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THE SORPTION OF METAL SALTS BY FILTER PAPER

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SUMMARY

A detailed study has been made of the sorption of copper(II) ions by Whatman 41 filter paper. With low concentrations of copper ion, adsorption of the cation can be attributed to ion exchange, at higher values ingestion of the salt into the fibres occurs. The observed relationship between the extent of adsorption and the exchange capacity is explained in terms of a hypothesis based on the Donnan membrane theory.

INTRODUCTION

There is ample qualitative¹⁻⁶ and quantitative⁷⁻¹⁰ evidence that filter paper can act as an ion-exchange medium and a number of workers have discussed the role of ion exchange in the differential migration of cations on paper chromatograms. One recent article⁶ even proposes a simple equation to relate the extent of migration to the cation concentration and ion-exchange capacity.

However, the idea of a simple cation-exchange process is challenged by the observation that hydroxyl ions⁴ and other anions^{11,12} can be adsorbed by filter paper. Views also differ in regard to the nature of the exchange sites. The ash content of Whatman 1 paper is about 0.06 % and its ion-exchange capacity is about 8 mequiv./g. Thus the paper contains a significant amount of non-bound metal salts and/or insoluble impurities such as silicates; together with some ions attached to carboxyl groups. From neutron activation studies¹³, in which the sodium content of paper as received, after pre-washing and after chromatography was determined, it has been concluded⁶ that there is a large amount of unbound sodium ion in the paper, some bound sodium ion which can be replaced in chromatography, and some which is seemingly inaccessible to replacement.

Additional information on the nature of the adsorption process on paper has therefore been sought through a detailed isothermal study of the sorption of copper (II) ions by an acid washed filter paper (Whatman 41).

EXPERIMENTAL

Samples of Whatman 41 filter paper were washed repeatedly with either hydrochloric acid or sodium chloride solutions. The excess electrolyte was then removed

by repeated washing with distilled water, the washings being tested on each occasion for pH or sodium content respectively. At the end of this process the exchange groups were considered to be either in the hydrogen or sodium ion form.

The papers were dried in an oven at 110° , but were subsequently allowed to come to equilibrium with atmospheric moisture before use. To allow calculation of adsorption in terms of dry weight, the moisture content of test samples was determined by titration with Karl Fischer reagent.

Multiple 2 g samples of either the sodium or acid form of the paper were placed in glass vials and allowed to come to equilibrium (24 h at 25° with constant rotation) with 20 or 25 ml of standard copper nitrate solutions (10^{-4} to 10^{-2} M).

The concentration of copper ions in the test solutions was determined accurately after establishment of equilibrium and blanks of the original solutions were run simultaneously to compensate for any sorption or exchange by the glass vials used, or absorption of carbon dioxide. Changes in pH were measured with a Beckman research pH meter and the sodium content of the solutions was determined in a flame photometer based on a Techtron A4 atomic absorption spectrophotometer unit.

All solutions were prepared using A.R. grade copper nitrate and deionised distilled water. Stock copper solutions were standardised by electro-deposition, while the copper content of the diluted solutions was determined colorimetrically, using the absorption of the blue copper tetramine ion at 610 nm. Measurements were made in a Unicam SP500 spectrophotometer using either 1 or 4 cm cells.

The amount of copper ion sorbed and sodium or hydrogen ion released was calculated from changes in the solution composition. The results of these studies are summarised graphically in Figs. 1 and 2, each point being the mean of several tests.

DISCUSSION

Fig. 1 shows the amount of Cu^{2+} adsorbed and $\text{Na}^{+}/2$ released (both in mmoles/g dry paper) as a function of the equilibrium copper concentration.

