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Anion-Exchange Studies of the Copper(II) Acetate, Glycolate, and Tartrate Systems

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The complex formation between copper and acetate, glycolate and tartrate ions has been studied at a temperature of 20°C, using an anion-exchange method.[1] The anion exchanger was saturated in advance with the ligand, and the complex solutions had varying ionic strength.

The distribution of the central ion between the anion exchanger and the solution at equilibrium was studied, and the existence of anionic complexes was confirmed by the appearance of distinct maxima in the distribution functions. The ligand numbers computed from the anion exchange data are in good agreement with those obtained by other methods [2] in the whole investigated region.

Attempts have also been made to compute the stability constants of the systems. The agreement between the values obtained and those previously found [2] in a potentiometric investigation at $I = 1$ M is satisfactory.

The possibility of using anion exchanger resins for the study of anionic complex formation in water solutions has been investigated previously by Fronæus.[1] A method was developed, based on measurements of the distribution of the central ion between the anion exchanger saturated with the ligand and the complex solution at equilibrium between the two phases.

First of all, an anion exchange study can give qualitative information about the formation of anionic complexes in a system. To test the method further and to see if it can be used also for quantitative measurements of complex formation it has been applied in the present paper to the copper acetate, glycolate, and tartrate systems, which have been thoroughly investigated by potentiometric, extinctiometric, and polarimetric methods in an earlier work by Fronæus.[2] The method has been tested previously by Sonesson [3] on the gadolinium glycolate system. Another approach to a quantitative treatment of the sorption by an anion exchanger of metal anion complexes is given by Marcus.[4–7]

THEORY OF THE METHOD

In the derivation of the equations below it is assumed that only mononuclear complexes are formed both in the solution and in the ion-exchanger. This assumption is reasonable because of the low total metal ion concentration in the solution.

The central ion is called M and the ligand A without marking the ionic charges. An index R indicates the resin phase.

For the formation of the complex MA_n we have the following equilibrium

$$MA_{n-1} + A \rightleftharpoons MA_n$$

The corresponding complexity constant β_n is by definition

$$\beta_n = \frac{[MA_n]}{[M]\,[A]^n}$$

Thus introducing the complexity constants we can express the total concentrations of the central ion in the solution, C_M, and in the exchanger phase, C_{MR}, as functions of the ligand concentrations [A] and $[A]_R$, respectively.

$$C_M = [M]\ (1 + \sum_{j=1}^{N} \beta_j\ [A]^j) \tag{1}$$

$$C_{MR} = [M]_R\ (1 + \sum_{j=1}^{N} \beta_{jR}\ [A]_R^j) \tag{2}$$

or $$C_M = [M] \cdot X \tag{3}$$

$$C_{MR} = [M]_R \cdot X_R \tag{4}$$

The distribution of the ion M between the resin and the solution is determined by the Donnan equation

$$[M]_R \cdot [A]_R^{\nu} = K\ [M] \cdot [A]^{\nu} \tag{5}$$

where ν is the ratio between the absolute values of the ionic charges of the central ion and the ligand. The factor K includes the activity coefficients of the ionic species in the two phases.

A combination of eqns. (3)—(5) yields the following expression for the distribution φ

$$\varphi = \frac{C_{MR}}{C_M} = K \cdot \frac{X_R}{[A]_R^{\nu}} \cdot \frac{[A]^{\nu}}{X} \tag{6}$$

If ν is a whole number and if the uncharged complex MA_ν exists, the relation can be given in the following form

$$\varphi = l_\nu \cdot \frac{\alpha_\nu}{\alpha_{\nu R}} \tag{7}$$

with $l_\nu = K\,\beta_{\nu R} \cdot \beta_\nu^{-1}$.

l_ν is the Nernst distribution coefficient for the uncharged complex. α_ν and $\alpha_{\nu R}$ denote the fractions $[MA_\nu] \cdot C_M^{-1}$ and $[MA_\nu]_R \cdot C_{MR}^{-1}$, respectively.

