

A Study of the Complex Formation between Copper(II) and Acetate, Glycolate, and Tartrate Ions in an Anion Exchanger Phase

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The complex formation of the copper acetate, glycolate and tartrate systems in an anion exchanger, containing quaternary ammonium groups (Dowex 2 × 8) has been studied at a temperature of 20.0°C. The ionic strength of the water phase was approximately constant, 1 M, with sodium perchlorate as supporting electrolyte. Owing to a slight dependence of the swelling factor on the ligand concentration of the resin, the ionic strength in the exchanger was not quite constant.

The ligand number in the resin phase, \bar{n}_R , was calculated from the distribution of copper between the complex solutions and the anion exchanger at equilibrium. It was found to increase with increasing ligand concentrations towards the limiting value 4.

Stability constants were computed for the complex systems in the resin phase and compared with those previously found in water solutions at the ionic strength 1 M.

For the study of anionic complex formation in water solutions an anion-exchange method has previously been devised by Fronæus.¹ It was 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. When this method was applied to the copper(II) acetate, glycolate, and tartrate systems² it was found that the sorption of copper was remarkably low in comparison with, *e.g.*, the sorption of cadmium in the bromide system,¹ though the tartrate system at least has a stronger tendency to anionic complex formation in water solutions. The differences could be due to a very slight formation of anionic copper complexes in the resin phase, perhaps because of a steric hindrance preventing the formation of higher complexes. In order to answer this question and to find out how the stepwise complex formation proceeds in an exchanger phase at increasing concentrations of large anionic ligands, the present investigation was started.

The method used has been elaborated by Fronæus *et al.*³ The ionic strength of the water solution is kept approximately constant by addition of a salt medium, and thus the ligand concentration in the resin phase varies with the corresponding concentration in the solution. If the complexity constants in the outer solution are known, the theory permits calculation of the ligand number and also of the complexity constants in the resin phase.

The method has previously been tested in two complex systems, the cadmium bromide system³ and the gadolinium glycolate system.⁴ In the present investigation it is applied to three copper(II) systems, the complexity of which in water solutions is well known at the ionic strength 1 M (*cf.* Fronæus⁵), *viz.* the acetate, glycolate, and tartrate systems.

THEORY OF THE METHOD

In the present paper only definitions of the symbols and a summary of the equations used are given. For further details about the theoretical treatment the original paper³ should be consulted.

The following notations are used:

C'_M, C'_A = the total concentrations of metal ion and ligand in the solution before addition of the ion-exchanger.

C_M, C_A = the total concentrations of metal ion and ligand in the solution at equilibrium with the ion exchanger.

C_{MR}, C_{AR} = the loads of metal ion and ligand on the exchanger.

$[M], [MA_j], [A]$ = the equilibrium concentrations of the species in the solution.

$[M]_R, [MA_j]_R, [A]_R$ = the equilibrium concentrations of the species in the resin phase.

β_j = the complexity constant for the complex MA_j in the solution.

β_{jR} = the complexity constant for the complex MA_{jR} in the resin phase.

$$X = 1 + \sum_{j=1}^N \beta_j [A]^j$$

$$X_R = 1 + \sum_{j=1}^N \beta_{jR} [A]_R^j$$

$$X_{jR} = \frac{X_{j-1,R} - \beta_{j-1,R}}{[A]_R} \quad (X_{0R} = X_R, \beta_{0R} = 1)$$

$$\bar{n} = (C_A - [A]) / C_M$$

$$\bar{n}_R = (C_{AR} - [A]_R) / C_{MR}$$

v = the volume of the solution before the resin is added.

m = the weight in grams of the air-dried resin.

δ = the swelling factor of the ion-exchanger.

For the distribution ($\varphi = C_{MR} / C_M$) of the central ion between the anion exchanger and the aqueous solution the following relation has been obtained³

$$\varphi = K \frac{X_R}{[A]_R^p} \cdot \frac{[A]^p}{X} \quad (1)$$

where the factor K includes activity coefficients of the ionic species M and A in the two phases. ν is the ratio between the absolute values of the ionic charges of the central ion and the ligand. The ionic strength of the water phase is kept approximately constant by addition of a neutral salt.

Calculation of \bar{n}_R . If the activity coefficients for the two phases can be presumed to be approximately constant under the experimental conditions, the ligand number in the resin phase, \bar{n}_R , can be obtained from the relation:³

$$\bar{n}_R = \nu + \frac{d \ln \varphi}{d \ln [A]_R} + (\bar{n} - \nu) \frac{d \ln [A]}{d \ln [A]_R} \quad (2)$$

Thus, to be able to compute \bar{n}_R , we must determine φ , $[A]_R$ and $[A]$ by experiment. The derivatives in eqn. (2) can then be obtained from plots of $\log \varphi$ and $\log [A]$ against $\log [A]_R$. The ligand number in the outer solution, \bar{n} , is computed from the known complexity constants in the water phase. The following relation holds:⁵

$$\bar{n} = \frac{C_A - [A]}{C_M} = \frac{X'[A]}{X} \quad (3)$$

X' stands for the derivative of X with respect to $[A]$.

