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THE EXTRACTION OF COPPER(II) IONS WITH LIQUID ANION EXCHANGERS USING SALICYLATE AS COMPLEX-FORMING AGENT

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SUMMARY

The extraction of copper(II) ions in the presence of salicylate ions, using a solution of the salicylate form of Aliquat 336 in chloroform, involves two simultaneous processes depending on the pH and on the salicylate concentration of the aqueous phase. The composition of the species formed in the chloroform phase can be described as follows: $\text{Cu}(\text{HL})_3\text{R}_4\text{N}$ and $\text{Cu}(\text{HL})\text{LR}_4\text{N}$, where HL is the monovalent salicylate anion. The corresponding extraction constants are: $\log K_1^c = 6.47 \pm 0.03$; $\log K_2^c = 1.80 \pm 0.01$. In solutions of $\text{pH} > 9$, if the chloride form of Aliquat 336 is used, a compound of composition $\text{CuL}_2(\text{R}_4\text{N})_2$ is also formed; the extraction constant found for this species is $\log K_3^c = 3.85 \pm 0.05$.

INTRODUCTION

It was shown earlier¹ that the separation of several metal ions in the presence of the chelate-forming compound tiron could be achieved by using a liquid anion exchanger. In the present work, the liquid-liquid distribution of copper(II) ions in the presence of salicylate ions was investigated, with use of a quaternary-ammonium-group-containing liquid anion exchanger (Aliquat 336) in chloroform solution.

EXPERIMENTAL

Reagents

In all experiments reagent-grade chemicals were used; aqueous solutions were prepared with deionised water.

Chloroform solution of Aliquat 336 (chloride), about 0.1 M. Fifty grams of Aliquat 336 (methyltrioctylammonium chloride; Serva Entwicklungslabor, Heidelberg, G.F.R.) were dissolved in 680 ml of chloroform. To determine the concentration of the quaternary ammonium chloride 10 ml of the solution were shaken several times with excess of a solution of sodium salicylate, and the concentration of chloride ions in the aqueous solution after separation was determined by potentiometric titration with silver nitrate solution.

Chloroform solution of Aliquat 336 (salicylate). Fifty millilitres of the chloroform solution of Aliquat 336 (chloride) and 50 ml of 0.5 M sodium salicylate (in

aqueous solution) were shaken together. After equilibration, the phases were separated, a fresh solution of salicylate was added to the chloroform solution, and the mixture was shaken again. This procedure was repeated until chloride in the aqueous phase was not detectable by means of silver nitrate. The aqueous layer was discarded.

Sodium salicylate, 0.1 M. A 16.0120-g portion of sodium salicylate was dissolved in water, and the solution was diluted to 1 litre.

Copper(II) sulphate, 0.01 M. A 2.4968-g portion of copper sulphate pentahydrate was dissolved in water, and the solution was diluted to 1 litre.

Sodium chloride, 0.5 M. A 29.224-g portion of sodium chloride was dissolved in water, and the solution was diluted to 1 litre.

Polarographic base solution for determination of copper(II) ions. A 26.2-g portion of ammonium chloride was dissolved in water, 38 ml of concentrated aqueous ammonia were added, and the solution was diluted with water to 500 ml.

Instruments

An OH-104 square-wave polarograph (Radelkis).

An SP-700 spectrophotometer (Unicam).

A pH meter, model 25 (Radiometer, Copenhagen, Denmark).

Distribution experiments

In these experiments, 10 ml of aqueous and 10 ml of chloroform solutions were pipetted into a shaking bottle. The time of shaking was 3 min. After settling and separation of the phases, the aqueous phase was centrifuged. The equilibrium pH of the solution was determined by using glass and calomel electrodes, and the concentrations of the ions being investigated were determined in the aqueous phase, copper ions by square-wave polarography and salicylate by spectrophotometry.