To get a simple relation between φ and [A] the value of $[A]_R$ must be kept approximately constant and thus a neutral salt medium must be spared. Then on the other hand the activity coefficients of the ionic species in the outer solution possibly vary at increasing ligand concentrations. Nevertheless, l_ν can be presumed to be approximately constant, since it refers to an uncharged complex.

As the ligand concentration in the resin phase is approximately constant, $\alpha_{\nu R} = \beta_{\nu R} \cdot [A]_R^{\nu} \cdot X_R^{-1}$ is also a constant, and thus, according to eqn. (7), φ will be proportional to α_ν, that is to the fraction of the central ion in the outer solution being present as an uncharged complex.

If anionic complexes are formed in a system, φ will increase at first with increasing values of [A], then pass through a maximum at the value of [A], where the ligand number $\bar{n}$ in the outer solution is equal to ν, and finally decrease again. On the other hand, if no anionic complexes are formed, φ may be expected to increase uniformly with increasing values of [A] but will always be very slight.

However, the possibility must be taken into consideration that at small values of φ an appreciable part of the sorption C_{MR}, especially at lower values of [A], may be due to adsorption on the surface of the resin, as has been pointed out by Fronæus.[1,8] In addition to the quaternary ammonium groups the anion exchanger may contain amine groups which, even if present in very small concentrations, may form complexes with the central ion M and to a much lesser extent with the complexes MA_j. Thus the presumed amine complexes should be found preferably on the surface of the resin and cause the adsorption mentioned. As [M] decreases when [A] increases, this surface adsorption may be expected to decrease with increasing values of [A].

Calculation of the complexity constants β_j. Eqn. (7) can be transformed to

$$\frac{[A]^{\nu}}{\varphi} = k \cdot X = k + k\beta_1[A] + k\beta_2[A]^2 + \ldots k\beta_N[A]^N \qquad (8)$$

where k is a constant.

If φ and [A] are experimentally determined, the function kX can be calculated for varying ligand concentrations [A]. Then the constants k and $k\beta_j$ are obtained by extrapolations to [A] = 0 of the functions kX_j defined by the relation

$$kX_j = \frac{kX_{j-1} - k\beta_{j-1}}{[A]} \qquad (9)$$

$$(X_0 = X,\ \beta_0 = 1)$$

In reality, the kX-function often decreases so rapidly with decreasing [A] that it is impossible to obtain even an approximate value of k. If k cannot be determined, the complexity constants cannot be computed either. However, even if k is unknown, the stability constants of the system $b_j = \beta_j/\beta_{j-1}$, can be obtained for $j > 1$.

Calculation of $\bar{n}$. The ligand number $\bar{n} = (C_A - [A])/C_M$ can be determined by means of eqn. (6). Derivation of $\ln\varphi$ with respect to $\ln[A]$ yields, if K and $[A]_R$ are considered as constants,

$$\frac{d\ln\varphi}{d\ln[A]} = \nu - \frac{d\ln X}{d\ln[A]} \tag{10}$$

For the ligand number $\bar{n}$ we have the relation $\bar{n} = d\ln X/d\ln[A]$ (Fronæus [2]). Hence

$$\bar{n} = \nu - \frac{d\ln\varphi}{d\ln[A]} \tag{11}$$

The derivative in eqn. (11) can be obtained graphically from plots of $\ln\varphi$ against $\ln[A]$.

MEASUREMENTS AND CALCULATIONS

Chemicals used. All chemicals were, if not stated otherwise, of analytical grade and used without further purification.

Copper perchlorate was prepared in the following manner. From a hot solution of copper sulphate, copper oxide was precipitated by sodium carbonate. The precipitate was dissolved in a perchloric acid solution and the excess of perchloric acid was removed by repeated crystallization. A stock solution was prepared, the concentration of which was determined by electrolysis.

Stock solutions of acetic acid and sodium acetate were prepared and standardized, the first one by an alkalimetric titration, the second one by passing a known volume of the solution through an ion exchanger in the hydrogen form followed by an alkalimetric titration of the acid. A buffer stock solution was prepared by mixing acetic acid and sodium acetate in the proportion 1:5. The concentrations of acid and acetate were controlled.