Calculation of the complexity constants β_{jR} . If corresponding values of φ , $[A]_R$, and $[A]$ are known, the function KX_R can be computed from eqn. (1) for varying ligand concentrations $[A]_R$. Then it is at least theoretically possible to calculate the constants K and $K\beta_{jR}$ by extrapolations to $[A]_R = 0$ of the quantities KX_R .

In general, however, it is not possible to obtain a safe value of K by extrapolation, owing to the uncertain determination of φ at low $[A]_R$ -values and the rapid decrease of the KX_R -function at decreasing $[A]_R$. Consequently, even the obtained complexity constants will be rather uncertain. However, the stability constants of the system, $b_{jR} = \beta_{jR}/\beta_{j-1,R}$, can be calculated for $j > 1$ even if K is unknown.

Eqn. (1) is general and does not presuppose the existence of an uncharged complex, MA_ν . In those cases where such a complex does exist, however, the Nernst distribution coefficient for this complex, l_ν , can be determined by means of the relation³

$$K = l_\nu \cdot \beta_\nu \cdot \beta_{\nu R}^{-1} \quad (4)$$

MEASUREMENTS AND CALCULATIONS

Chemicals used. The solutions used in the present investigation were prepared and analysed in the way described in the preceding parts.^{2,3}

The anion exchanger was, as before, Dowex 2×8 , containing quaternary ammonium groups. It was transferred into the acetate, glycolate or tartrate forms and air-dried.

Method of investigation. The complex acetate and glycolate solutions had the initial composition C'_M mM $\text{Cu}(\text{ClO}_4)_2 + C'_A$ mM $\text{NaA} + 0.2 C'_A$ mM $\text{HA} + (1000 - C'_A)$ mM NaClO_4 .

The complex tartrate solutions could not be prepared from a tartrate buffer stock solution, however, as in such a case, the ion HA^- , would have appeared as a ligand in addition to A^{2-} . The composition of the complex tartrate solutions was consequently C'_M mM $\text{Cu}(\text{ClO}_4)_2 + C'_A$ mM $\text{Na}_2\text{A} + (1000 - 3 C'_A)$ mM NaClO_4 .

The value of C'_M ought to be as low as possible to avoid polynuclear complex formation and the influence of variations in the total concentrations of C_M and C_{MR} on the constancy of the activity coefficients. A lower limit of the applicable concentration range of C'_M is set by the sensitivity of the analytical method used. It is best, of course if it is possible to work at tracer concentrations. Unfortunately, there is no copper isotope with a half-life suitable for activity measurements and so a not quite so sensitive extinctionometric method of analysis had to be chosen. C'_M was kept constant at 0.3240 mM in the measurement series and the initial ionic strength of the solutions was always 1.00 M, sodium perchlorate being added to give the correct ionic strength.

A fixed volume (v litres) of the complex solution was shaken for 20 h in a thermostat at 20.0°C with a fixed amount (m grams) of the air-dried resin. The value of $v \cdot m^{-1}$ was 0.015 l·g⁻¹.

After attaining a distribution equilibrium the resin phase was separated from the solution by means of a glass-filter funnel. The resin grains were transferred to a second funnel and were eluted by v_1 litres 1 M NaClO₄ in small portions. The value of $v_1 \cdot m^{-1}$ was here 0.030 l·g⁻¹, an amount which proved to be sufficient for the complete elution of the resin phase.

The total concentrations of copper and ligand ions in the outer solution (C_M, C_A) and in the eluate (C''_M, C''_A) were determined according to methods which will be described below and the loads on the exchanger (C_{MR}, C_{AR}) were calculated by means of the relations

$$C_{MR} = v_1 m^{-1} C''_M \text{ and } C_{AR} = v_1 m^{-1} C''_A$$

As the resin particles could not be completely freed from adherent solution before the elution of the resin, there was a certain contribution in the thus calculated C_{MR} and C_{AR} values due to outer solution adsorbed. In order to obtain the real C_{MR} and C_{AR} values we must make an estimate of the volume of the adhering solution. In the present investigation this estimate was performed from measurements of the copper perchlorate system. The choice is based on the assumption that with this system the load on the exchanger can be regarded as being an almost pure contribution of adherent solution. 1 g of the air-dried, perchlorate-saturated exchanger was shaken with 15 ml of a solution, the initial composition of which was C'_M mM Cu(ClO₄)₂ + C'_A mM NaClO₄. The resin was separated from the solution and eluted in the same way as before. The φ -values obtained in this case were low and rather constant. From the measurements it was concluded that the volume of the adhering solution was about 0.15 ml·g⁻¹. Therefore, in the calculations of C_{MR} and C_{AR} this quantity has been subtracted as a correction.

