

# INVESTIGATION OF COMPLEX EQUILIBRIA BY MEANS OF CHROMATOGRAPHY WITH ION-EXCHANGE PAPERS

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It has been shown<sup>1-3</sup> that chromatography on resin papers makes it possible to obtain information about the nature of ions existing in solution, to determine their charge and consequently to establish whether complexes are formed; the conclusions obtained with these procedures are, however, essentially qualitative.

Since chromatography with ion-exchange papers has a number of interesting features, such as rapidity and simplicity of operation, the present work was carried out with the aim of developing a suitable treatment of the chromatographic data in order to obtain quantitative information about the equilibria in solutions and to determine the stability constants.

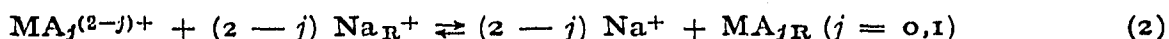
To achieve this aim the method of calculation suggested by FRONAEUS for the quantitative determination of stepwise constants<sup>4-7</sup> has been extended to resin paper chromatography. The procedure developed has been applied to the study of the system copper-acetate, which had previously been investigated by FRONAEUS by means of cation-exchange resins<sup>4</sup>.

## THEORETICAL

Complex formation between a bivalent central ion  $M^{2+}$  and a monovalent ligand  $A^-$  according to the reaction:



the constants of which are  $\beta_1, \beta_2 \dots \beta_N$ , can be determined by means of the exchange equilibria of the ionic species existing in the solution on a cationic exchanger ( $Na_R^+$ ):



The relationship between exchange equilibria and equilibria of complex formation can be obtained according to FRONAEUS by introducing a distribution function  $\varphi$ ; this function, which can be experimentally determined, is given by the following relationship:

$$\varphi = \frac{C_{MR}}{C_M}$$

where  $C_{MR}$  and  $C_M$  are the total concentrations of the metal species at the equilibrium on the resin and in the solution respectively;  $\varphi$  can also be expressed as a function

of the formation constants and of the concentration of ligand

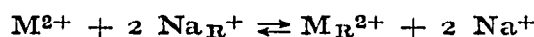
$$\varphi = \frac{[M^{2+}]_R + [MA^+]_R}{[M^{2+}] \left( 1 + \sum_{j=1}^N \beta_j [A^-]^j \right)} \quad (3)$$

It has been shown by MARTIN AND SYNGE<sup>8</sup> that the partition coefficient,  $\alpha$ , of a certain species which distributes between a stationary and a mobile phase is related to the chromatographic  $R_F$  value by the equation:

$$\alpha = \left( \frac{1}{R_F} - 1 \right) \frac{A_L}{A_S} \quad (4)$$

where  $A_L/A_S$  is the ratio of the amount of solvent to the amount of resin in a cross section of the paper; the validity of the above relationship has been verified in the case of equilibria on ion-exchange papers<sup>1,9</sup>.

In the absence of a ligand the equilibrium constant  $K_e$ , of an exchange reaction



can be expressed as

$$\log K_e = \log \frac{[M^{2+}]_R}{[M^{2+}]} + \log [H^+] - 2 \log [H^+]_R$$

where:

$$\log \frac{[M^{2+}]_R}{[M^{2+}]} = \log \alpha.$$

In the presence of a ligand the numerator represents the total concentration of the metal species on the resin and the denominator the total concentration of the metal ions in solution; as a consequence  $\alpha$  has the same meaning as  $\varphi$  (eqn. (3)), and the same theoretical treatment applied to the  $\varphi$  function can be extended to  $\alpha$ .

