QUANTITATIVE DETERMINATION OF THE EQUILIBRIA OF COPPER, COBALT, NICKEL AND CADMIUM IONS IN CHLORIDE SOLUTIONS BY MEANS OF ION-EXCHANGE PAPERS

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In a previous investigation[1] it was shown that the equilibria established in a solution containing a cation and a ligand may be determined quantitatively by means of chromatography with ion-exchange papers.

The rapidity and simplicity of operation with ion-exchange papers are, indeed, attractive factors which recommend their use for quantitative measurements, but since the results of the calculation depend upon the accuracy with which the R_F values are measured, caution should be applied before a general application of this method.

The purpose of this study was the application of the procedure, developed previously[1], to solutions of copper, cobalt, nickel and cadmium ions in the presence of chloride in order to evaluate the possibilities and the limitations of this method.

EXPERIMENTAL

Ion-exchange paper SA-2 (Rohm and Haas) containing about 45 % Amberlite IR-120 (a sulphonic resin) was used. The sodium ion of the resin was replaced by hydrogen ion by equilibrating the ion-exchange papers with 3 M hydrochloric acid for 30 min; the papers were washed several times by allowing them to equilibrate with distilled water for 30 min after each wash.

Copper, cobalt, nickel and cadmium perchlorate solutions were prepared by adding 3 M perchloric acid to an excess of the solid carbonates; the solutions were filtered and then boiled to eliminate carbon dioxide. The copper content was determined iodometrically and the other cations were determined by means of titrations with ethylenediaminetetraacetic acid (EDTA). The working solutions were 0.1 M Cu^{2+}, 0.01 M Co^{2+}, 0.4 M Ni^{2+} and 0.4 M Cd^{2+} at these concentrations well defined, round spots were obtained when samples of about 10 μl were eluted with the solutions described below.

The experimental procedure was the same as outlined in the previous paper[1]. The chromatograms were run at 25° by the ascending technique.

The various cations were detected by spraying the ion-exchange papers with a solution of hexacyanoferrate, $K_4Fe(CN)_6$, for copper, with H_2S for cadmium, dimethylglyoxime for nickel and α-nitroso-β-naphthol for cobalt.

All the systems were investigated at constant ionic strength (3000 mM, except for the Cd^{2+}–Cl$^-$ system which was 1000 mM) and at a constant hydrogen ion concentration. The ligand concentration was made to vary by adding hydrochloric acid, H$^+$(Cl$^-$ + ClO$_4^-$) = 3000 mM, except for the Cd^{2+} system where H$^+$(Cl$^-$ + ClO$_4^-$) = 1000 mM. A different ligand range was chosen for the latter system as the cadmium–chloride complexes are more stable than the others; with a high ligand concentration the spots travel with the front.

RESULTS

The experimental results obtained for the investigated cations are collected in Table I. [A$^-$] is the concentration by analysis of the ligand of the eluting solution, which is assumed to be equal to the equilibrium concentration; A_L/A_S is the ratio of the amount of solvent to the amount of resin in a cross section of the paper. The partition coefficient (α) is related to the chromatographic R_F value by the equation:

$$\alpha = \left(\frac{1}{R_F} - 1 \right) \frac{A_L}{A_S}$$

In Fig. 1 the partition coefficient α is plotted against the ligand concentration for the systems investigated.