Glycolic acid (Fluka *puriss.*) was dried *in vacuo* over concentrated sulphuric acid. After drying the equivalent weight was determined to 76.0 (calc. 76.0). A buffer stock solution of glycolic acid and sodium glycolate in the proportion 1:5 was prepared by partial neutralization of calculated amounts of dried acid by carbonate-free sodium hydroxide. Afterwards the concentrations of glycolic acid and sodium glycolate were checked.

A sodium D-tartrate stock solution was prepared and standardized by means of a cation exchanger column in the hydrogen state.

The anion exchanger was Dowex 2 × 8, containing fixed quaternary ammonium groups. It was converted to the acetate, glycolate or tartrate forms and air-dried.

Method of investigation. In the measurements of the copper acetate and glycolate systems the complex solutions had the initial composition

$$C_M'\ \text{mM}\ Cu(ClO_4)_2 + C_A'\ \text{mM}\ NaA + 0.2\ C_A'\ \text{mM}\ HA$$

For the copper tartrate system no buffer solution could be used, as in such a case the ion HA^- would have appeared as a ligand too. The initial composition of the complex tartrate solutions was consequently

$$C_M'\ \text{mM}\ Cu(ClO_4)_2 + C_A'\ \text{mM}\ Na_2A$$

C_M' had a constant value in the same measurement series. m grams of the air-dried exchanger were shaken for 20 h in a thermostat at 20.0°C with v litres of the complex solution. It was checked that a longer time of shaking did not affect the distribution of copper. The value of vm^{-1} was always constant (0.015 lg^{-1}).

When a distribution equilibrium had been reached, the exchanger was carefully separated from the outer solution by means of a small glass-filter funnel, and the equilibrium concentration C_M of the water phase was deter-

mined. As the sorption was found to be very slight at all concentrations of acetate, glycolate and tartrate ions, C_{MR} could not be obtained indirectly with great accuracy by means of the relation $C_{MR} = vm^{-1}(C_M' - C_M\delta)$, where δ represents the swelling factor of the resin, but had to be determined directly by eluting the resin. After the resin had been transferred to another glass-filter funnel it was treated with v_1 litres 1 M $NaClO_4$ in small portions. The value of v_1m^{-1} was here 0.030 lg^{-1}. After this treatment the elution was tested as to completeness with regard to copper as well as acetate, glycolate and tartrate ions. The copper concentration C_M'' of the eluate was determined, and the load C_{MR} was calculated by means of the relation $C_{MR} = v_1m^{-1}C_M''$.

However, a certain amount of the outer solution adhered to the particles of the resin, which could not be washed before the elution (*cf.* Fronæus[9]). An approximate value of the contribution to C_M'' due to the adhering solution and also to the phenomenon "surface adsorption" mentioned above was obtained in the following way. In special measurements m grams of an air-dried exchanger in the perchlorate form were shaken with a solution of the volume v and of the composition: C_M' mM $Cu(ClO_4)_2$ + C_A' mM $NaClO_4$. The experiments were performed in the same manner as before and the eluates were analysed with regard to copper. The C_M''-value arrived at in these measurements was subtracted as a correction term.

The copper(II) concentrations were determined extinctiometrically by means of "tetra", a shortening of the name of the colorimetric copper reagent disodium ethyl bis(5-tetrazolylazo)acetate.[10]

Tetra forms a stable, intensely coloured 1 to 1 complex with copper(II) ions, with an adsorption peak (among others) at 535 mμ. As a copper reagent it is very sensitive. The pH-values of the solutions to be measured ought to be between 5 and 8, because the light absorption characteristics of the acid form of tetra are different and, at too high pH-values, a precipitation of the copper(II) hydroxide may taken place. The extinction is not quite unaffected by the presence of varying amounts of acetate, glycolate and tartrate ions, but the effects of the disturbing ions are rather small and can easily be corrected for.