The copper concentration in the complex solutions was determined in the way described in the preceding paper,² by extinctionometric measurements at 535 m μ after addition of the colorimetric copper reagent "tetra".⁶

To find good methods for the determination of the free ligand concentration in the solutions was more problematic. Different methods were tried. Those giving the best reproducibility, will be described below.

For the acetate and the glycolate systems the concentration of free ligand, [A⁻], can be determined by means of the relation

$$[A^-] = K_c \cdot [HA]/[H^+] \quad (5)$$

K_c stands for the dissociation constant of the acid.

In the present investigation [H⁺] was determined potentiometrically by means of a quinhydrone electrode. The total concentration of acid $C_{HA} = [HA] + [H^+]$ was obtained by an alkalimetric titration. Then, if the dissociation constant of the acid is known for the ionic medium in question, the ligand concentration [A⁻] can be calculated according to eqn. (5).

It is to be noticed, however, that in spite of the use of a salt medium, K_c is not a constant. As is evident from measurements made by Ahrlund⁷ and Sonesson,⁸ the addition of undissociated glycolic acid as well as the exchange of perchlorate for glycolate ions have a marked influence on the ionic medium. If C'_A is kept constant, K_c increases with C'_{HA} and if C'_{HA} is kept constant, K_c varies with C'_A . If the ratio between C'_{HA} and C'_A is kept as low as 0.2, however, as in the present investigation, these effects are negligible and K_c may be regarded as a constant.

The dissociation constant of acetic acid is not affected to the same extent as that of glycolic acid by changes in the ionic medium⁹ and can be regarded as a constant in the investigated concentration range.

Of course, the method cannot be applied to the complex tartrate solutions, as no secondary tartrate buffer was used in the present investigation.

Another method to determine the ligand concentration, applicable to all the three complex systems studied, is a spectrometric one. The glycolate concentration, for instance, can be determined by measuring the extinction of a solution to which a constant amount of $\text{Cu}(\text{ClO}_4)_2$ has been added so that the glycolate ions are forming copper glycolate complexes. According to Frønaes,⁵ the copper glycolate system has an intense light absorption in the ultra-violet range. A suitable wave-length for extinctionometric measurements is about 290 $\text{m}\mu$, at which wave-length neither $\text{Cu}(\text{ClO}_4)_2$, NaClO_4 , nor glycolic acid have any observable light absorption. The glycolate concentration in the measuring solution is then obtained from a calibration curve, showing the extinction as a function of the glycolate concentration in the solution.

The spectrometric method of analysis is applicable to the acetate and tartrate systems as well. Suitable wave-lengths for extinctionometric measurements are here 300 $\text{m}\mu$ and 290 $\text{m}\mu$, respectively.

The two analytical methods described have been used parallelly, each acetate and glycolate solution being analysed according to both the methods. The reproducibility as well as the agreement between data obtained by different methods were quite satisfactory. The tartrate solutions were analysed according to the spectrometric method only.

To be able to express the concentrations in the resin phase in moles per litre, the volume of water in the resin phase must be known. It can be obtained as the sum of two contributions, *viz.* the water still left in the air-dried resin and the water taken up by the exchanger during the swelling procedure. The first quantity can be determined as the loss of weight of the air-dried resin when dried further at about 80°C till a constant weight is reached. The values obtained for the resin in the acetate, glycolate and tartrate states were 0.144, 0.117, and 0.107 g water per g air-dried resin, respectively. The volume of water absorbed during the swelling procedure was 15 (1- δ) ml per g air-dried resin, the symbol δ representing the swelling factor of the resin.

The swelling factor is approximately given as the ratio between the initial concentration and the equilibrium one of sodium ions in solutions with $C'_M = 0$. These concentrations were determined by means of a cation exchanger column in the hydrogen state. In the measurements of the acetate and glycolate systems, where the solutions were