Investigation of the distribution of salicylate and some other anions between water and the chloroform solution of Aliquat 336 (chloride)

To determine the ion-exchange equilibrium constant of the salicylate referred to the chloride ions ($K_{Cl,HL}^x$), the stoichiometry of the exchange, *i.e.*, the form in which the salicylate was bound to the quaternary amine in the pH range of 4–11, had to be established. The ratio of salicylate and Aliquat 336 was determined by distribution measurements. In a series of experiments, the concentration of salicylate in the aqueous solution was varied from 0.02 to 0.25 *M* while the concentration of Aliquat 336 was kept constant at 0.072 *M* (pH \approx 6). After equilibration, the concentration of salicylate (after acidification of the solution with hydrochloric acid) was determined spectrophotometrically at 300 or 237 nm. The concentration of salicylate in the organic phase was calculated from the original and equilibrium concentrations of salicylate in the aqueous phase. The calculated ratio of the salicylate concentration and Aliquat 336 concentration in the organic phase was plotted against the original concentration of salicylate in the aqueous phase (C_{sal}^0). The graph is shown in Fig. 1, from which it can be seen that, above a certain concentration of salicylate, the molar ratio of salicylate to the amine is 1:1. Thus, the composition of the compound formed can be written R_4NHL , where HL denotes the once-protonated, monovalent, salicylate ion.

The distribution of salicylate was also investigated at various pH values

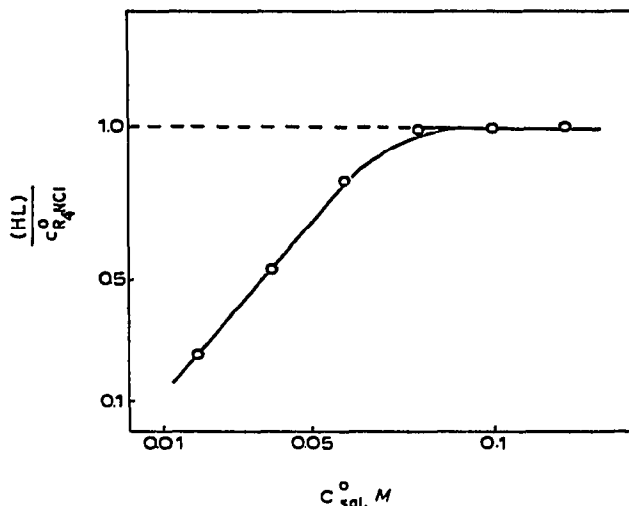


Fig. 1. Ratio of salicylate and amine concentrations in the organic phase plotted against the initial salicylate concentration in the aqueous phase: $C_{R_4NCl}^0 = 0.072 M$; $\text{pH} \approx 6$.

of the solution. The distribution coefficient was practically independent of pH in the pH range 4–10. The distribution coefficient was also determined at various initial concentrations of salicylate, but at constant concentration of chloride. The results were used to calculate the values of $K_{Cl,HL}^x$.

In order to compare the ion-exchange constants of some other anions referred to chloride, experiments were also carried out with these other anions. Aqueous solutions of these anions were shaken with a chloroform solution of Aliquat 336 (chloride). After equilibration, the pH of the aqueous phase and the concentration of chloride ion in the aqueous phase were determined. The concentration of the anion in question in the organic phase, and its distribution coefficient, were also calculated. For sulphosalicylate ions, a portion of the aqueous phase was diluted to a known volume with hydrochloric acid, the optical density of the acid solution was measured spectrophotometrically at 237 nm, and the concentration was determined by reference to a calibration graph.

Investigation of the distribution of copper(II) ions in the presence of salicylate

During the investigation of the extraction of copper ions, the concentration of metal ions was kept low (1 to 5 mg-ions per litre) compared with that of the salicylate ions ($>0.01 M$) and with that of the quaternary amine ($>0.05 M$). After equilibration and separation of the phases, the concentration of Cu(II) ions in the aqueous phase was determined by square-wave polarography using calibration graphs, and the distribution coefficient of copper (D_{Cu}) was calculated.

