

The Use of Cation Exchangers for the Quantitative Investigation of Complex Systems

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For the investigation of complex systems and the determination of the complexity constants, in the first place of the mononuclear complexes, especially potentiometric and extinctionometric methods have been applied. In previous papers¹⁻³ the present author has developed and used different such methods. But the application of those presupposes that suitable electrodes can be found, or that the complexes have absorption bands within available wave length ranges.

Therefore it is very important to search for new and more generally applicable investigation methods. Then it is near at hand to try to use cation exchangers, as acid-resistant, synthetic cation exchangers with reproducible exchange equilibria are available. Some investigations of this kind have been performed by Samuelson⁴ and especially by Schubert⁵. Their calculation methods, however, presuppose that only complexes with zero or net negative charges are formed, and the methods then result in a determination of the concentration of free central group in the solutions. The calculation method of Schubert also presupposes that only one complex is formed. Very often, however, these conditions are not fulfilled, and then none of the complexity constants of the system can be determined according to those methods.

It is the aim of the present investigation to develop a method, the applicability of which is not limited by such conditions, and to prove it on a complex system, that has been thoroughly investigated before by potentiometric and extinctionometric methods. As a model system the cupric acetate system was chosen.

The investigation method

As in previous investigations by the present author the ionic strength of the complex solutions was kept constant, $I = 1$ C, with sodium perchlorate as a neutral salt. The sodium form of a cation exchanger was used, and the distribution of copper at equilibrium between the ion exchanger and the complex solution was determined at different cupric and acetate ion concentrations. The calculations of the complexity constants are based on these determinations.

Deduction of the equations necessary for the calculations

We presuppose that the central group is a divalent cation M^{2+} , and that the ligand is a monovalent anion A^- , as is the case with the model system chosen. According to the Donnan equilibrium the concentration of complexes with zero or negative charges in the cation exchanger is negligible, as the sodium ion concentration is much higher in the resin phase than in the solution. So we have only to take into consideration the taking up of M^{2+} and MA^+ by the sodium form of the ion exchanger.

The following notation is used (*cf.* Fronæus¹):

C'_M, C'_A = total concentrations of M^{2+} and A^- in the solution before the ion exchanger is added.

C_M, C_A = total concentrations in the solution at equilibrium with the ion exchanger.

$(MR_2), (MAR), (NaR)$ = moles of $M^{2+}, MA^+,$ and Na^+ contained in one unit weight of the exchanger at equilibrium.

$$C_{MR} = (MR_2) + (MAR)$$

$$\varphi = \frac{C_{MR}}{C_M}; \varphi_1 = (1/\varphi - 1/l_0)/[A^-]; (l_0 = \text{a constant}).$$

β_j = the complexity constant of the complex MA_j^{2-j} ($j \leq N$).

$$X = 1 + \sum_{j=1}^N \beta_j [A^-]^j; X_j = (X_{j-1} - \beta_{j-1})/[A^-]; (X_0 = X, \beta_0 = 1).$$

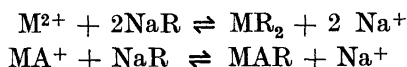
$$\bar{n} = (C_A - [A^-])/C_M; \bar{n}_R = (MAR)/C_{MR}$$

v = the initial volume of the solution.

$v \cdot \delta$ = the volume at equilibrium.

m = the weight of the exchanger.

If we apply the law of mass action to the exchange equilibria:



we obtain:

$$\frac{(\text{MR}_2)}{[\text{M}^{2+}]} = k_0 \cdot \frac{(\text{NaR})^2}{[\text{Na}^+]^2}; \quad \frac{(\text{MAR})}{[\text{MA}^+]} = k_1 \cdot \frac{(\text{NaR})}{[\text{Na}^+]} \quad (1)$$

In eq. (1) k_0 and k_1 are presumed to be constants at a fixed value of C_{MR} , as the ionic strength is practically constant in the resin phase and in the solution. Then we put:

$$l_0 = k_0 \cdot \frac{(\text{NaR})^2}{[\text{Na}^+]^2}; \quad l_1 = k_1 \cdot \frac{(\text{NaR})}{[\text{Na}^+]} \quad (2)$$