By assuming complex formation between an ion and a chloride ligand (M^{n+} + j Cl$^-$ ⇌ MCl$^{(n-j)+}$) and considering the partition on the resin of the various chemica
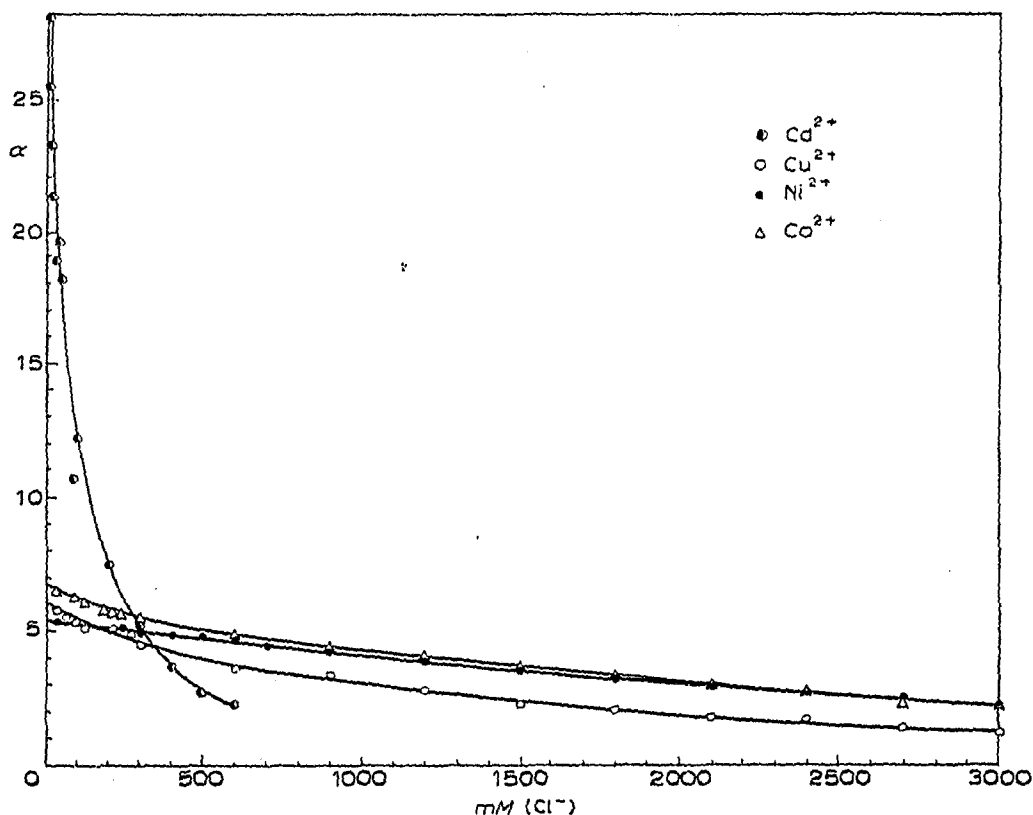

Fig. 1. Values of α plotted against chloride concentration for various cations.

TABLE I

R_F AND A_L/A_S VALUES AT VARIOUS LIGAND CONCENTRATIONS FOR THE INVESTIGATED CATIONS

[A⁻]mM	A_L/A_S	Cu²⁺ R_F	Cu²⁺ α	Co²⁺ R_F	Co²⁺ α	Ni²⁺ i_F	Ni²⁺ α	[A⁻]mM	A_L/A_S	Cd²⁺ R_F	Cd²⁺ α
0								0			30.8
30	3.52	0.38	5.74	0.35	6.54	0.40	5.28	5	3.367	0.11	27.24
60	3.52	0.39	5.50					10	3.365	0.12	24.68
90	3.51	0.40	5.27	0.36	6.25			15	3.363	0.13	22.51
120	3.51			0.37	5.98			20	3.361	0.14	20.65
150	3.50	0.41	5.04					30	3.357	0.15	18.32
180	3.50							40	3.353	0.16	17.60
210	3.50			0.38	5.71			50	3.349	0.17	16.35
240	3.50					0.41	5.03	100	3.328	0.22	11.80
270	3.49					0.41	5.02	200	3.286	0.32	7.15
300	3.49	0.44	4.45	0.39	5.46	0.42	4.82	300	3.244	0.40	4.97
600	3.45	0.49	3.60	0.42	4.96	0.43	4.57	400	3.203	0.48	3.47
900	3.43	0.51	3.29	0.44	4.37	0.45	4.19	500	3.162	0.56	2.48
1200	3.40	0.55	2.78	0.46	3.99	0.47	3.83	600	3.120	0.60	2.08
1500	3.36	0.60	2.24	0.48	3.64	0.49	3.50				
1800	3.33	0.62	2.04	0.50	3.33	0.51	3.20				
2100	3.30	0.65	1.78	0.53	2.95	0.53	2.93				
2400	3.27	0.66	1.68	0.54	2.79	0.55	2.68				
2700	3.24	0.70	1.39	0.58	2.35	0.57	2.44				
3000	3.21	0.73	1.19	0.59	2.23	0.59	2.23				