The concentration of the metal species in the resin phase (eqn. (3)) can be expressed by means of the exchange constant  $K_j$  (eqn. (2)).

$$[MA_{j(2-j)^+}]_R = [MA_{j(2-j)^+}] \frac{[Na^+]_R^{2-j}}{[Na^+]^{2-j}} K_j = [MA_{j(2-j)^+}] l_j$$

and the function  $\alpha$  by means of the following equation:

$$\alpha = l_0 \frac{1 + l [A^-]}{1 + \sum_{j=1}^N \beta_j [A^-]^j} \quad (5)$$

where:

$$l = \frac{\beta_1 l_1}{l_0} \text{ and } l_0 = \frac{[M^{2+}]_R}{[M^{2+}]} = \lim_{[A^-] \rightarrow 0} \alpha \quad (6)$$

The terms  $K_j$  and  $l_j$  are functions of the activity coefficients in the resin paper and in the solution; in the case of ion-exchange papers, if a medium of constant ionic strength, is used, the activity coefficients in solutions may be considered to be constant. To

relate the  $\alpha$  values to a constant  $C_{MR}$ , according to the FRONAEUS method, experiments were carried out in which the metal ion concentration was changed over a fairly wide range; it was found that the effect upon the  $\alpha$  value is within the range of the experimental errors. We conclude therefore that changes of activity coefficients in the resin paper have only a minor influence and may be neglected in the present treatment.

The formation constants have been calculated by means of the following procedure. From the experimental data,  $\alpha$  and  $A^-$ , the following function is calculated

$$\alpha_1 = \left( \frac{l_0}{\alpha} - 1 \right) \frac{1}{[A^-]} \quad (7)$$

which by extrapolation for  $[A^-] \rightarrow 0$  gives  $\alpha_1^\circ = \beta_1 - l$ . From this value a new function containing the two quantities  $l_0$  and  $\beta_1 - l$  is introduced

$$f = \frac{l_0}{\varphi} \{ [(\beta_1 - l) [A^-] - 1] + 1 \} \frac{1}{[A^-]^2} \quad (8)$$

and by extrapolation, for  $[A^-] \rightarrow 0$ , the limiting value  $f^\circ$  is obtained:

$$f^\circ = \beta_1 (\beta_1 - l) - \beta_2 \quad (9)$$

To obtain the formation constants the following function can be determined

$$\frac{\Delta f}{[A^-]} = \beta_1 \frac{\Delta \alpha_1}{[A^-]} - \sum_{j=3}^N \beta_j [A^-]^{j-3} \quad (10)$$

where  $\Delta f = f - f^\circ$  and  $\Delta \alpha_1 = \alpha_1 - \alpha_1^\circ$ .

By plotting  $\Delta f/[A^-]$  against  $\Delta \alpha_1/[A^-]$ ,  $\beta_1$  can be obtained. When  $\Delta f/[A^-]$  and  $\Delta \alpha_1/[A^-]$  are almost constant over the entire  $[A^-]$  range investigated, eqn. (10) cannot be applied, and  $\beta_1$  is approximatively given by the quotient  $\Delta f/\Delta \alpha_1$ . In order to obtain higher complexity constants, the function

$$g = \left\{ f - \beta_1 \alpha_1 + \frac{l_0}{\alpha} \beta_2 \right\} \frac{1}{[A^-]} \quad (11)$$

is calculated. By introducing the functions  $\alpha_1$ ,  $f$  and  $g$ , eqn. (4), at small ligand concentrations, can be written in the form:

$$g = \beta_1 \alpha_1 - \beta_3 \quad (12)$$

Thus  $g$  is a linear function of  $\alpha_1$ , the slope gives  $\beta_2$  and the intercept  $\beta_3$ .

#### EXPERIMENTAL

Amberlite ion-exchange paper SA-2 (Rohm & Haas) containing ca. 45% of a strong cation exchanger (Amberlite IR-120 sulphonic resin in the sodium form) was used.

The paper was cut in pieces of about  $22 \times 3$  cm size. These strips were kept for about 30 min in 1 M NaCl and then washed with distilled water. The treatment was repeated several times; the papers were air-dried before use.

Chromatograms were run according to the ascending technique, keeping the temperature constant at 30°. The eluting solution was allowed to reach the same height in every strip; 25 min were needed for this. The copper solution was about 0.1 *M* in copper perchlorate; a few microliters were used for each chromatogram.

In order to realize the conditions required for this investigation (to keep the ionic strength and the hydrogen ion concentration in the solution constant and to carry out chromatograms on a wide range of ligands) the eluants were prepared by mixing sodium acetate and acetic acid, of various concentrations, in the molar ratio 2:1 and adding sodium perchlorate to keep the ionic strength constant. The composition of every eluant was:  $C_{A'} = mM$  AcONa,  $0.5 C_{A'} = mM$  AcOH and  $1000 - C_{A'} = mM$  NaClO<sub>4</sub>. The ligand concentration was varied in the range 10–400 *mM*.