If the values of C_{M} are low, compared with the ionic strength, then $[\text{Na}^+]$ is approximately constant in all the solutions. For (NaR) we have the expressions:

$$(\text{NaR}) = a - 2(\text{MR}_2) - (\text{MAR}) \quad (3 \text{ a})$$

$$(\text{NaR}) = a - (2 - \bar{n}_{\text{R}}) \cdot C_{\text{MR}} \quad (3 \text{ b})$$

Here a is the exchange capacity, and at certain cation exchangers it is a function of pH. From the definition of C_{MR} and eq. (1—2) we obtain:

$$C_{\text{MR}} = l_0 \cdot [\text{M}^{2+}] + l_1 \cdot [\text{MA}^+] \quad (4)$$

This relation is combined with the expressions $[\text{MA}^+] = \beta_1[\text{M}^{2+}][\text{A}^-]$ and $C_{\text{M}} = [\text{M}^{2+}] \cdot X$ (cf. Fronæus¹), and then, putting $l_1\beta_1/l_0 = l$, we get:

$$\varphi = l_0 \frac{1 + l \cdot [\text{A}^-]}{X} \quad (5)$$

From eq. (2—3) it is evident that at a constant value of a (that is of pH) and so small C_{MR} that the term $(2 - \bar{n}_{\text{R}}) \cdot C_{\text{MR}}$ in eq. (3b) can be neglected, the quantities l_0 , l_1 and l are constants, and for \bar{n}_{R} we have the relation:

$$\bar{n}_{\text{R}} = \frac{l \cdot [\text{A}^-]}{1 + l \cdot [\text{A}^-]} \quad (6)$$

If at greater C_{MR} the term $(2 - \bar{n}_{\text{R}}) \cdot C_{\text{MR}}$ cannot be neglected, but C_{MR} is kept constant, l_0 and l_1 are polynomials of \bar{n}_{R} . Then only at rather low values of $[\text{A}^-]$ the numerator in the expression for φ is approximately linear in $[\text{A}^-]$, and if the coefficients are still called l_0 and l , it is easily shown that in this case they have not exactly the same meaning as before, and eq. (6) is no longer valid.

Thus we see that C_{MR} should be kept constant and as small as possible, so that eq. (5) with constant l_0 and l can be used within a concentration range of $[A^-]$ that is large enough for the calculation of the complexity constants.

At the deduction up till now it has been tacitly assumed that only mononuclear complexes are formed. If also polynuclear complexes are formed, the expression for φ will contain in the numerator and in the denominator terms with $[M^{2+}]$, $[M^{2+}]^2$ etc. as factors. But for $C_{MR} \rightarrow 0$ and consequently $C_M \rightarrow 0$ these terms cancel, and thus at small C_{MR} eq. (5) is *general* for complex systems of the type $M^{2+}-A^-$.

For the calculation of the values of C_{MR} and φ we have the relation:

$$C_{MR} = \frac{v}{m} (C'_M - C_M \cdot \delta) \quad (7)$$

C'_M , C_M and δ are determined at the measurements. Because of the swelling of the dried ion exchanger, when it is added to the solution, δ is always < 1 . δ is obtained as the quotient between the initial and the equilibrium concentrations of the ligand in solutions with $C_M = 0$. As will be shown below, δ is independent of C_A at a constant ionic strength. It can be assumed to be independent also of C_M at small C_{MR} , but this cannot be proved exactly at the measurements because of the taking up of the complex MA^+ by the exchanger. However, the exchanger takes up about m ml of water from v ml of the solution, $\delta \simeq 1 - m/v$, and at a small value of m/v only an approximate determination of δ is required.

At the measurements, described below, on the cupric acetate system it is shown, how the φ -values, corresponding to different C_A and a constant C_{MR} , are obtained. For a rough approximation of \bar{n} we can use the relation:

$$\bar{n} \simeq - \frac{C_A}{\varphi} \cdot \left(\frac{\partial \varphi}{\partial C_A} \right)_{C_{MR}} \quad (8)$$

obtained from eq. (5) by putting $l \simeq 0$ and $C_A \simeq [A^-]$. Then the $[A^-]$ -values are computed from the relation $[A^-] = C_A - \bar{n} \cdot C_M$. The approximation is quite satisfactory for the calculation of $[A^-]$, as C_M is kept small.