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

C_M mM	δ	$C_{MR} \times 10^4$ mmole·g ⁻¹	C_{MR} mM	C_A M	C_{AR} mmole·g ⁻¹	C_{AR} M	φ
0.338	0.996	0.011	0.005	0.195	0.010	0.050	0.015
0.338	0.996	0.016	0.008	0.275	0.017	0.083	0.024
0.338	0.996	0.016	0.008	0.355	0.027	0.130	0.024
0.338	0.995	0.019	0.009	0.440	0.034	0.160	0.027
0.337	0.995	0.022	0.010	0.520	0.047	0.225	0.030
0.337	0.995	0.028	0.013	0.605	0.055	0.255	0.039
0.335	0.995	0.035	0.016	0.675	0.076	0.350	0.048
0.334	0.994	0.042	0.019	0.760	0.108	0.480	0.057
0.334	0.994	0.057	0.024	0.850	0.156	0.670	0.072
0.334	0.992	0.130	0.050	0.900	0.325	1.25	0.150
0.332	0.990	0.235	0.079	0.915	0.530	1.80	0.240
0.329	0.987	0.425	0.125	0.935	0.850	2.50	0.380
0.328	0.984	0.800	0.205	0.950	1.32	3.40	0.625
0.327	0.981	1.07	0.250	0.960	1.66	3.90	0.765
0.326	0.978	1.67	0.350	0.975	2.25	4.75	1.07
0.324	0.977	2.08	0.420	0.990	2.65	5.40	1.30

buffered, the data obtained in this way represent the total concentrations of sodium salts and acid in the solutions. The concentration of acid was then solely determined by a separate alkalimetric titration and so the concentration of sodium ions could be computed.

The copper acetate system. The anion-exchange data from the measurements of the copper acetate system are collected in Tables 1–3. The initial concentration of copper (C'_M) was always 0.3240 mM. In Table 1, columns 3–4 and 6–7, the loads on the exchanger of metal ion and ligand, C_{MR} and C_{AR} , are given in two concentration units, viz. in mmoles per gram air-dried resin and in mmoles or moles per litre. In column 8 the distribution φ has been computed, the values of C_{MR} in molarity being used, and in Fig. 1 φ is graphically represented as a function of the ligand concentration C_{AR} .

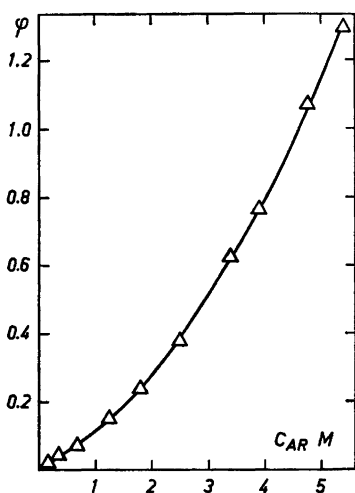


Fig. 1. The distribution φ of the copper acetate system as a function of the acetate concentration in the resin phase, C_{AR} .

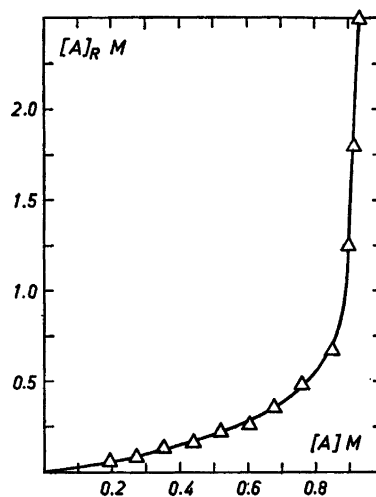


Fig. 2. The acetate ion concentration in the resin phase, $[A]_R$, as a function of the acetate ion concentration in the outer solution, $[A]$.

As the amount of water in the resin phase varies with the ionic composition in the resin, the condition prescribed in the theoretical part, that the ionic strength should be constant, is not entirely fulfilled in the resin phase. From the decreasing δ -values in Table 1, column 2, it is evident that the amount of water, absorbed during the swelling, decreases strongly when acetate ions, originally bound to the resin, are exchanged for perchlorate ones. Accordingly, the highest values of the ionic strength are found in the resin solutions with the lowest ligand concentrations.

From the anion-exchange data obtained, the ligand number in the resin phase, \bar{n}_R , has been computed, in accordance with eqn. (2). The value of ν was here 2. As a first approximation it may be allowed to consider $[A] \approx C_A$ and $[A]_R \approx C_{AR}$, the correction terms $\bar{n}C_M$ and $\bar{n}_R C_{MR}$, due to ligand ions bound

in the complexes MA_j and MA_{jR} , respectively, being very small in comparison with the corresponding concentrations of free ligand. The derivatives in eqn. (2) were obtained from plots of $\log \varphi$ and $\log[A]$ against $\log[A]_R$, and \bar{n} was computed according to eqn. (3). For the calculation of the X- and X'-functions the following values of the complexity constants were used (*cf.* Fronæus⁵): $\beta_1 = 47 \text{ M}^{-1}$, $\beta_2 = 450 \text{ M}^{-2}$, $\beta_3 = 1150 \text{ M}^{-3}$, $\beta_4 = 750 \text{ M}^{-4}$.

Table 2. Computation of \bar{n}_R for the copper acetate system.