The spots were detected with K<sub>4</sub>Fe(CN)<sub>6</sub>;  $A_L$  was obtained from the difference in weight of a strip of pure air-dried exchange paper in the sodium form before and after impregnation with the eluting solution;  $A_S$  is known from the concentration of the resin in the paper (45 %).

The ratio  $A_L/A_S$  was calculated for several concentrations of the eluting solutions and the results were plotted *versus* the acetate concentration; by graphic interpolation this ratio could therefore be obtained for any concentration of ligand.

The experimental results are collected in Table I. In the treatment of these data according to the procedure described it was assumed that the equilibrium concentration of the ligand [A<sup>-</sup>] is equal to the analytical concentration of the eluting solution; the factor due to the swelling of the resin and the correction due to the change of concentration of the ligand because of the formation of complexes in solution have been neglected. These approximations are justified considering the experimental conditions of the chromatographic technique and the degree of accuracy obtainable in the measurement of the  $R_F$  value.

TABLE I  
CORRESPONDING VALUES OF [A<sup>-</sup>],  $R_F$ ,  $A_L/A_S$  AND  $\alpha$  FOR THE COPPER-ACETATE SYSTEM

[A <sup>-</sup> ] mM	$R_F$	$A_L/A_S$	$\alpha$
0			23.7
10	0.16	3.27	17.2
20	0.21	3.26	12.3
30	0.23	3.26	10.9
40	0.24	3.25	10.3
60	0.32	3.25	6.59
80	0.39	3.24	5.06
100	0.45	3.23	3.94
120	0.48	3.23	3.48
140	0.54	3.22	2.74
160	0.56	3.21	2.54
180	0.58	3.21	2.31
200	0.65	3.20	1.73
225	0.63	3.19	1.88
250	0.66	3.18	1.62
275	0.76	3.16	0.98
300	0.71	3.15	1.29
360	0.74	3.14	1.10
400	0.80	3.13	0.78

In Fig. 1  $\alpha$  is plotted against the ligand concentration  $[A^-]$ . To calculate  $l_0$  according to eqn. (6),  $1/\alpha$  is plotted against  $[A^-]$  (Fig. 2); by extrapolating to zero free ligand concentration the  $l_0$  value (23.7) is obtained.

In Table II the calculated values for  $\alpha_1$ ,  $f$ ,  $g$ ,  $\Delta f/[A^-]$  and  $\Delta\alpha_1/[A^-]$  are reported;  $\alpha_1^\circ$  and  $f^\circ$  were determined by graphical extrapolation as shown in Fig. 3.

Since the values of  $\Delta f/[A^-]$  and  $\Delta\alpha/[A^-]$  in Table II are, within the limits of experimental error, almost constant,  $\beta_1$  was calculated as the ratio  $\Delta f/\Delta\alpha_1$ :

$$\beta_1 = (43 \pm 10) M^{-1}$$

From the limiting values of  $l_0$  and  $\alpha^\circ$ , it is evident that  $l_0 > l$ , as  $\text{Cu}^{2+}$  is more strongly sorbed than  $\text{CuAc}^+$ .

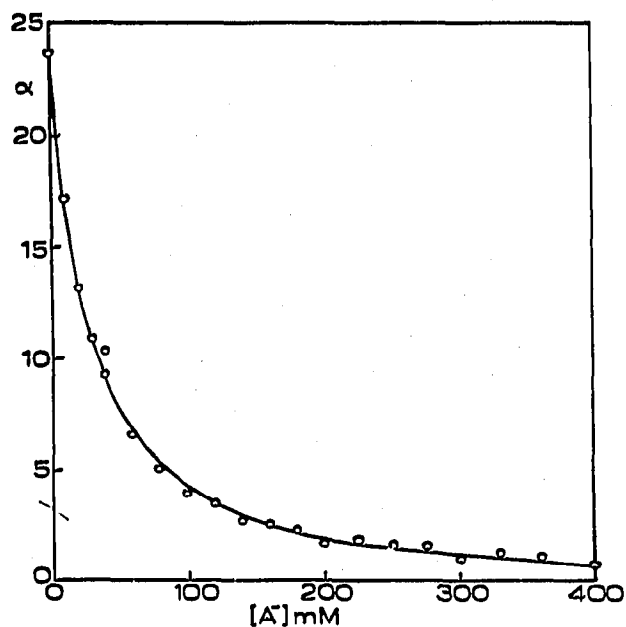


Fig. 1. Plot of the partition coefficient  $\alpha$  versus ligand concentration.

