

THE DISTRIBUTION OF ACIDS, WATER AND BUTAN-1-OL ON CHROMATOGRAMS MADE BY THE ASCENDING TECHNIQUE

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In a previous paper¹ the author has described the way in which butanol and water were distributed on an ascending chromatogram. As most chromatographic solvents contain an acid as well as the other constituents, the factors governing the distribution of acid are of importance and the aim of this paper is to show some of the relations which hold during chromatography.

EXPERIMENTAL

The work was divided into two broad groups. The first of these dealt with solvents made by varying the proportions of butan-1-ol, hydrochloric acid and water, while the second was concerned with variations in the nature of the acid while still using butanol and water as the basis of the solvent.

The method used in making the chromatograms was the same for both groups and has been described previously¹. However, there were differences between the two groups in regard to the paper used and the height to which the chromatogram was ran. In the first group the chromatograms were 18 cm long and made on Schleicher and Schüll 598 paper. For the other group Munktell's 20/150 paper was used and the height of the chromatogram was 20 cm.

Butanol-water-hydrochloric acid series

The solvents were of two types for the butanol-water-hydrochloric acid series. The first type was made by shaking equal volumes of aqueous acid and butanol together for a period of 4-5 min and then using the butanol layer as solvent and the aqueous layer to saturate the atmosphere of the development vessel. Four solvents were made based on aqueous solutions of hydrochloric acid of the following concentrations, 0.1, 0.5, 1.0 and 2.0 *M*. The other type of solvents was made by taking a butanol-water mixture of 0.3 mol fraction of water and adding dry HCl gas to form a series of six solvents which had acid concentrations, in the solvent itself, varying from 0.04 *M* to 1.19 *M* (see Table I).

Series using butanol-water and various acids

The second group of solvents was prepared by shaking equal volumes of butanol and 2 *M* aqueous acid. The acids were tartaric, acetic, hydrochloric, hydrobromic, nitric and perchloric acid. The actual concentrations of these acids in the solvents is given in Table II.

Butanol for the solvents was prepared from a commercial product by fractional distillation. The fraction boiling between 116° and 118° was taken. It was shown to be free from significant quantities of acids and aldehydes. The water was freshly distilled from glass apparatus. All acids used were of analytical reagent grade.

The pattern of sampling and methods for the determination of water and total solvent were similar to those described in a previous paper¹. However the following modifications were necessary because of the acid in the solvent. Extra samples were taken immediately below and above the adsorption front which was apparent as a brown line on the paper. The acid concentration in the solvent and on the paper was determined by titration with sodium hydroxide solution to a potentiometric end point appropriate to the acid being titrated. Where water concentrations were determined, two separate chromatograms were made. The water content was determined on one, and, on the other, the total solvent and acid concentration.

The results of these tests are reported in a series of figures in which the concentration of each solvent constituent on the paper is plotted against the mean height of the sample taken from the chromatogram. Conductivities were determined with a Phillips conductivity bridge and cell. These measurements were made at 25° .

DISCUSSION

The distribution of water and butanol

Where the relative properties of butanol and water in the solvents were similar to those of solvents previously described, it was found that the distribution of these constituents on the chromatogram was almost the same as for the previous solvents. One modification, however, was significant. A dip in the curve representing water concentration *versus* height occurred at or near the height corresponding to the adsorption front. The lower concentration ahead of the adsorption front was presumably due to the absorption of some water with the hydronium ion. The extent of the change

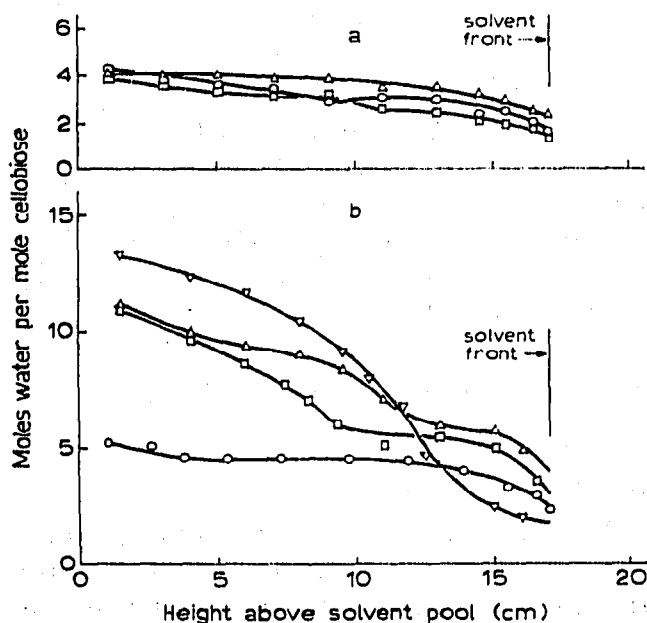


Fig. 1. The distribution of water on paper chromatograms made using both series of solvents.

was indefinite and did not seem to bear a constant relationship to the hydronium ion concentration in the solvent. This was true of both series of experiments though the change in aqueous concentration was smaller for the series in which the total butanol-water ratio in the solvent was fixed. Examples for each series are given in Fig. 1.