φ	[A] M	[A] _R M	$\frac{d \ln \varphi}{d \ln [A]_R}$	$\frac{d \ln [A]}{d \ln [A]_R}$	\bar{n}	\bar{n}_R
0.015	0.195	0.050			2.0	
0.024	0.275	0.083			2.2	
0.024	0.355	0.130	0.3	0.8	2.4	2.6
0.027	0.440	0.160	0.4	0.6	2.6	2.7
0.030	0.520	0.225	0.5	0.6	2.7	2.9
0.039	0.605	0.255	0.6	0.5	2.8	3.0
0.048	0.675	0.350	0.7	0.3	2.9	3.0
0.057	0.760	0.480	0.8	0.3	2.9	3.1
0.072	0.850	0.670	0.9	0.2	3.0	3.1
0.150	0.900	1.25	1.2	0.1	3.0	3.3
0.240	0.915	1.80	1.3	0.1	3.0	3.4
0.380	0.935	2.50	1.5	0.1	3.1	3.6
0.625	0.950	3.40	1.6	0.1	3.1	3.7
0.765	0.960	3.90	1.6	0.1	3.1	3.7
1.07	0.975	4.75	1.7	0.1	3.1	3.8
1.30	0.990	5.40	1.8	0.1	3.1	3.9

Table 3. Calculation of the stability constants of the copper acetate system in the resin phase.

[A] _R M	KX_R	KX_{1R} M ⁻¹	KX_{2R} M ⁻²	KX_{3R} M ⁻³	KX_{4R} M ⁻⁴
0		1.0	20	120	90
0.050	(0.04)				
0.083	0.17	2.0			
0.130	0.44	3.4			
0.160	0.84	5.3			
0.225	2.0	8.9			
0.255	3.8	15	55		
0.350	9.6	27	74		
0.480	24	50	100		
0.670	66	99	150		
1.25	500	400	320		
1.80	1700	940	520	280	90
2.50	5300	2100	840	330	80
3.40	16×10^3	47×10^2	1400	410	90
3.90	27×10^3	69×10^2	1800	460	90
4.75	56×10^3	12×10^3	2500	530	90
5.40	90×10^3	17×10^3	3100	570	80

The results are shown in Table 2. The ligand number \bar{n}_R increases with increasing values of $[A]_R$ and approaches the limiting value 4. Thus, one can exclude the possibility that, because of the size of the acetate ion, there should not be space enough in the resin network for the formation of higher complexes.

From the values obtained of the distribution φ and of the acetate concentrations $[A]_R$ and $[A]$ (with $[A]_R$ expressed in moles per litre), the KX_R -function was computed, according to eqn. (1). The results are shown in Table 3. As it was not possible to determine φ experimentally with sufficient accuracy at low ligand concentrations for the performance of a safe extrapolation of the KX_R -function, no value of the constant K could be obtained.

By successive extrapolations of the KX_{jR} -functions, the following values of $K\beta_{jR}$ are found (cf. Table 3):

$$\begin{aligned} K\beta_{1R} &= 1.0 \pm 0.4 \text{ M}^{-1}, & K\beta_{2R} &= 20 \pm 5 \text{ M}^{-2}, \\ K\beta_{3R} &= 120 \pm 30 \text{ M}^{-3}, & K\beta_{4R} &= 90 \pm 30 \text{ M}^{-4} \end{aligned}$$

As K is unknown, only the stability constants of the system, $b_{jR} = \beta_{jR}/\beta_{j-1,R}$, can be computed for $j > 1$. The values obtained are:

$$\begin{aligned} b_{2R} &= 20 \pm 10 \text{ M}^{-1}, & b_{3R} &= 6 \pm 3 \text{ M}^{-1}, \\ b_{4R} &= 0.8 \pm 0.4 \text{ M}^{-1} \end{aligned}$$

The values are possibly influenced by the variation of the ionic strength in the resin phase and thus the values obtained are rather uncertain.

According to relation (4), the Nernst distribution coefficient for the uncharged complex, l_2 , can be determined, if β_2 and $K\beta_{2R}$ are known. Inserting the values above, we get $l_2 = 0.04 \pm 0.01$.

The copper glycolate system. The experimental data from the present system are found in Table 4. As the absorbed amount of water was much dependent on the resin composition, the ionic strength in the resin phase could not be

Table 4. Anion exchange measurements of the copper glycolate system. $C'_M = 0.3240 \text{ mM}$.