Investigation of the distribution of copper(II) ions using Aliquat 336 (salicylate) in chloroform solution

The values of D_{Cu} were investigated at different pH values of the solution, the concentrations of salicylate and Aliquat 336 (salicylate) being kept constant. The

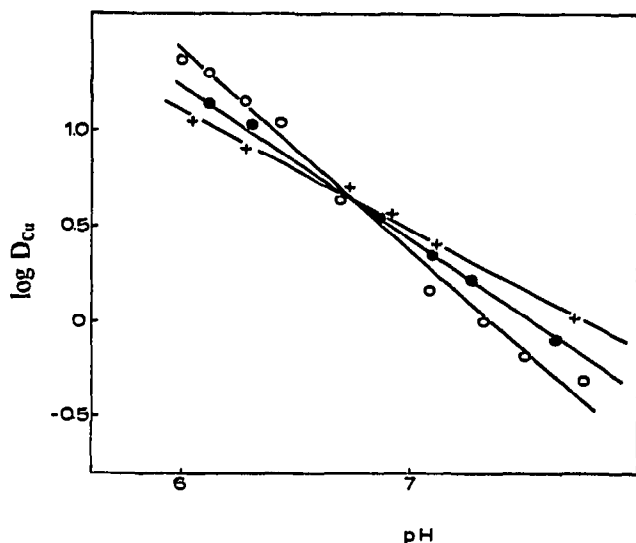


Fig. 2. Logarithmic diagram of the dependence of D_{Cu} on pH at different concentrations of salicylate: $C_{Cu}^0 = 1 \text{ mM}$; $C_{R_4NH}^0 = 0.071 \text{ M}$; $C_{sal}^0 = 0.1 \text{ M}$ (○—○); 0.06 M (●—●); 0.04 M (+—+).

values obtained for $\log D_{Cu}$ were plotted against pH for different initial concentrations of sodium salicylate; the results are shown in Fig. 2, from which it can be seen that $\log D_{Cu}$ decreases with increasing pH. However, the slope of the curve depends on the concentration of salicylate in the aqueous phase. The colour of the chloroform phase gradually changes from bluish-green to green with increasing pH; this can be explained by the fact that different extraction processes take place simultaneously, depending on the pH and on the salicylate concentration.

The change in $\log D_{Cu}$ plotted against the log of the concentration of Aliquat 336 (salicylate) gave a linear graph with a slope of 1.28. This showed that the concentration of copper ions in the organic phase increased almost in proportion with the increasing concentration of the quaternary ammonium salicylate.

Investigation of the distribution of copper(II) ions using Aliquat 336 (chloride) in chloroform solution

It was found by the distribution measurements using Aliquat 336 (chloride) that the extent of extraction of copper ions increased with increasing pH; the colour of the chloroform phase was yellowish-green. The values of $\log D_{Cu}$ plotted against pH at different initial concentrations of salicylate are shown in Fig. 3. The concentration of chloride (0.5 M) in the original solution was relatively high. From the results obtained, it can be seen that $\log D_{Cu}$ is nearly constant above pH 9, and that, at lower concentrations of salicylate, higher values of $\log D_{Cu}$ can be obtained. The change in D_{Cu} as a function of the concentration of the quaternary ammonium salt at $\text{pH} > 9$ was also investigated. Using the determined ion-exchange constant value for the salicylate-chloride exchange reaction, the fraction of Aliquat 336 was calculated for any given condition. Thus, using the values for D_{Cu} and the concentration

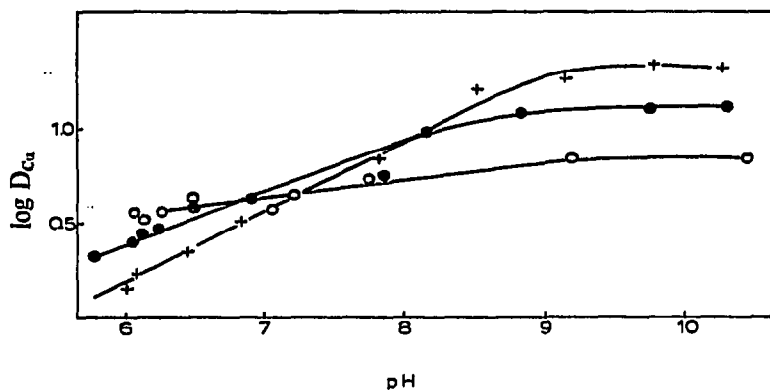
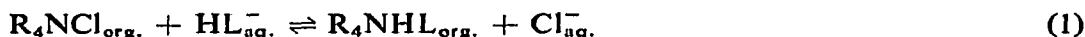