The equilibrium concentration [A] of the free ligand in the solution was computed from C_A'. At low values of C_A' the small amounts of perchlorate ions in the solutions are nearly completely exchanged for the ions A. Thus, taking into consideration the swelling of the resin, we have the relation $[A] = C_A' \cdot \delta^{-1} + \nu C_M$. Other correction terms, due to *e.g.* ligand ions bound in the complexes MA_j and to ligand ions produced by the protolysis of the acid HA, can safely be neglected in the present investigation.

The swelling factor is approximately given as the ratio between the initial and equilibrium concentrations of sodium ions. These concentrations were determined by means of a cation exchanger column in the hydrogen form. The sum of the concentrations of sodium salt and acid was obtained in this way at first. The concentration of acid was then obtained separately by an alkalimetric titration.

Fig. 1 shows the variation of the swelling factor δ with the ligand concentration in the outer solution for the three systems investigated.

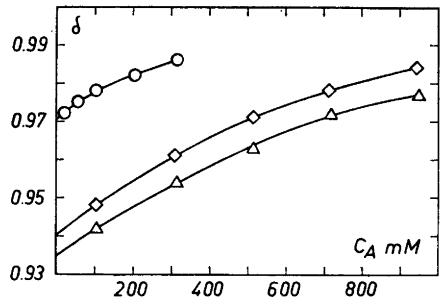

Fig. 1. The variation of the swelling factor δ with the total concentration of ligand in the solution. The curves refer to a) the acetate system (△), b) the glycolate system (◇) and c) the tartrate system (○).

The copper acetate system. The data from the anion exchange measurements of the copper acetate system are collected in Tables 1 and 2. In Fig. 2 the distribution φ has been plotted against [A]. It can be seen that φ has a maximum at [A] $\approx$ 250 mM, indicating that $\bar{n}$ has attained the value 2. Then, at ligand concentrations $>$ 250 mM, φ decreases at increasing values of [A], owing to the formation of anionic complexes.

The ligand number in the outer solution, $\bar{n}$, was calculated by means of eqn. (11). In this case $\nu = 2$. The term $d\ln\varphi/d\ln[A]$ was obtained graphically from a plot of $\log\varphi$ against $\log[A]$ (Fig. 3). The values obtained of the ligand number are given in Table 1, column 6. For the sake of comparison, $\bar{n}$ was also computed by means of the values of the complexity constants, previously obtained[2] in potentiometric measurements at a constant ionic strength 1 M. The agreement between the two sets of ligand numbers is very good.

Attempts have also been made to use the kX_j-functions for calculations of k and the products $k\beta_j$. However, $\bar{n}$ is already equal to 1.0 at the lowest

Table 1. Anion exchange measurements of the copper acetate system. $C_M' = 0.3240$ mM.

[A] mM	C_M mM	$C_{MR} \times 10^4$ mmole·g^{-1}	$\varphi \times 10^4$ l·g^{-1}	$\frac{d\ln\varphi}{d\ln[A]}$	$\bar{n}$	$\bar{n}_{pot}$
18.5	0.334	0.36	1.10			0.60
36.0	0.332	0.70	2.10	1.0	1.0	0.90
71.0	0.332	1.06	3.20	0.6	1.4	1.28
105	0.330	1.24	3.75	0.4	1.6	1.54
160	0.323	1.34	4.15	0.2	1.8	1.81
210	0.320	1.41	4.40	0.1	1.9	2.02
265	0.317	1.43	4.50	−0.1	2.1	2.16
315	0.322	1.40	4.35	−0.2	2.2	2.32
365	0.323	1.38	4.25	−0.3	2.3	2.43
415	0.325	1.34	4.10	−0.4	2.4	2.51
515	0.327	1.25	3.80	−0.5	2.5	2.67
615	0.328	1.15	3.50	−0.6	2.6	2.78
720	0.329	1.07	3.25	−0.7	2.7	2.88
815	0.331	0.98	2.95	−0.8	2.8	2.96
950	0.332	0.88	2.65	−1.0	3.0	3.04

Table 2. Calculation of the stability constants of the copper acetate system.