Acid distribution

Although the general pattern of acid distribution was the same for both series of experiments (see Fig. 2), the relationship between R_F value and acid concentration differed. For the first series, in which the solvent was made by shaking butanol with

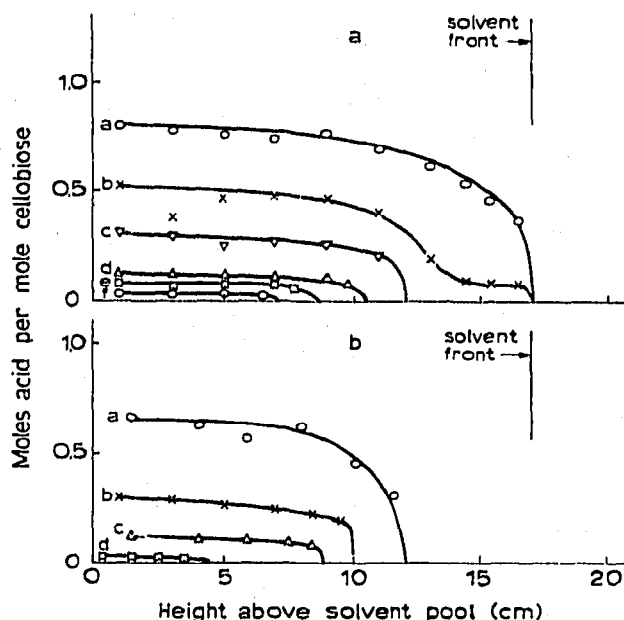


Fig. 2. The distribution of hydrochloric acid on paper chromatograms made using both series of solvents.

an aqueous acid until at equilibrium, the R_F values were related to the logarithm of the actual concentration of the acid in the solvent by the relationship:

$$R_F = n + k \log C_{acid}$$

as is shown by the following data:

Aqueous acid concentration (M)	0.1	0.5	1	2
Actual concentration in solvent (M)	0.014	0.11	0.27	0.84
Log (acid concentration $\times 10^2$)	1.146	2.041	0.431	2.924
R_F	0.25	0.50	0.59	0.70

Later experiments showed that the linearity of this relationship is limited to $R_F = 0.85$. Above this value the region of complete miscibility of aqueous acid and butanol is approached. It was found that the constants n and k were, at least partly, properties of the filter paper used.

No simple relationship was found for the second series of solvents.

Nature of acid adsorption

The hypothesis that the hydronium ions of the solvent are adsorbed to produce the adsorption or acid front may be tested as follows. As it has been found¹ that the paper swells during the course of a chromatogram approximately in proportion to the water concentration of the solvent, the series of solvents which have a constant butanol-water ratio were chosen for this study. It can be assumed that all chromatograms were swollen to about the same amount.

The total weight of acid A_t at any height on a chromatogram is then equal to the sum of the weights of adsorbed acid (A_a) and the acid remaining in solution (A_s), the quantities being referred to 1 g of cellulose. The solvent is assumed to travel sufficiently slowly for equilibrium to be reached for the adsorption process.

Thus:

$$A_t = A_s + A_a \quad (1)$$

The weight of acid in any section may then be taken as $A_s = V_s \times C_a$, where V_s is the volume of solvent and C_a the acid concentration.

Further, if it is assumed that the hydronium ions are held on the cellulose by some type of adsorption the adsorbed acid can be described by an equation of the Langmuir isotherm type.

$$A_a = \alpha\beta C_a / (1 + \beta C_a) \quad (2)$$

where α and β are constants.

Hence:

$$A_t = V_s C_a + \alpha\beta C_a / (1 + \beta C_a) \quad (3)$$

Eqn. (2) may be arranged to give:

$$\frac{C_a}{A_a} = \frac{1}{\alpha\beta} + \frac{C_a}{\alpha}$$

a standard procedure for testing such data.

Table I shows the values of some of the terms involved in the latter relationship calculated, where necessary, from the data given in Fig. 2. α here is taken as the number of moles of acid required completely to cover 1 g of cellulose (paper).

From the data in Table I, a regression line was calculated which had a slope of 1900 and intercepted the ordinate ($C_a = 0$) at 1100. The correlation coefficient of

TABLE I

VALUES OF SOME TERMS INVOLVED IN EQN. (2)

C_a is molar concentration; A_t , $V_s C_a$ and A_a are moles acid/g of paper $\times 10^5$.