Fig. 3. Logarithmic diagram of the dependence of D_{Cu} on pH at different concentrations of salicylate: $C_{\text{Cu}}^0 = 1 \text{ mM}$; $C_{\text{R}_4\text{NCl}}^0 = 0.072 \text{ M}$; $C_{\text{Cl}^-}^0 = 0.5 \text{ M}$; $C_{\text{sal.}}^0 = 0.06 \text{ M}$ (○—○); 0.05 M (●—●); 0.04 M (+—+).

of the chloride form of Aliquat 336 in the organic phase, a logarithmic diagram was constructed; this was a straight line with a slope of *ca.* 2. It was also found that $\log D_{\text{Cu}}$ decreased with increasing concentration of chloride in the aqueous phase.

RESULTS AND DISCUSSION

The ion-exchange process between the chloride and monovalent salicylate anions can be described by the equation



The equilibrium constant is given by

$$K_{\text{Cl,HL}}^x = \frac{(\text{R}_4\text{NHL}) [\text{Cl}^-]}{(\text{R}_4\text{NCl}) [\text{HL}^-]} = \frac{D_{\text{HL}} [\text{Cl}^-]}{C_{\text{R}_4\text{NCl}}^0 - (\text{R}_4\text{NHL})} \quad (2)$$

in which the concentrations shown in square brackets refer to the aqueous phase and those shown in parentheses refer to the organic phase, D_{HL} is the distribution coefficient of salicylate, and $C_{\text{R}_4\text{NCl}}^0$ denotes the initial concentration of quaternary ammonium chloride in the organic phase.

The ion-exchange equilibrium constant was calculated from eqn. 2 using the experimentally found value of D_{HL} , the concentration of salicylate anion in the organic phase (R_4NHL), the concentration of chloride in the equilibrated aqueous phase and the initial concentration of Aliquat 336 in the chloroform phase. The ion-exchange equilibrium constants of the other anions were calculated in a similar way. The results are presented in Table I.

The $\text{Cu}(\text{II})$ ions in the presence of salicylate may form complexes having the compositions CuL and CuL_2^- , depending on the pH and the concentration of salicylate. We calculated the mole fractions of the various species in the aqueous

TABLE I
ION-EXCHANGE EQUILIBRIUM CONSTANTS OF DIFFERENT ANIONS REFERRED TO CHLORIDE

Anions (A^{n-})	Equilibrium constant ($\log K^x$)
Salicylate (HL^-)	2.43 ± 0.02
Sulphosalicylate (HA^{2-})	2.24 ± 0.05
Bromide (A^-)	1.34 ± 0.04
Nitrate (A^-)	1.33 ± 0.06
Oxalate (A^{2-})	-1.28 ± 0.07
Acetate (A^-)	-1.74 ± 0.05
Sulphate (A^{2-})	-3.6 ± 0.2

phase in the pH range investigated (pH 4–8), using the “ α ” functions introduced by Ringbom². Thus,

$$\alpha_{Cu} = \frac{C_{Cu}}{[Cu^{2+}]} = 1 + [L] \beta_1 + [L]^2 \beta_2 = 1 + \frac{C_{sal.}^0}{\alpha_{L(H)}} \beta_1 + \left(\frac{C_{sal.}^0}{\alpha_{L(H)}} \right)^2 \beta_2 \quad (3)$$

where C_{Cu} is the concentration of Cu(II) ions in the aqueous phase, $C_{sal.}^0$ is the initial concentration of sodium salicylate in the aqueous phase, β_1 and β_2 are the overall stability constants of the copper–salicylate complexes ($\log \beta_1 = 10.6$ and $\log \beta_2 = 18.45$; see ref. 3), and $\alpha_{L(H)}$ is the side-reaction function of protonation of the salicylate ligand. The value of $\alpha_{L(H)}$ can be calculated using the following equation

$$\alpha_{L(H)} = 1 + [H^+] K_1 + [H^+]^2 K_1 K_2 \quad (4)$$

in which K_1 and K_2 are protonation constants of the divalent salicylate ion. The value of $\log K_1$ is 13.6, whereas $\log K_2 = 3$ (see ref. 3). Thus,