Thus we have determined φ as a function of $[A^-]$ with l_0 and l as constants. For the calculation of the complexity constants β_i the product $\varphi \cdot X$ is differentiated twice with respect to $[A^-]$, and from eq. (5) we get:

$$\varphi'' \cdot X + 2 \varphi' \cdot X' + \varphi \cdot X'' = 0 \quad (9)$$

($\varphi' = \frac{d\varphi}{d[A^-]}$, $\varphi'' = \frac{d^2\varphi}{d[A^-]^2}$ etc.). Putting in the expressions for X , X' , and X'' , we obtain:

$$\varphi'' + \sum_{j=1}^N ([A^-]^j \cdot \varphi'' + 2j [A^-]^{j-1} \cdot \varphi' + j(j-1) [A^-]^{j-2} \cdot \varphi) \cdot \beta_j = 0 \quad (10 \text{ a})$$

or abbreviated:

$$\varphi'' + \sum_{j=1}^N a_j \beta_j = 0 \quad (10 \text{ b})$$

From a graphic representation of φ as a function of $[A^-]$ we can determine φ' and then φ'' in the same way from a graphic representation of φ' . Then φ'' and the coefficients a_j in eq. (10 b) are determined at N values of $[A^-]$, spread out within the concentration range used. Thus we have a system of N equations, from which the complexity constants β_j can be computed.

At the measurements on the cupric acetate system it was found, however, that only β_1 could be determined accurately in this way, and it is very likely that this fact is general. The reason will be discussed below (p. 868) in connection with the calculations. The remaining constants, $\beta_2 \dots \beta_N$, can be computed according to the following method. $1/\varphi$, which is a monotonously increasing function of $[A^-]$ (as $l < \beta_1$), is easily extrapolated graphically to $[A^-] = 0$. From eq. (5) we have:

$$\frac{1}{l_0} = \lim_{[A^-] \rightarrow 0} \frac{1}{\varphi}$$

Here it should be mentioned that l_0 cannot be determined directly at measurements on a solution with $C_A = 0$, unless the solution has the same value of pH as the solutions with $C_A > 0$.

Then the function $\varphi_1 = (1/\varphi - 1/l_0)/[A^-]$ is extrapolated to $[A^-] = 0$. Putting in the expression for X in eq. (5) we obtain:

$$\frac{\beta_1 - l}{l_0} = \lim_{[A^-] \rightarrow 0} \varphi_1$$

When l_0 and l have been determined in this way, the polynomial X can be calculated, and from corresponding values of X and $[A^-]$ the complexity constants can be computed from the relation:

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

It is obvious that if we have a complex system of the form $M^{v+}-A^{v-}$, where all complexes have zero or negative charges (that is $l = 0$), the calculation method is considerably simplified. Then l_0 and the complexity constants β_i can be obtained directly from corresponding values of $[A^{v-}]$ and the function $1/\varphi$.

THE MEASUREMENTS ON THE $\text{Cu}^{2+}-\text{Ac}^-$ SYSTEM

In order to prove the method, described above, it was applied to the cupric acetate system, that has been investigated in a previous work¹ by the present author.

Chemicals used. Cupric perchlorate, sodium perchlorate, perchloric acid, sodium acetate and acetic acid were prepared or purified as in previous investigations^{1,2}, and stock solutions of an ionic strength of 1 C were prepared. The sodium form of the cation exchanger Amberlite IR-105 with a particle size of 20-40 mesh was used. A portion of the exchanger, sufficient for all the measurements, was dried on a water bath and stored in a closed bottle, so that the content of water was kept constant. The exchange capacity was about 2.4 meq. per gram of the dried hydrogen form of the exchanger.

The measurements were carried out in the following way. To v liters of the complex solution

$$\left\{ \begin{array}{l} C'_M \text{ mC Cu}(\text{ClO}_4)_2 \\ C'_A \text{ mC NaAc} \\ 0.5 C'_A \text{ mC HAc} \\ (1000 - 3C'_M - C'_A) \text{ mC NaClO}_4 \end{array} \right.$$

m grams of the dried cation exchanger were added. The value of the quotient m/v was the same at all the measurements and equal to $40.0 \text{ g} \cdot \text{l}^{-1}$ and m was about 0.4 g. The solution was shaken with the exchanger for twenty-four hours in a thermostat at 20.0°C , and then the solution was separated from the exchanger and analysed. It was controlled that a longer time of shaking did not affect the distribution of the copper.