[A] mM	$\frac{[A]^2}{\varphi} = kX$ $M^2 \cdot g \cdot l^{-1}$	kX_1 $M \cdot g \cdot l^{-1}$	kX_2 $g \cdot l^{-1}$	kX_3 $M^{-1} \cdot g \cdot l^{-1}$
0	*<2*	*90*	*1100*	*2700*
18.5	3.1			
36.0	6.2			
71.0	15.8	190		
105	29.4	260		
160	62	380		
210	100	470		
265	156	580	1850	2800
315	228	720	2000	2900
365	310	850	2100	2700
415	420	1010	2200	2700
515	700	1360	2500	2700
615	1080	1760	2700	2600
720	1600	2200	2900	2500
815	2250	2800	3300	2700
950	3400	3600	3700	2700

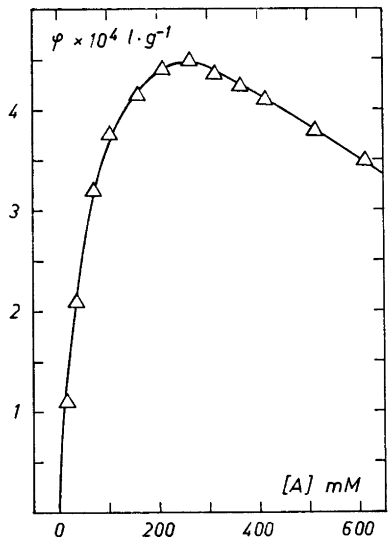

Fig. 2. The distribution φ of the copper acetate system as a function of the free acetate concentration in the solution, [A].

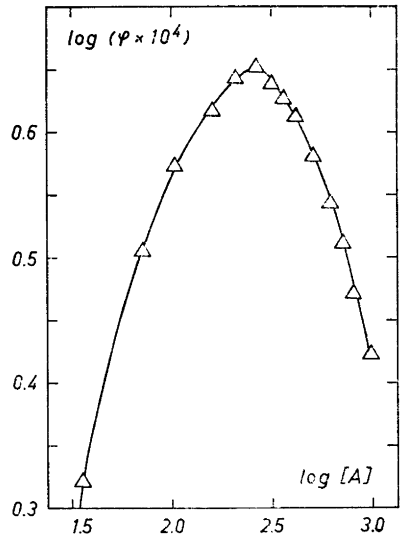

Fig. 3. Logφ represented as a function of log[A] for the copper acetate system. The slope of the curve gives the derivative in eqn. (11), $d\ln\varphi/d\ln[A]$.

value of [A] for which φ can be measured with sufficient accuracy. This means that the term k in eqn. (8) cannot be determined separately. By extrapolation of the function kX only an upper limit, *viz.* $k<2$ M²·g·l⁻¹, is obtained. Successive extrapolations to [A] = 0 of the kX$_j$-functions give the following values of $k\beta_j$:

$k\beta_1 = 90 \pm 20$ M·g·l⁻¹, $\quad k\beta_2 = 1100 \pm 300$ g·l⁻¹,
$k\beta_3 = 2700 \pm 800$ M⁻¹·g·l⁻¹

No value of $k\beta_4$ can be obtained, since the small increase in $\bar{n}$ at the highest ligand concentrations used lies nearly within the limits of the random errors in $\bar{n}$. Thus the present measurements can indicate the formation of only three complexes with certainty.

As no value of k can be obtained, only the stability constants $b_j = \beta_j/\beta_{j-1}$ can be computed for $j>1$. The following values are found:

$b_1>45$ M⁻¹, $\quad b_2 = 12 \pm 5$ M⁻¹,
$b_3 = 2.5 \pm 1.2$ M⁻¹

These values agree very well with those found previously in potentiometric measurements.[2] In Table 7 a comparison is given between the two sets of constants.

The copper glycolate system. The data from the measurements of the copper glycolate system are collected in Tables 3 and 4. In Fig. 4 the distribution φ is plotted against the ligand concentration [A]. The φ-function shows a distinct maximum at the ligand concentration 150 mM, indicating that anionic glycolate complexes are formed at higher ligand concentrations. The φ-values of the glycolate system are about six times higher than the corresponding ones of the acetate system, but the form of the φ-curve is similar.