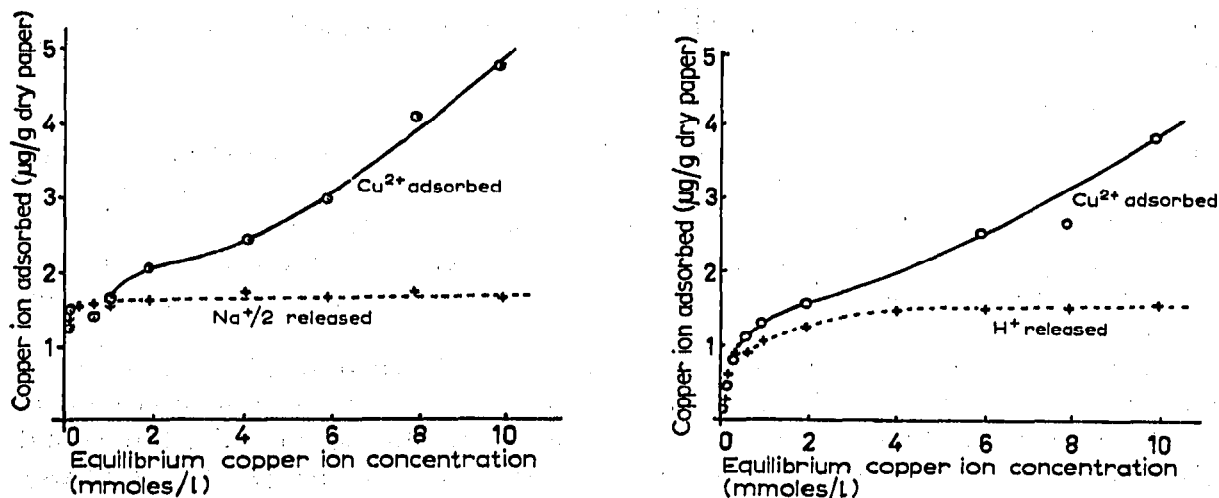


Fig. 1. The sorption isotherm for copper ions on Whatman 41 filter paper (exchange groups in Na^{+} form) at 25° .

Fig. 2. The sorption isotherm for copper ions on Whatman 41 filter paper (exchange groups in H^{+} form) at 25° .

The divergence of the curves at higher copper concentrations indicates that two sorption processes may be involved. The first, which predominates at concentrations of less than 1 mmole/l, is undoubtedly the exchange of Cu^{2+} for Na^+ in a manner similar to that observed in any cation-exchange resin. However, with equilibrium concentrations above this value, the sodium ion released remained constant, indicating that all the exchange sites were occupied by an equivalent number of copper ions.

The reaction may be written

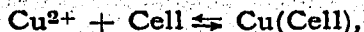


where Cell represents the cellulose matrix and R represents the functional groups responsible for the ion exchange.

Whatman 41 filter paper is an acid (HCl and HF) washed paper and as such should be virtually free from impurities. However, comparison of Figs. 1 and 2 shows that further washing of this paper with HCl reduces the exchange capacity from 3.4 mequiv./dry g (in Na^+ form) to 1.5 mequiv./dry g (in H^+ form). The type of functional groups (R) therefore appears to be about equally divided between carboxyl groups attached to the cellulose and acid-soluble impurities.

After saturation of the exchange sites, the amount of copper ion adsorbed increases near linearly with increased solution concentration. This second sorption process can be attributed to ingestion of electrolyte into a cellulose-water complex¹⁴, adsorption by cellulose microfibrils, or complex formation¹⁵.

If "complex" formation occurs between the cellulose unit (Cell) and Cu^{2+} (for example, at selected OH groups in the glucose unit in non-crystalline regions or at pentosans bound to the microfibril), then the reaction may be described as



the position at equilibrium being defined by the equation

$$K = [\text{Cu}(\text{Cell})] / [\text{Cu}^{2+}] [\text{Cell}]$$

From the magnitude of the adsorption it can be seen that only a small fraction of the total glucose units is involved. Thus [Cell] can be assumed to be effectively constant and

$$K' = [\text{Cu}(\text{Cell})] / [\text{Cu}^{2+}]$$

If the amount of copper ion adsorbed at higher solution concentrations is taken to indicate [Cu(Cell)], then the near linearity of the second leg of the copper sorption curves (Figs. 1 and 2) is taken support of the complex formation theory.

However, the slope of the two graphs is not similar, and for this reason, the preferable explanation is one which relates the amount of sorption to the maximum exchange capacity.

This aim can be achieved by treating the two-phase distribution in terms of the Donnan membrane theory¹⁶. The interface between the cellulose fibres and external solution can be considered to act as a semi-permeable membrane, and the functional groups (R) can be regarded as non-diffusible ions trapped in a swollen paper phase.

According to the Donnan theory, an electrolyte (*e.g.*, A_xB_y) from the external solution will pass through the membrane until the relationship

$$\left[a_{A^{y+}} \right]_p^x \cdot \left[a_{B^{x-}} \right]_p^y = \left[a_{A^{y+}} \right]_w^x \cdot \left[a_{B^{x-}} \right]_w^y$$

is satisfied. (The subscripts "p" and "w" indicate the paper and external aqueous phases respectively.)

For the dilute solutions used in this study, activity coefficients can be considered to cancel and the appropriate equation becomes

$$[\text{Cu}^{2+}]_p [\text{NO}_3^-]_p^2 = [\text{Cu}^{2+}]_w [\text{NO}_3^-]_w^2$$

Because the paper also contains the anions, R, the principle of electrical neutrality requires that

$$2[\text{Cu}^{2+}]_p = [\text{R}]_p + [\text{NO}_3^-]_p$$

For calculation of the concentrations of the various species within the swollen fibrils, it is necessary to know the internal void volume. This cannot be determined directly, but an estimate can be made from the adsorption results.