C_M mM	δ	$C_{MR} \times 10^4$ mmole·g ⁻¹	C_{MR} mM	C_A M	C_{AR} mmole·g ⁻¹	C_{AR} M	φ
0.340	0.994	0.088	0.043	0.165	0.033	0.160	0.125
0.340	0.994	0.100	0.049	0.205	0.050	0.245	0.145
0.339	0.994	0.133	0.064	0.310	0.060	0.290	0.190
0.339	0.994	0.139	0.067	0.415	0.071	0.340	0.200
0.338	0.994	0.160	0.077	0.500	0.080	0.385	0.230
0.338	0.994	0.180	0.086	0.580	0.086	0.410	0.255
0.337	0.994	0.225	0.107	0.675	0.105	0.500	0.320
0.336	0.994	0.270	0.127	0.750	0.124	0.585	0.380
0.336	0.994	0.330	0.154	0.825	0.166	0.775	0.460
0.334	0.993	0.485	0.220	0.880	0.250	1.15	0.660
0.331	0.993	0.795	0.350	0.910	0.395	1.75	1.06
0.325	0.992	1.35	0.560	0.935	0.630	2.60	1.72
0.322	0.990	2.35	0.890	0.965	1.08	4.10	2.75
0.313	0.988	3.75	1.29	0.980	1.56	5.35	4.10
0.300	0.987	4.90	1.54	0.995	2.05	6.45	5.15
0.296	0.985	6.70	1.92	1.00	2.60	7.45	6.50

kept constant throughout the measurement series but decreased at increasing ligand concentrations. In column 8 the distribution φ is shown. The values obtained are about five times higher than the corresponding ones of the preceding system, indicating a stronger tendency to complex formation in the glycolate system than in the acetate one (*cf.* Ref.²).

Table 5. Computation of \bar{n}_R for the copper glycolate system.

φ	[A] M	[A] _R M	$\frac{d\ln \varphi}{d\ln[A]_R}$	$\frac{d\ln[A]}{d\ln[A]_R}$	\bar{n}	\bar{n}_R
0.125	0.165	0.160			2.1	
0.145	0.205	0.245			2.2	
0.190	0.310	0.290			2.4	
0.200	0.415	0.340			2.6	
0.230	0.500	0.385			2.6	
0.255	0.580	0.410			2.7	
0.320	0.675	0.500			2.8	
0.380	0.750	0.585			2.9	
0.460	0.825	0.775	0.7	0.2	2.9	2.9
0.660	0.880	1.15	0.9	0.1	3.0	3.0
1.06	0.910	1.75	1.0	0.1	3.0	3.1
1.72	0.935	2.60	1.2	0.1	3.0	3.3
2.75	0.965	4.10	1.3	0.1	3.0	3.4
4.10	0.980	5.35	1.4	0.1	3.0	3.5
5.15	0.995	6.45	1.6	0.1	3.0	3.7
6.50	1.00	7.45	1.7	0.1	3.0	3.8

Table 6. Calculation of the stability constants of the copper glycolate system in the resin phase.

$\frac{[A]_R}{M}$	KX_R	KX_{1R} M ⁻¹	KX_{2R} M ⁻²	KX_{3R} M ⁻³	KX_{4R} M ⁻⁴
0		50	2.0×10^3	7×10^3	2.0×10^3
0.160	27	170			
0.245	74	300			
0.290	150	520			
0.340	250	740			
0.385	410	1060			
0.410	570	1400			
0.500	12×10^2	24×10^2			
0.585	21×10^2	36×10^2	6.1×10^3		
0.775	49×10^2	63×10^2	8.1×10^3		
1.15	16×10^3	14×10^3	12×10^3		
1.75	63×10^3	36×10^3	21×10^3		
2.60	23×10^4	88×10^3	34×10^3	12×10^3	2.0×10^3
4.10	95×10^4	23×10^4	56×10^3	13×10^3	1.0×10^3
5.35	25×10^5	47×10^4	88×10^3	16×10^3	2.0×10^3
6.45	46×10^5	71×10^4	11×10^4	17×10^3	2.0×10^3
7.45	77×10^5	103×10^4	14×10^4	19×10^3	2.0×10^3

The ligand number \bar{n}_R was calculated from eqn. (2) in the way described before. No correction had to be applied to the values of C_{AR} and C_A in order to determine $[A]_R$ and $[A]$, as the concentration of the central ion in the resin phase as well as in the outer solution was very low throughout. The ligand number \bar{n} was computed from eqn. (3), the following values of the complexity constants being used:⁵

$$\beta_1 = 220 \text{ M}^{-1}, \beta_2 = 5.1 \times 10^3 \text{ M}^{-2}, \beta_3 = 1 \times 10^4 \text{ M}^{-3}, \beta_4 = 6 \times 10^3 \text{ M}^{-4}$$

As seen in Table 5, the ligand number \bar{n}_R increases with increasing ligand concentrations towards the value 4, the maximum coordination number of copper in a glycolate solution. Also the highest anionic complexes can thus be formed within the resin phase in spite of the comparatively low values of the found sorption. Thus no steric hindrance seems to be present.