The cupric concentration C_M of the solution was determined extinc-tio-metrically. A surplus of 2 C ammonia was added, and the extinction was measured with a Beckman Quartz Spectrophotometer (Model DU) at the wave length 6200 \AA and with a thickness of 1 cm of the absorbing layer. The molar extinction was obtained from solutions with known cupric concentrations. At the ammonia concentration used the molar extinction was independent of the acetate concentration C'_A .

Table 1. Ion exchange measurements on the cupric acetate system.
 $M^{2+} = Cu^{2+}$, $A^- = Ac^-$

C'_M mC	C_A mC	C_M mC	$C'_M - C_M \cdot \delta$ mC	$\varphi \cdot 10^3$ $l \cdot g^{-1}$
6.67	20.2	1.47	5.27	89.6
»	39.0	1.86	4.90	65.9
»	68.5	2.14	4.64	54.2
»	106.0	2.49	4.30	43.2
»	162.0	3.05	3.77	30.9
»	215	3.42	3.42	25.0
»	266	3.68	3.17	21.5
»	319	3.93	2.94	18.7
»	423	4.28	2.60	15.2
»	526	4.67	2.23	11.9
10.00	21.3	3.05	7.10	58.2
»	42.0	3.45	6.72	48.7
»	71.4	4.05	6.15	38.0
»	109.1	4.55	5.68	31.2
»	161.0	5.14	5.12	24.9
13.33	19.3	5.11	8.48	41.5
»	39.0	5.84	7.78	33.3
»	68.5	6.33	7.32	28.9
»	109.0	7.03	6.65	23.6
»	159.0	7.69	6.02	19.6
»	216	8.31	5.44	16.4
»	264	9.04	4.74	13.1
»	313	9.49	4.31	11.4
»	417	10.2	3.64	8.9
»	521	10.8	3.07	7.1
20.0	215	14.2	6.40	11.3
»	266	14.7	5.90	10.0
»	318	15.1	5.50	9.1
»	422	15.8	4.80	7.6
»	526	16.4	4.25	6.5

The concentration C_A at equilibrium could be determined with sufficient accuracy only by extinctionometric titration with perchloric acid. These measurements were performed at the wave length 3 000 Å, where the molar extinctions of the complexes are great, while the other ions in the solution practically do not absorb at this wave length. When so much acid has been added that $C_A < C_M$, approximately only the first complex is formed and $[A^-] \ll C_A$.

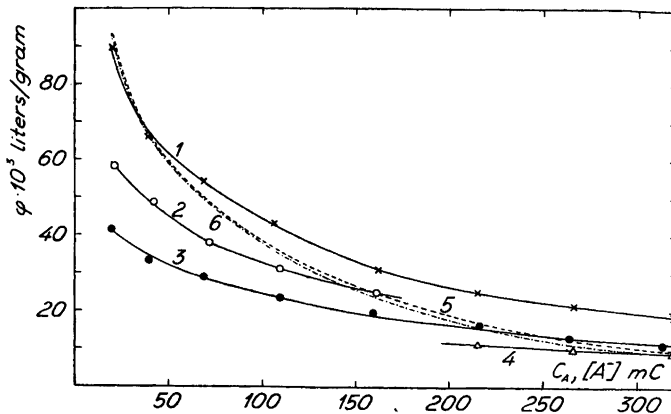


Fig. 1. Fulldrawn curves: φ as a function of C_A at different values of C'_M . 1. $C'_M = 6.67$ mC; 2. $C'_M = 10.00$ mC; 3. $C'_M = 13.33$ mC; 4. $C'_M = 20.0$ mC. — Dashed curves: 5. φ as a function of C_A at $C'_M - C_M \cdot \delta = 5.00$ mC; 6. φ as a function of $[A^-]$ at $C'_M - C_M \cdot \delta = 5.00$ mC.