In the experiments, 2 g of paper were suspended in 25 ml of solution, and either Na^+ or H^+ were displaced into the external solution. After saturation of the exchange sites,

$$[\text{Na}^+]_w \text{ or } [\text{H}^+]_w = \frac{\text{exchange capacity} \times 2 \times 10^3}{25} \text{ moles/l}$$

From which $[\text{Na}^+]_w = 2.7 \times 10^{-4}$ moles/l and $[\text{H}^+]_w = 1.2 \times 10^{-4}$ moles/l. From electro-neutrality considerations,

$$[\text{NO}_3^-]_w = 2[\text{Cu}^{2+}]_w + [\text{Na}^+]_w \text{ or } [\text{H}^+]_w$$

Thus for any equilibrium value of $[\text{Cu}^{2+}]_w$, a value of $[\text{NO}_3^-]_w$ can be calculated, and used to determine the magnitude of the function $[\text{Cu}^{2+}]_w [\text{NO}_3^-]_w^2$. This function, assuming the Donnan theory applies, should equal the term $[\text{Cu}^{2+}]_p [\text{NO}_3^-]_p^2$.

In the swollen fibres,

$$[\text{NO}_3^-]_p = 2[\text{Cu}^{2+}]_p - [\text{Exchange groups}]_p$$

If A represents the mmoles of Cu^{2+} adsorbed/g paper and V is the volume of the internal phase/g,

$$[\text{Cu}^{2+}]_p = \frac{A \times 10^{-6} \times 10^3}{V}, \text{ and}$$

$$[\text{Exchange groups}]_p = \frac{3.4 \times 10^{-3}}{V} \text{ for Na}^+ \text{ paper or } \frac{1.55 \times 10^{-3}}{V} \text{ for H}^+ \text{ paper}$$

$$\therefore [\text{NO}_3^-]_p = \frac{2A \times 10^{-3}}{V} - \frac{3.4 \times 10^{-3}}{V} \text{ or } \frac{(2A - 1.55) \cdot 10^{-3}}{V} \text{ and}$$

$$[\text{Cu}^{2+}]_p [\text{NO}_3^-]_p^2 = \frac{A(2A - 3.4)^2 \cdot 10^{-9}}{V^3} \text{ or } \frac{A(2A - 1.55)^2 \cdot 10^{-9}}{V^3}$$

Values of A corresponding to particular $[\text{Cu}^{2+}]_w$ values were read off Figs. 1 and 2, and substituted in this equation; and by equating the two segments of the Donnan equation, values of V were calculated. These values are summarised in Table I.

The variations in V values about the mean figure of $0.33 \text{ cm}^3/\text{g}$ can be attributed to small errors in the measured copper adsorbance, variations in the degree of swelling with electrolyte concentration, and small differences in activity coefficients.

TABLE I
VOLUME OF INTERNAL PORES OF PAPER

$[Cu^{2+}]_w$ (mmole/l)	Paper in Na^+ form		Paper in H^+ form	
	Cu^{2+} adsorbed (μ moles/g)	Calculated ($V, cm^3/g$)	Cu^{2+} adsorbed (μ moles/g)	Calculated ($V, cm^3/g$)
2	2.1	0.33	1.65	(0.53)
3	2.1	0.33	1.85	(0.44)
4	2.45	0.27	2.05	0.37
5	2.75	0.29	2.3	0.35
6	3.1	0.30	2.6	0.34
7	3.5	0.32	2.9	0.33
8	4.15	0.36	3.2	0.33
9	4.45	0.36	3.55	0.33
10	4.85	0.36	3.9	0.33

The significant point is the similarity of the two sets of figures, since it indicates that the membrane hypothesis allows correlation of the results obtained with exchangers of different capacity. In addition, this hypothesis provides an explanation for the observed adsorption of anions by the support in paper chromatography, since any ingested cations must be accompanied by an equivalent number of anions.

CONCLUSIONS

Ion exchange plays an important role in determining the extent of migration of cations when a solution of an acid or a salt continuously ascends a strip of paper.

However, use of the extent of migration to calculate the exchange capacity is only valid if the threshold of salt ingestion into the fibres is not exceeded.

This threshold is a function of the exchange capacity of the paper. On Whatman 41 paper using copper ions it was $8 \times 10^{-4} M$ when the capacity was 3.4 mequiv./g and about half this value when the capacity was reduced to 1.5 mequiv./g by acid washing. With Whatman 1 the threshold is predicted to be 0.003 M with untreated paper. However, KNUDSON *et al.*⁶ have shown that the capacity of this paper can be reduced from 8 to 3.2 or 2.5 mequiv./g by washing with 2 M acetic acid or 1 M perchloric acid respectively.

Thus in interpreting the migration of cations on paper in terms of ion exchange, one must consider both the type of paper and its pretreatment; and once the applied solution concentration exceeds the threshold value, sorption is best considered in terms of a permeable membrane model. This model has the added advantage that it allows semi-quantitative prediction of the extent to which anion adsorption can occur in chromatographic studies.

The functional groups, present in chromatography paper either as carboxyl groups on the cellulose or as impurities, influence the sorption characteristics of the support in a number of ways, and their role cannot be considered solely in terms of the exchange of cations which can occur at these sites.

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