Table 3. Anion exchange measurements of the copper glycolate system. $C_M' = 0.3240$ mM.

[A] mM	C_M mM	$C_{MR} \times 10^4$ mmole·g⁻¹	$\varphi \times 10^3$ l·g⁻¹	$\frac{d\ln\varphi}{d\ln[A]}$	$\bar{n}$	$\bar{n}_{pot}$
0.7	0.334	1.00	0.30			0.15
9.5	0.313	2.95	0.94			0.70
27.0	0.296	5.10	1.70	0.8	1.2	1.20
44.5	0.292	6.45	2.20	0.5	1.5	1.50
71.0	0.288	7.50	2.60	0.2	1.8	1.70
105	0.287	7.95	2.75	0.1	1.9	1.88
160	0.287	8.05	2.80	−0.1	2.1	2.06
210	0.288	7.75	2.70	−0.2	2.2	2.18
260	0.288	7.50	2.60	−0.2	2.2	2.30
310	0.290	7.20	2.50	−0.3	2.3	2.38
415	0.292	6.75	2.30	−0.4	2.4	2.53
515	0.294	6.30	2.15	−0.5	2.5	2.64
615	0.296	5.80	1.95	−0.6	2.6	2.75
715	0.298	5.35	1.80	−0.7	2.7	2.83
815	0.301	5.05	1.70	−0.8	2.8	2.90
945	0.303	4.55	1.50	−1.0	3.0	2.98

Table 4. Calculation of the stability constants of the copper glycolate system.

[A] mM	$\frac{[A]^2}{\varphi} = kX$ $M^2 \cdot g \cdot l^{-1}$	kX_1 $M \cdot g \cdot l^{-1}$	kX_2 $g \cdot l^{-1}$	kX_3 $M^{-1} \cdot g \cdot l^{-1}$
0		*9*	*230*	*450*
0.7	0.002			
9.5	0.096	10.1		
27.0	0.43	15.9		
44.5	0.90	20.0		
71.0	1.94	27.0	250	
105	4.0	38.0	280	480
160	9.1	57.0	300	440
210	16.3	78.0	330	480
260	26.0	100	350	460
310	38	123	370	450
415	75	181	410	430
515	123	240	450	430
615	194	320	500	440
715	284	400	550	450
815	390	480	580	430
945	600	630	660	460

The values of $\bar{n}$ in Table 3, column 6 were calculated by means of eqn. (11) in the way described before. As a comparison the values found in potentiometric measurements [2] at the ionic strength 1 M are given. The agreement between the two sets of values is good.

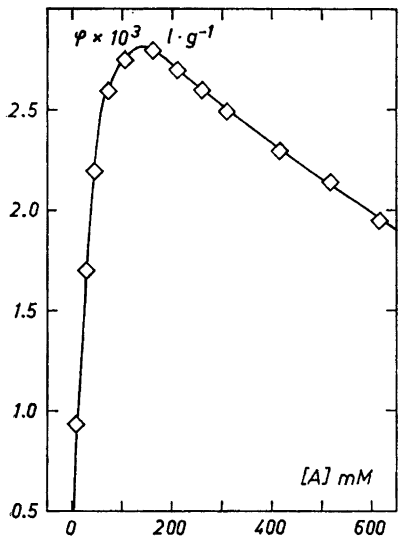

Fig. 4. The distribution φ as a function of the ligand concentration [A] for the copper glycolate system.

Values of the kX_j-functions for different ligand concentrations are given in Table 4. The kX-function decreases so rapidly with decreasing [A] that it is impossible to obtain even an approximate value of k, but the functions with $j \geq 1$ give the following values at extrapolations to [A] = 0:

$k\beta_1 = 9 \pm 2$ M·g·l^{-1}, $k\beta_2 = 230 \pm 60$ g·l^{-1},

$k\beta_3 = 450 \pm 150$ M^{-1}·g·l^{-1}

The fourth complex is not formed in sufficient amounts to permit a determination of $k\beta_4$ in this investigation.