TABLE II

FORMATION CONSTANTS FOR CHLORIDE COMPLEXES WITH VARIOUS CATIONS

Ion-exchange papers (t = 25°)	Other investigations	

Cu²⁺

$\beta_1 = 0.94 \pm 0.05\ M^{-1}$
$\beta_2 = 0.16 \pm 0.07\ M^{-2}$
$\beta_3 = 0.05 \pm 0.08\ M^{-3}$

$\beta_1 \cong 1\ M^{-1}$
$\beta_2 = 0.1 - 0.4\ M^{-2}$
$\beta_3 = 0.02 - 0.06\ M^{-3}$
$\beta_4 = 0.003 - 0.01\ M^{-4}$

Spectrophotometry[2]
(t = 22°)

Ni²⁺

$\beta_1 = 0.23 \pm 0.03\ M^{-1}$
$\beta_2 = 0.06 \pm 0.03\ M^{-2}$
$\beta_3 = 0.001 \pm 0.006\ M^{-3}$

No evidence of anionic complex even in 12 M HCl

Anion exchange[3]

Co²⁺

$\beta_1 = 0.61 \pm 0.05\ M^{-1}$
$\beta_2 = 0.11 \pm 0.04\ M^{-2}$

$K_1 = 4 \cdot 10^{-3}\ M^{-1}$
$K_2 K_3 = 3 \cdot 10^{-4} M^{-2}$

Spectrophotometry[4]
(t = 18°)

Cd²⁺

$\beta_1 = 18 \pm 3\ M^{-1}$
$\beta_2 = 90 \pm 55\ M^{-2}$

$\beta_1 = 38.9\ M^{-1}$
$\beta_2 = 170\ M^{-2}$
$\beta_3 = 257\ M^{-3}$

Cd–Hg/3 M NaClO₄[5]
(t = 25°)

species, the data have been treated, according to the procedure of the previous paper[1], to determine the unknown values of the equation:

$$\alpha = l_0 \frac{1 + l\,[Cl^-]}{1 + \sum\limits_{j=1}^{N} \beta_j\,[Cl^-]^j}$$

Table II shows the values obtained in this investigation and compares them with the values available from the literature.

DISCUSSION

The data reported in Table II show that equilibria which establish in solution can be determined by means of ion-exchange papers by applying the FRÖNAEUS method. Satisfactory results are obtained for the determination of equilibrium constants for the first or second step of weak complexes. When a system has a higher degree of complexity and the complexes are very stable, the inaccuracy connected with the R_F determination affects the calculations much more and renders the graphic extrapolations unreliable. For example, an error corresponding to ± 0.01 in the determination of R_F, affects the calculation of α by about ± 0.2.

In general therefore, the results are less accurate than ones obtained by means of ion-exchange resins and other standard methods. The procedure, however, offers the advantage of a greater rapidity so that it can be satisfactorily applied, especially on a qualitative basis, to obtain information on the strength of various complexes. The behaviour of α, which is obtained by simple calculations and the trend of the graph α versus ligand concentration, is particularly indicative. The degree of steepness of the curve is an indication of the stability of the complexes. When complexes are also formed at a very low ligand concentration, as in the case of the Cd^{2+}–Cl system, the curve is quite steep.

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SUMMARY

Equilibria which establish in a solution containing a cation (Cu^{2+}, Co^{2+}, Ni^{2+} or Cd^{2+}) and chloride have been studied by means of chromatography on ion-exchange papers; complex formation constants have been determined and the possibilities of this method are discussed and evaluated.

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