Then the extinction is almost proportional to C_A , and thus the extinction, corrected for the dilution, is a linear function of the volume of perchloric acid added. After the equivalence point the corrected extinction is constant, and is due to the small extinction of the acetic acid. In this way the acetate concentration could be determined graphically with great accuracy. At very small values of C_M cupric perchlorate was added before the titration.

The values obtained from the distribution measurements on the cupric acetate system are collected in Table 1, the columns 1—3. At the calculation of $C'_M - C_M \cdot \delta$ and φ in the columns 4 and 5 the value $\delta = 0.95$ was used. δ was determined in the way, described above.

In Fig. 1 φ is represented as a function of C_A and in Fig. 2 $C'_M - C_M \cdot \delta$ as a function of C_A , in both cases with C'_M as a parameter. From these curves the values in the columns 2—9 of Table 2 have been obtained. The relation between φ and $C'_M - C_M \cdot \delta$ at a constant value of C_A proves to be practically linear, when graphically represented. So it is easy to determine by graphic interpolation the φ -values corresponding to a constant and low value of C_{MR} , that is of $C'_M - C_M \cdot \delta$. The value $C'_M - C_M \cdot \delta = 5.00$ mC or $C_{MR} = 0.125$ mmoles $\cdot g^{-1}$ was selected, and the φ -values are to be found in column 10 of Table 2. The values of C_M in the column 11 have been calculated from the definition of φ . The $[A^-]$ -values in the last column of Table 2 have been determined in the way, described above. The values of $(\partial\varphi/\partial C_A)_{C_{MR}}$ in eq. (8) have

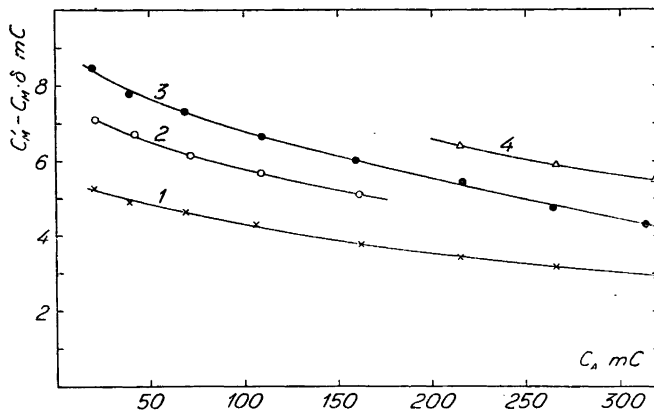


Fig. 2. $C'_M - C_M \cdot \delta$ as a function of C_A at different values of C'_M . 1. $C'_M = 6.67$ mC; 2. $C'_M = 10.00$ mC; 3. $C'_M = 13.33$ mC; 4. $C'_M = 20.0$ mC.

been obtained from the curve 5 in Fig. 1. It is evident that the difference between C_A and $[A^-]$ is rather small. For the H^+ -concentration we have the relation:

$$[H^+] = K_c \cdot \frac{0.5 C_A}{[A^-]}$$

K_c is the dissociation constant of the acetic acid. As $C_A/[A^-]$ is almost constant at the different C_A , $[H^+]$ is also practically unchanged, and the conditions for

Table 2. Determination of corresponding values of C_A , C_M and φ at a constant value of $C'_M - C_M \cdot \delta$

C_A mC	$C'_M = 6.67$ mC		$C'_M = 10.00$ mC		$C'_M = 13.33$ mC		$C'_M = 20.0$ mC		$C'_M - C_M \cdot \delta = 5.00$ mC		
	$C'_M - C_M \cdot \delta$ mC	$\varphi \cdot 10^3$ $l \cdot g^{-1}$	$C'_M - C_M \cdot \delta$ mC	$\varphi \cdot 10^3$ $l \cdot g^{-1}$	$C'_M - C_M \cdot \delta$ mC	$\varphi \cdot 10^3$ $l \cdot g^{-1}$	$C'_M - C_M \cdot \delta$ mC	$\varphi \cdot 10^3$ $l \cdot g^{-1}$	$\varphi \cdot 10^3$ $l \cdot g^{-1}$	C_M mC	$[A^-]$ mC
20.0	5.25	89.0	7.15	59.0	8.40	41.0			93.5	1.34	19.4
40.0	4.95	66.5	6.70	48.5	7.90	34.5			66.0	1.89	39.0
70.0	4.60	53.5	6.15	38.5	7.30	28.5			49.5	2.53	68.4
100.0	4.30	44.0	5.75	32.5	6.80	24.5			38.5	3.25	97.5
150.0	3.85	33.0	5.20	26.0	6.15	19.5			26.5	4.72	145
200	3.50	26.3			5.55	16.5	6.60	11.7	19.0	6.58	191
250	3.25	22.5			5.00	13.7	6.05	10.4	13.7	9.12	235
300	3.05	19.7			4.45	12.0	5.60	9.3	10.5	11.9	280
400	2.65	15.7			3.75	9.3	4.95	8.0	7.9	15.8	375
500	2.35	12.7			3.20	7.5	4.40	6.7	6.2	20.2	465