As no value of k can be obtained, the complexity constants of the system cannot be computed either. For the stability constants the following values are found:

$b_2 = 26 \pm 10$ M^{-1}, $b_3 = 2.0 \pm 1.0$ M^{-1}

The values calculated above are in accordance with those previously found in a potentiometric investigation [2] (*cf.* Table 7).

The copper tartrate system. The data from the measurements of the tartrate system are given in Tables 5 and 6, and in Fig. 5 the function φ is graphically represented.

At [A] $\approx$ 6 mM a pronounced maximum in the φ-curve is obtained, indicating that anionic complexes are formed in appreciable amounts at higher tartrate concentrations, in agreement with already established facts.[2] The φ-values of the tartrate system are much higher than the corresponding ones of the two systems earlier described, owing to the stronger tendency to complex formation within the tartrate system.

The ligand numbers $\bar{n}$ at varying tartrate concentrations are collected in Table 5, column 6. In this case $\nu = 1$. A comparison between the values

Table 5. Anion exchange measurements of the copper tartrate system. $C_M' = 0.3240$ mM.

[A] mM	C_M mM	$C_{MR} \times 10^3$ mmole·g^{-1}	$\varphi \times 10^2$ l·g^{-1}	$\frac{d\ln\varphi}{d\ln[A]}$	$\bar{n}$	$\bar{n}_{pot}$
0.3	0.0246	4.50	18.5			0.35
0.9	0.0154	4.65	30.0	0.4	0.6	0.65
1.5	0.0134	4.65	34.5	0.3	0.7	0.80
2.6	0.0121	4.70	39.0	0.2	0.8	0.98
4.9	0.0115	4.70	41.0	0.0	1.0	1.19
7.8	0.0115	4.70	41.0	−0.3	1.3	1.30
10.6	0.0131	4.65	35.5	−0.5	1.5	1.44
15.7	0.0160	4.65	29.0	−0.5	1.5	1.55
20.9	0.0184	4.60	25.0	−0.6	1.6	1.64
26.0	0.0210	4.55	21.5	−0.7	1.7	1.70
31.0	0.0234	4.50	19.0	−0.8	1.8	1.76
41.5	0.0305	4.45	14.5	−0.9	1.9	1.85
51.5	0.0366	4.35	12.0	−1.0	2.0	1.94
102	0.0710	3.80	5.35	−1.2	2.2	2.30
204	0.1450	2.75	1.90	−1.7	2.7	2.95
315	0.2040	1.85	0.90	−2.2	3.2	3.40

Table 6. Calculation of the stability constants of the copper tartrate system.

[A] mM	$\frac{[A]}{\varphi} = kX$ M·g·l^{-1}	kX_1 g·l^{-1}	kX_2 M^{-1}·g·l^{-1}	kX_3 M^{-2}·g·l^{-1}
0	*0.001*	*1.4*	*100*	*700*
0.3	0.0016			
0.9	0.0030			
1.5	0.0043			
2.6	0.0067			
4.9	0.0120			
7.8	0.0190	2.30		
10.6	0.0299	2.70		
15.7	0.054	3.40		
20.9	0.084	4.00		
26.0	0.121	4.60		
31.0	0.163	5.20		
41.5	0.286	6.90	130	700
51.5	0.43	8.40	140	800
102	1.91	18.7	170	700
204	10.7	53.0	250	700
315	35.0	111	350	800

obtained by the anion-exchange method and those computed from previous potentiometric data [2] shows that in spite of the differences in ionic strength the agreement between the two sets of values is good.

Calculated values of the polynomial kX are given in Table 6, column 2. By extrapolation of this function to [A] = 0 we obtain $k = (1.0 \pm 0.1) \times 10^{-3}$

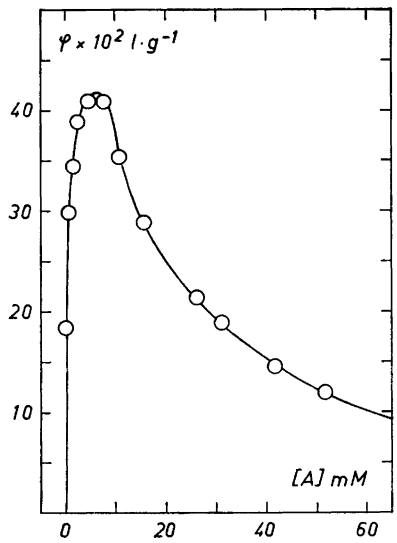

Fig. 5. The distribution function $\varphi([A])$ for the copper tartrate system.