Attempts have also been made to compute the complexity constants for the ionic species in the resin phase. Owing to experimental difficulties at low ligand concentrations, however, it was not possible to obtain even an approximate value of K by the extrapolation procedure described, but for the KX_{jR} -functions with $j \geq 1$, the following values are found (*cf.* Table 6):

$$\begin{aligned} K\beta_{1R} &= 50 \pm 20 \text{ M}^{-1}, & K\beta_{2R} &= (2.0 \pm 0.5) \times 10^3 \text{ M}^{-2}, \\ K\beta_{3R} &= (7 \pm 2) \times 10^3 \text{ M}^{-3}, & K\beta_{4R} &= (2.0 \pm 0.6) \times 10^3 \text{ M}^{-4} \end{aligned}$$

The stability constants, computed from the values of $K\beta_{iR}$ above, are

$$\begin{aligned} b_{2R} &= 40 \pm 20 \text{ M}^{-1}, & b_{3R} &= 3.5 \pm 1.5 \text{ M}^{-1}, \\ b_{4R} &= 0.30 \pm 0.15 \text{ M}^{-1} \end{aligned}$$

From the value of $K\beta_{2R}$ above, a value of the distribution coefficient l_2 for the second uncharged complex can also be determined. We get $l_2 = 0.4 \pm 0.1$.

The copper tartrate system. The data from the present system are collected in Tables 7–9. The anion-exchange measurements as well as the subsequent calculations were performed in complete accordance with the two systems previously described.

Table 7. Anion exchange measurements of the copper tartrate system. $C'_M = 0.3240 \text{ mM}$.

C_M mM	δ	$C_{MR} \times 10^4$ mmole·g ⁻¹	C_{MR} mM	C_A M	C_{AR} mmole·g ⁻¹	C_{AR} M	φ
0.336	0.999	0.002	0.0017	0.297	0.013	0.110	0.005
0.336	0.999	0.004	0.0034	0.306	0.022	0.185	0.010
0.335	0.999	0.007	0.0058	0.311	0.030	0.250	0.017
0.334	0.999	0.025	0.020	0.318	0.054	0.430	0.060
0.332	0.998	0.090	0.066	0.322	0.096	0.705	0.200
0.317	0.996	0.420	0.250	0.325	0.196	1.20	0.790
0.282	0.994	1.51	0.735	0.327	0.370	1.80	2.60
0.234	0.991	3.65	1.50	0.328	0.595	2.45	6.40
0.196	0.989	6.35	2.25	0.331	0.845	3.00	11.5
0.161	0.988	9.70	3.30	0.332	1.08	3.65	20.5
0.142	0.986	12.4	3.90	0.335	1.30	4.05	27.5

In Table 7 the distribution φ has been computed at increasing loads of ligand on the exchanger, C_{AR} . From a comparison between the orders of magnitude of the φ -values for the three complex systems investigated, it is evident that the sorption of copper by the ion-exchanger increases in the order: acetate, glycolate and tartrate, in agreement with the increasing tendency to anionic complex formation, previously stated in water solutions.²

In Table 8 approximate values of the ligand number in the resin phase, \bar{n}_R , have been computed according to eqn. (2). The value of ν was here 1. As both C_{MR} and C_M were very low, no correction terms had to be applied to C_{AR} and C_A in order to compensate for ligand ions bound in copper complexes. At the calculation of \bar{n} from eqn. (3), the following values of the complexity constants in the outer solution were used:⁵

$$\beta_1 = 1.6 \times 10^3 \text{ M}^{-1}, \beta_2 = 1.3 \times 10^5 \text{ M}^{-2}, \beta_3 = 0.6 \times 10^5 \text{ M}^{-3}, \beta_4 = 3.2 \times 10^6 \text{ M}^{-4}$$

From the values of \bar{n}_R , given in Table 8, it is obvious that the ligand number in the resin phase attains the limiting value 4 already at moderate tartrate concentrations.

At the calculation of $K\beta_{jR}$, the following values are obtained (cf. Table 9):

$$K\beta_{2R} = (4 \pm 1) \times 10^3 \text{ M}^{-2}, \quad K\beta_{3R} = (3 \pm 1) \times 10^3 \text{ M}^{-3}, \\ K\beta_{4R} = (7 \pm 2) \times 10^4 \text{ M}^{-4}$$

Owing to the rapid decrease of the KX_R -function and the uncertainty in the experimental data at low ligand concentrations, no values of K and $K\beta_{1R}$ can be computed.

From the extrapolated values of $K\beta_{jR}$ the stability constants of the two highest anionic species in the resin phase can be determined. We get:

$$b_{3R} = 0.8 \pm 0.4 \text{ M}^{-1}, \quad b_{4R} = 20 \pm 10 \text{ M}^{-1}$$

The Nernst distribution coefficient l_1 of the uncharged complex MA cannot be determined for the present system, as the value of $K\beta_{1R}$ is unknown.