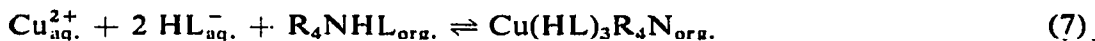
$$\alpha_{CuL} = \frac{C_{Cu}}{[CuL]} = 1 + \frac{\alpha_{L(H)}}{C_{sal.}^0 K_{CuL}} + \frac{C_{sal.}^0 K_{CuL}}{\alpha_{L(H)}} \quad (5)$$

and

$$\alpha_{CuL_2} = \frac{C_{Cu}}{[CuL_2^{2-}]} = 1 + \left(\frac{\alpha_{L(H)}}{C_{sal.}^0} \right)^2 \cdot \frac{1}{\beta_2} + \frac{\alpha_{L(H)}}{C_{sal.}^0 K_{CuL_2}} \quad (6)$$

where K_{CuL} and K_{CuL_2} are the stability constants of the copper–salicylate complexes.

The values of α_{Cu} , α_{CuL} and α_{CuL_2} were calculated at various pH and at various concentrations of salicylate (0.1, 0.06 and 0.04 M); their reciprocal values are the mole fractions of the species. The calculations showed that in the pH range 4–6, mainly Cu^{2+} and complex of composition CuL are present in the aqueous phase. At the extraction, using a chloroform solution of Aliquat 336 (salicylate) therefore, the following reactions were assumed



The corresponding extraction equilibrium constants are

$$K_1^c = \frac{\text{Cu}(\text{HL})_3 \text{R}_4\text{N}}{[\text{Cu}^{2+}] [\text{HL}^-]^2 (\text{R}_4\text{NHL})} = \frac{D_{1\text{Cu}} \alpha_{\text{Cu}}}{C_{\text{sal.}}^0 (\text{R}_4\text{NHL})} \quad (9)$$

$$K_2^c = \frac{(\text{Cu HL}_2\text{R}_4\text{N})}{[\text{CuL}] (\text{R}_4\text{NHL})} = \frac{D_{2\text{Cu}} \alpha_{\text{CuL}}}{(\text{R}_4\text{NHL})} \quad (10)$$

where

$$D_{1\text{Cu}} = \frac{(\text{Cu}(\text{HL})_3\text{R}_4\text{N})}{C_{\text{Cu}}} = \frac{(\text{Cu}(\text{HL})_3\text{R}_4\text{N})}{[\text{Cu}^{2+}] \alpha_{\text{Cu}}} \quad (11)$$

and

$$D_{2\text{Cu}} = \frac{(\text{Cu HL}_2\text{R}_4\text{N})}{C_{\text{Cu}}} = \frac{(\text{CuHL}_2\text{R}_4\text{N})}{[\text{CuL}] \alpha_{\text{CuL}}} \quad (12)$$

By combining eqns. 9 and 10, the equation for the overall distribution coefficient of the copper can be obtained

$$D_{\text{Cu}} = (\text{R}_4\text{NHL}) \left[\frac{K_1^c (C_{\text{sal.}}^0)^2}{\alpha_{\text{Cu}}} + \frac{K_2^c}{\alpha_{\text{CuL}}} \right] \quad (13)$$

The D_{Cu} values were determined by experiment and the values of α , the side-reaction functions, were calculated by using the known pH value and the concentration of salicylate. By substituting these values at various experimental conditions in eqn. 11, an equation system with two unknown quantities was obtained; by solving this system, the values of the K_1 and K_2 extraction constants were calculated. These were

$$\log K_1^c = 6.47 \pm 0.03$$

$$\log K_2^c = 1.80 \pm 0.01$$

To verify the assumptions and calculations, we compared the calculated and experimentally found values of $\log D_{\text{Cu}}$ at various pH values; these are shown in Fig. 4, from which it can be seen that the calculated and experimental values are in close agreement. Thus the assumption was correct.