Table 3. φ , φ' , and φ'' as functions of $[A^-]$ at $C_{MR} = 0.125$ millimoles/gram.

$[A^-]$ mC	$\varphi \cdot 10^3$ $1 \cdot g^{-1}$	$-\varphi' \cdot 10^3$ $1 \cdot g^{-1} \cdot C^{-1}$	$\varphi'' \cdot 10^3$ $1 \cdot g^{-1} \cdot C^{-2}$
20.0	92.5	2 200	$1.00 \cdot 10^5$
40.0	65.5	780	$2.05 \cdot 10^4$
70.0	49.0	445	5 900
100.0	37.7	315	3 600
150	25.5	190	1 900
200	17.7	130	1 000
250	12.5	78	1 000
300	9.6	38	480
400	7.3	20	75

the use of eq. (5) are fulfilled. Curve 6 in Fig. 1 represents graphically φ as a function of $[A^-]$ at $C_{MR} = 0.125$ mmoles $\cdot g^{-1}$.

In Table 3 the values of the first two derivatives φ' and φ'' at different $[A^-]$ are to found. They have been graphically determined. In Table 4 the coefficients a_i in eq. (10 b) have been computed at $[A^-] = 20, 100, 200,$ and 400 mC. a_1 is obtained with great accuracy, especially at $[A^-] = 20$ and 100 mC, but for the other coefficients a_i the relative errors are much greater. However, as the values of φ'' and a_1 are so great at $[A^-] = 20$ mC, compared with the values at the other $[A^-]$, the first complexity constant β_1 is easily calculated from our system of equations (10 b). The value $\beta_1 = 45 \pm 2 C^{-1}$ is obtained. Approximately the same value is found from eq. (10 b) at $[A^-] = 20$ mC, if the small terms $a_2\beta_2 - a_4\beta_4$ are neglected. The errors in the values of $a_2 - a_4$ make a determination of the constants $\beta_2 - \beta_4$ from the system of equations impossible.

In Table 5, column 2 the function φ^{-1} is computed. The connection between φ^{-1} and $[A^-]$, graphically represented, is at lower $[A^-]$ almost linear, and by

Table 4. Determination of the coefficients a_i in eq. (10 b) at different values of $[A^-]$.

$[A^-]$ mC	a_1 $1 \cdot g^{-1} \cdot C^{-1}$	a_2 $1 \cdot g^{-1}$	a_3 $1 \cdot g^{-1} \cdot C$	a_4 $1 \cdot g^{-1} \cdot C^2$
20	- 2 400	49	6.6	0.3
100	- 270	- 14	7.3	2.4
200	- 60	- 28	2.0	1.8
400	- 10	- 5.4	3.1	5.7

Table 5. Corresponding values of $[A^-]$, φ^{-1} , φ_1 and the polynomials X , X_1 , X_2 , and X_3 .