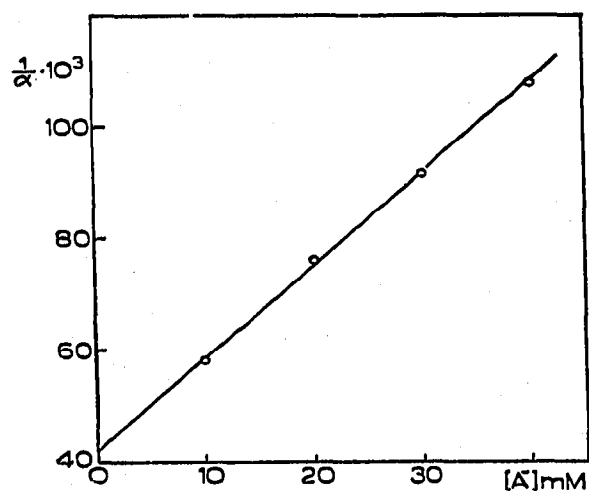


Fig. 2. Determination of the limiting value of  $\alpha$ . Plot of  $1/\alpha$  as a function of  $[A^-]$ .

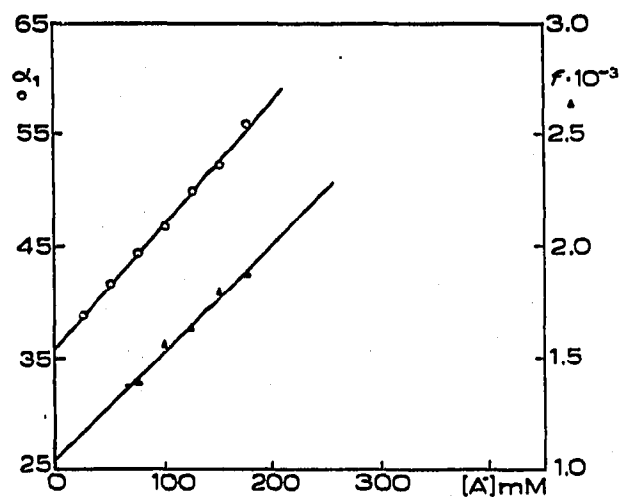


Fig. 3. Determination of the limiting values of  $\alpha_1$  and  $f$ . Plot of  $\alpha_1$  ( $-O-O-$ ) and  $f$  ( $-\Delta-\Delta-$ ) as functions of  $[A^-]$ .

TABLE II  
CORRESPONDING VALUES OF  $[A^-]$ ,  $\alpha_1$ ,  $f$ ,  $g$ ,  $\Delta f/[A^-]$  AND  $\Delta\alpha_1/[A^-]$

$[A^-]$ mM	$\alpha_1$ $M^{-1}$	$f \times 10^{-3}$ $M^{-2}$	$g \times 10^{-3}$ $M^{-3}$	$\Delta f/[A^-] \times 10^{-3}$ $M^{-3}$	$\Delta\alpha_1/[A^-]$ $M^{-2}$
0	36	1.06			
25	38.8	1.33			
50	41.6	1.40	22.2	6.80	112
75	44.3	1.39	21.4	4.40	110
100	46.6	1.57	23.3	5.10	106
125	49.8	1.64	24.2	4.67	111
150	52.3	1.81	25.8	5.03	108
175	55.8	1.87	27.0	4.65	113
200	56.5	1.93	27.6	4.37	102
225	57.3	1.95	27.9	3.89	94.8
250	58.4	2.03	28.5	3.89	89.6
275	60.4	2.09	29.3	3.76	88.6
300	60.9	2.11	29.6	3.50	83.0
325	63.2	2.19	30.8	3.47	83.8
350	68.3	2.38	33.1	3.76	92.6
375	76.3	2.61	36.8	4.14	107
400	96.3	3.31	46.1	5.63	151