In the distribution experiments carried out at pH > 9 we found that the D_{Cu} values increased with the concentration of the quaternary ammonium chloride in the organic phase. It was found also, by calculation, that in the pH range mentioned and under the given concentration conditions, the CuL_2^{2-} complex was predominant in the aqueous phase. Therefore the following extraction reaction was assumed



The extraction equilibrium constant is given by

$$K_3^c = \frac{(\text{CuL}_2(\text{R}_4\text{N})_2)}{[\text{CuL}_2^{2-}] (\text{R}_4\text{NCl})^2} = \frac{D_{3\text{Cu}} \alpha_{\text{CuL}} [\text{Cl}^-]^2}{(\text{R}_4\text{NCl})^2} \quad (15)$$

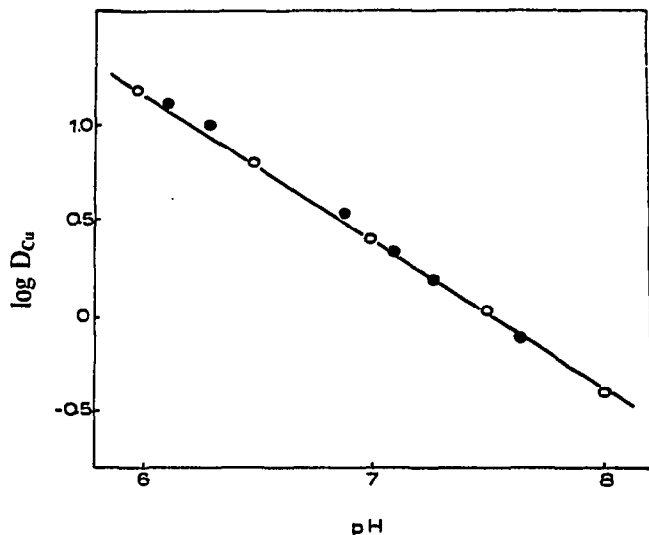


Fig. 4. Calculated and experimentally found values of $\log D_{Cu}$ at various pH values: $C_{Cu}^0 = 1 \text{ mM}$; $C_{NaCl}^0 = 0.06 \text{ M}$; $C_{R_4NHCl}^0 = 0.071 \text{ M}$; calculated (○—○), measured (●—●).

where

$$D_{3Cu} = \frac{(CuL_2(R_4N)_2)}{C_{Cu}} = \frac{(CuL_2(R_4N)_2)}{[CuL_2^{2-}] \alpha_{CuL_2}} \quad (16)$$

By using eqn. 15, we calculated, from known quantities, the value of the third extraction constant; this was

$$\log K_3^c = 3.85 \pm 0.05$$

So, if we want to calculate the distribution coefficient of the copper in the pH range 6–10, the process described by eqn. 8 must be taken into consideration. Thus, the

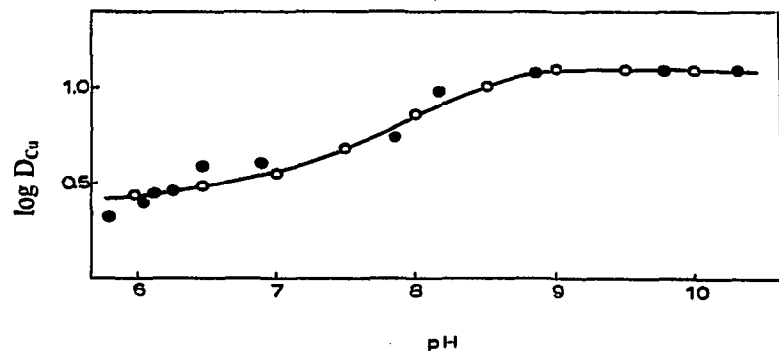


Fig. 5. Calculated and experimentally found values of D_{Cu} at various pH values: $C_{Cu}^0 = 1 \text{ mM}$; $C_{NaCl}^0 = 0.05 \text{ M}$; $C_{Cl}^0 = 0.5 \text{ M}$; $C_{R_4NC}^0 = 0.02 \text{ M}$; calculated (○—○), measured (●—●).

overall distribution coefficient, D_{Cu} is the sum of $D_{2\text{Cu}}$ and $D_{3\text{Cu}}$. The calculated and experimentally found values for D_{Cu} are shown in a logarithmic diagram in Fig. 5; it can be seen that agreement between them was reasonably good.

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