M·g·l^{-1}. Then by successive extrapolations to [A] = 0 of the functions kX_j the following values of $k\beta_j$ are found:

$k\beta_1 = 1.4 \pm 0.3$ g·l^{-1}, $k\beta_2 = 100 \pm 25$ M^{-1}·g·l^{-1},

$k\beta_3 = 700 \pm 200$ M^{-2}·g·l^{-1}

From the values of k and $k\beta_j$ above the following values of the complexity constants β_j are calculated:

$\beta_1 = (1.4 \pm 0.4) \times 10^3$ M^{-1}, $\beta_2 = (1.0 \pm 0.3) \times 10^5$ M^{-2},

$\beta_3 = (7 \pm 3) \times 10^5$ M^{-3}

For the stability constants b_j the following values are found:

$b_1 = 1400 \pm 400$ M^{-1}, $b_2 = 70 \pm 30$ M^{-1},

$b_3 = 7.0 \pm 3.0$ M^{-1}

The stability constants obtained are, with the exception of b_3, of the same order of magnitude as those determined potentiometrically [2] at the ionic strength 1 M (Table 7). The cause of the difference between the two b_3-values may be that in the present investigation, effects ascribed to the third complex are partly caused by a fourth complex.

DISCUSSION

According to Fronæus [1] the values of φ_{max} for systems of equal type give a qualitative measure of the strength of the anionic complexes formed in the resin phase. The increasing orders of magnitude of the φ_{max}-values for the copper systems investigated, combined with the fact that the maxima of the φ-functions appear at decreasing concentrations of the ligand in the outer solution, indicate accordingly that the tendency to anionic complex formation in both phases increases in the order: acetate, glycolate and tartrate, a conclusion that is in agreement with the measurements.

Anionic complexes can thus be formed in the solution as well as in the resin phase for all the three complex systems investigated. The sorption of

Table 7. The stability constants and the ratios between consecutive stability constants of the investigated copper(II) complexes

Ligand	Anion exchange measurements							Potentiometric measurements[2]						
	b_1	b_2	b_3	b_4	$\frac{b_1}{b_2}$	$\frac{b_2}{b_3}$	$\frac{b_3}{b_4}$	b_1	b_2	b_3	b_4	$\frac{b_1}{b_2}$	$\frac{b_2}{b_3}$	$\frac{b_3}{b_4}$
Ac^-	> 45	12	2.5		> 3.8	4.8		47	9.6	2.6	0.65	4.9	3.7	4.0
$AcOH^-$		26	2.0			13		220	23	2.0	0.60	9.6	11.5	3.3
T^{2-}	1400	70	7.0		20	10		1600	80	0.5	50	20	160	0.01

copper by an anion exchanger saturated with acetate, glycolate or tartrate ions is of a much lower order of magnitude than *e.g.* the sorption of cadmium in the cadmium bromide system,[1] though at least the tartrate system has a stronger tendency to anionic complex formation in water solution. This fact may indicate that the anionic complexes in the resin phase are not easily formed within the present systems, perhaps because of a steric hindrance, which reduces the tendency to complex formation.

The ligand numbers $\bar{n}$ as well as the stability constants b_j computed on the basis of the anion exchange data obtained are in good agreement with those found potentiometrically[2] in the whole concentration range of the investigated ligand (*cf.* Tables 1, 3, 5, and 7). The agreement between the two sets of values is unexpectedly good considering the fact that the potentiometric measurements were performed at a constant ionic strength, $I = 1$ M, whereas the complex solutions in the present anion-exchange study had an ionic strength, varying from about 0.1 to 1.0 for the values of [A] used in the calculations.

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