Table 8. Computation of \bar{n}_R for the copper tartrate system.

φ	[A] M	[A] _R M	$\frac{d \ln \varphi}{d \ln [A]_R}$	$\frac{d \ln [A]}{d \ln [A]_R}$	\bar{n}	\bar{n}_R
0.005	0.297	0.110	0.07	1.3	3.3	2.4
0.010	0.306	0.185	0.05	1.7	3.4	2.8
0.017	0.311	0.250	0.05	2.0	3.4	3.1
0.060	0.318	0.430	0.03	2.3	3.4	3.4
0.200	0.322	0.705	0.02	2.5	3.4	3.6
0.790	0.325	1.20	0.02	2.7	3.4	3.8
2.60	0.327	1.80	0.02	2.9	3.4	4.0
6.40	0.328	2.45	0.02	2.9	3.4	4.0
11.5	0.331	3.00	0.02	2.9	3.4	4.0
20.5	0.332	3.65	0.02	2.9	3.4	4.0
27.5	0.335	4.05	0.02	2.9	3.4	4.0

Table 9. Calculation of the stability constants of the copper tartrate system in the resin phase.

$\frac{[A]_R}{M}$	KX_R	KX_{1R} M^{-1}	KX_{2R} M^{-2}	KX_{3R} M^{-3}	KX_{4R} M^{-4}
0			4×10^3	3×10^3	7×10^4
0.110	7.1×10^1	6.5×10^2	5.9×10^3		
0.185	2.6×10^2	1.4×10^3	7.6×10^3		
0.250	6.1×10^2	2.4×10^3	9.6×10^3		
0.430	3.9×10^3	9.1×10^3	2.1×10^4		
0.705	2.2×10^4	3.1×10^4	4.4×10^4	5.7×10^4	
1.20	1.5×10^5	1.3×10^5	1.1×10^5	9.2×10^4	7×10^4
1.80	7.6×10^5	4.2×10^5	2.3×10^5	1.3×10^5	7×10^4
2.45	2.6×10^6	1.1×10^6	4.5×10^5	1.8×10^5	7×10^4
3.00	5.8×10^6	1.9×10^6	6.3×10^5	2.1×10^5	7×10^4
3.65	1.3×10^7	3.6×10^6	9.9×10^5	2.7×10^5	7×10^4
4.05	1.9×10^7	4.7×10^6	1.2×10^6	3.0×10^5	7×10^4

DISCUSSION

In Table 10 a comparison is given between the stability constants obtained in the present investigation, and those previously⁵ found to be valid in water solutions at the ionic strength 1 M. It is apparent that in spite of the differences in ionic strength, the two sets of values are of the same order of magnitude. Thus, the complex formation of the copper(II) acetate, glycolate and tartrate systems does not seem to be much influenced by changes in the ionic strength, a conclusion that is in agreement with previous measurements² of the systems. The stability constants in the resin phase are, as a rule, somewhat higher than the corresponding ones in the outer solution, a fact that can be explained by the very high ionic strength in the resin solution. One possible reason why such low b_{4R} -values are obtained, may be the fact mentioned above that the ionic strength in the resin phase is not constant throughout the measurement series.

Table 10. The stability constants of the investigated copper(II) complex systems.

Ligand	The stability constants in the resin phase.				The stability constants in the outer solution. ⁵ ($I = 1M$)			
	b_{1R}	b_{2R}	b_{3R}	b_{4R}	b_1	b_2	b_3	b_4
Ac ⁻		20	6	0.8	47	9.6	2.6	0.65
AcOH ⁻		40	3.5	0.30	220	23	2.0	0.60
T ²⁻			0.8	20	1600	80	0.5	50

For all the three complex systems investigated the ligand number \bar{n}_R approaches the limiting value 4, and so there does not seem to be any steric hindrance to the formation of higher complexes within the exchanger. In all probability, the systems behave in the resin phase as in an ordinary water solution, the complexes being stepwise built up until the fourth one has been formed and dominates in the system.

The fact, mentioned above that the sorption of copper by an anion-exchanger saturated with acetate, glycolate or tartrate ions, is very slight in comparison with *e.g.* the sorption of cadmium by an exchanger in the bromide state — though at least the tartrate system has a stronger tendency to anionic complex formation in water solutions at the ionic strength 1 M (*cf.* Refs.^{1,2}) — can be explained by the fact that the values of the distribution coefficients l_v and of the constants b_{3R} and $b_{3R}b_{4R}$ for the three copper systems in the present investigation are of a much lower order of magnitude than the corresponding values for the cadmium bromide system previously investigated.³

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