precipitation of different forms of the copper(II) and cobalt(II) phthalate compounds; *cf.* Refs. 5, 25–27 and 28.

The opinions presented above are also in agreement with the idea that the bonds between the metal and the ligand (M–O) in the complexes are mainly ionic by nature, because the precipitated iron(III) and chromium(III) phthalate complexes showed strong bands at 1530–1540 cm^{-1} due to the asymmetric CO_2^- stretching band.[2]

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