$[A^-]$ mC	φ^{-1} $l^{-1} \cdot g$	φ_1 $l^{-1} \cdot g \cdot C^{-1}$	X	X_1 C^{-1}	X_2 C^{-2}	X_3 C^{-3}
0	7.0	195		45	440	
20	10.8	190	2.07	53.5		
40	15.3	205	3.67	67		
70	20.4	190	6.38	77	460	
100	26.5	195	10.2	92	470	
150	39.0	215	19.8	125	530	
200	56.5	245	35.5	173	640	1 000
250	80	290	60.0	236	760	1 300
300	104	325	91	300	850	1 350
400	137	325	155	390	860	1 000

extrapolation to $[A^-] = 0$ we get $l_0^{-1} = 7.0$ liter $^{-1} \cdot$ gram. The function φ_1 is practically constant and equal to 195 liter $^{-1} \cdot$ gram \cdot C $^{-1}$ at $[A^-] \leq 100$ mC. Thus $(\beta_1 - l)l_0^{-1}$ can be determined with great accuracy, and we obtain $\beta_1 - l = 28.0$ C $^{-1}$ or $l = 17 \pm 2$ C $^{-1}$.

With the values determined of l_0 and l the polynomial X has been calculated in column 4 of Table 5. At the extrapolation of X_1 to $[A^-] = 0$ we find of course the same value of β_1 as before. By extrapolation of X_2 to $[A^-] = 0$ we obtain $\beta_2 = 440 \pm 60$ C $^{-2}$. The experimental error in this value is substantially dependent on the error in the value of l .

The polynomial X_3 has been calculated for such $[A^-]$ for which the difference $X_2 - \beta_2$ is not small compared with β_2 . From the values in the last column of Table 5 the complexity constant of the third complex is determined to $\beta_3 = 1000 \pm 300$ C $^{-3}$. No value of β_4 can be obtained from the measurements, and this is natural, as according to the potentiometric investigation^{1, p. 55} only about 10 % of C_M is present as the complex $CuAc_4^{2-}$ at an acetate ion concentration of 400 mC.

Discussion of the results

A comparison between the complexity constants obtained in this investigation and the constants potentiometrically determined shows that within the limits of the random errors the agreement is complete.

Ion exchange method:

β_1 :	45 ± 2 C $^{-1}$
β_2 :	440 ± 60 C $^{-2}$
β_3 :	$1\ 000 \pm 300$ C $^{-3}$
β_4 :	

Potentiometric method:

	47 ± 1 C $^{-1}$
	450 ± 50 C $^{-2}$
	$1\ 150 \pm 150$ C $^{-3}$
	750 ± 200 C $^{-4}$

This perfect agreement proves that the presumption, on which the use of eq. (5) is based, is fulfilled. Thus at a constant value of C_{MR} the quantities l_0 and l_1 or k_0 and k_1 are constants, so that the activity coefficients in the resin phase seem to be independent of the value of \bar{n}_R . It is conceivable that in the exchanger with its high concentration of fixed sulphonate ions there is some complex formation between these and the cupric ions. Then at increasing acetate ion concentration a mere ligand displacement with an unimportant influence on the activity coefficients occurs. On the other hand it is evident from Table 2 that the function φ at every value of C_A is highly dependent on C_{MR} . Thus the activity coefficients in the resin phase are very much affected by a variation of the total cupric concentration C_{MR} , even if this is small in comparison with the exchange capacity.

Concerning the taking up of complex cations by ion exchangers the present author has not found any quantitative data in the literature. In this investigation it has been proved by the determination of the value of the constant l that the complex $CuAc^+$ is taken up by the exchanger used. Further, from eq. (6) the ligand number \bar{n}_R in the resin phase is obtained as a function of the acetate ion concentration of the outer solution.

SUMMARY

A method for the investigation of complex systems by the use of synthetic resin cation exchangers is described. The calculation method is developed for systems of the type $M^{2+}-A^-$, where the central ion M^{2+} and the first complex MA^+ are taken up by the exchanger, whereas the concentration in the resin phase of the higher complexes with zero or negative charges can be neglected.

From the deduction of the equations it is obvious that it is possible to calculate the complexity constants of all the mononuclear complexes formed, even if also polynuclear complexes occur. For systems, where no cation complexes are formed, e. g. systems of the type $M^{v+}-A^{v-}$, the calculations are considerably simplified.

In order to prove the method it has been applied to the cupric acetate system. The measurements have been carried out at 20°C, and the ionic strength has been kept at 1 C by addition of sodium perchlorate. The complexity constants of the complexes $CuAc^+$, $CuAc_2$, and $CuAc_3^-$ have been computed, and the values obtained are in complete agreement with previous potentiometric determinations. On account of this it is to be expected that the new method will be of great use.

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