Using this value of  $\beta_1$ , and that of  $\beta_2$  obtained from eqn. (9), the function  $g$  can be calculated from eqn. (11) (Table II). According to eqn. (12)  $g$  is plotted against  $\alpha_1$ ;  $\beta_2$  and  $\beta_3$  are respectively obtained from the slope and the intercept with the  $g$ -axis (Fig. 4):

$$\beta_2 = (500 \pm 100) M^{-3}$$

$$\beta_3 = (800 \pm 600) M^{-3}$$

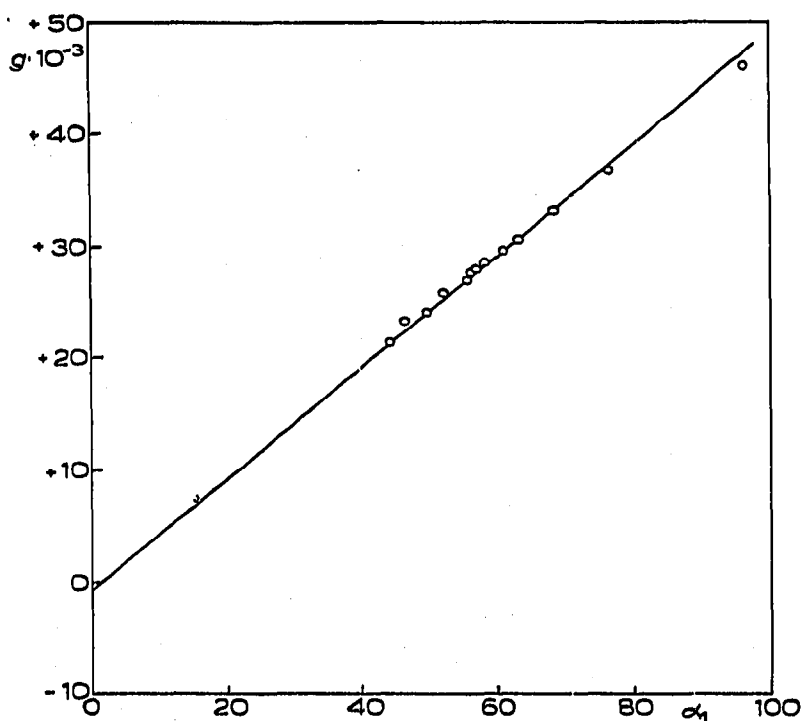


Fig. 4. Determination of the formation constants. Plot of  $g$  as a function of  $\alpha_1$ .

## CONCLUSION

A comparison between the complexity constants obtained in this work and those obtained by ion exchange, is presented:

<i>Fronaeus investigation (t = 20°)</i>	<i>Ion-exchange paper investigation (t = 30°)</i>
$\beta_1 = 45 \pm 2 M^{-1}$	$\beta_1 = 43 \pm 10 M^{-1}$
$\beta_2 = 440 \pm 60 M^{-2}$	$\beta_2 = 500 \pm 100 M^{-2}$
$\beta_3 = 1000 \pm 300 M^{-3}$	$\beta_3 = 800 \pm 600 M^{-3}$

The agreement is quite good; the use of ion-exchange paper yielding, as it was expected, a lower degree of accuracy. This result shows that the assumptions and approximations made in applying the FRONAEUS method are justified and that the method may be safely extended to the study of complex equilibria by resin paper chromatography. Though the use of chromatography with ion-exchange papers in the study of complex equilibria yields less accurate results because of the limited degree of precision afforded by paper chromatography in the determination of the  $R_F$  value, its application can be very useful because of the simplicity of operation and the speed with which experimental results can be obtained. The method should be very valuable for studying equilibria which occur on paper impregnated with ion exchangers of various nature.

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## SUMMARY

Chromatography with ion-exchange papers has been used for the study of complex equilibria. The FRONAEUS method of calculation has been applied to the quantitative determination of equilibria in solution and the procedure has been checked with the system copper-acetate.

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