C_a	A_t	$V_s C_a$	$A_a = A_t - V_s C_a$	$C_a/A_a \times 10^{-5}$
0.0412	10.5	7	4	1.03
0.0986	28.7	18	11	0.90
0.181	41.4	31	10	1.81
0.445	103	79	24	1.85
0.766	165	140	25	3.06
1.19	252	214	38	3.12

0.902 lies between the 0.02 and 0.01 levels of significance for four degrees of freedom. The Langmuir isotherm can therefore be claimed satisfactorily to present the data.

The parameters α and β are related to surface area and heat of adsorption respectively so the adsorption hypothesis may be tested further through these values.

From the slope of 1900 a value of $5.2 \cdot 10^{-4}$ is obtained for α . This gives an area of 33 m²/g of paper when calculated using 10.5 Å² (calculated from ionic radii) as the area occupied by an hydronium ion. It lies within the range of 10–100 m²/g found by FORZIATI *et al.*². This is not inconsistent with the area obtained by calculation, assuming the 10.8 Å × 8.4 Å surface of the cellulose crystal is exposed with its six hydroxy groups available for hydrogen bonding. Further, MASON³ has shown that the "freeness" of a paper pulp is related to the surface area of the fibre and freeness determinations made on a sample of the paper used in these experiments suggested a value of 11 m²/g; a value in reasonable agreement with that calculated above considering the diverse conditions of determination.

Heat of adsorption

An approximate heat of adsorption may be calculated from DE BOER's⁴ expression:

$$\beta = \frac{N \tau}{\sigma_0 \sqrt{2\pi} MRT}$$

where N, M, R, T are, respectively, Avogadro's number, the molecular weight of the adsorbed particle, the gas constant and the absolute temperature. τ is the time of adsorption and σ_0 the number of particles which can occupy 1 cm² of surface. Calculated from α , this gave a value lying between $6.5 \cdot 10^{11}$ and $2.9 \cdot 10^{12}$ for σ_0 , while β , obtained from the intercept of the regression line mentioned above, was 1.9.

Q , the heat of adsorption, may be calculated from Frenkels relationship (*vide* DE BOER⁴)

$$Q = \tau_0 \exp. Q/RT$$

τ_0 being the period of vibration of the adsorbed particle. It was taken as 10^{-13} sec in this case, a value given by DE BOER for the water molecule and probably not greatly in error for the hydronium ion.

These calculations give a heat of adsorption of 0.9 kcal/mol which, as a net value representing the heat change between solution and adsorption, is not inconsistent with the hypothesis of a hydrogen-bonded hydronium ion.

Composition of solvent on the chromatogram

It is interesting to compare the concentrations of the constituents in the solvent at various heights on the chromatogram, with their concentrations in the original solvent.

No data could be found in the literature on the partial pressures for the ternary system butanol–water–HCl. It seems reasonable to assume that the presence of hydrochloric acid in the butanol–water mixture would lower the partial pressure of the water in much the same way as the partial vapour pressure of aqueous hydrogen chloride is lowered by increasing the concentration of acid⁵. Weight balances were calculated on the basis of the acid concentrations and in most cases a slight loss of water was found. This was greater in the series where water was controlled in the

solvent and almost zero for the other series. The butanol loss, however, was much greater than the water losses in both cases and in this a comparison may be drawn with the results of the work with butanol and water solvents.

Fig. 3 shows a considerable variation between the acids. The curves for the strong acids, HCl, HBr, HClO₄ and HNO₃ are similar in outline and such differences as

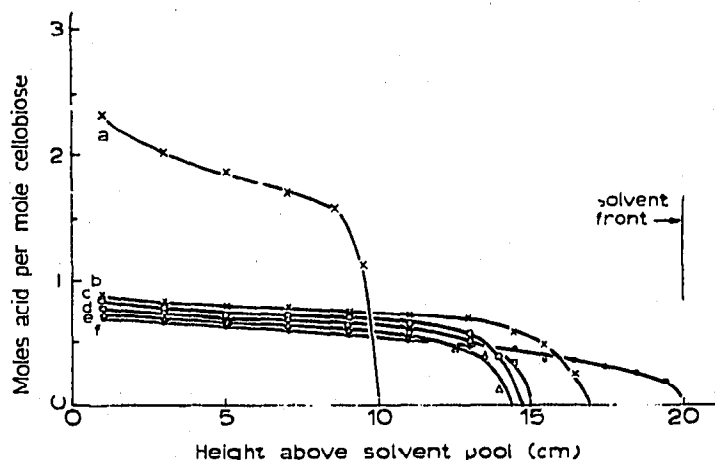


Fig. 3. The comparative distributions of acids on chromatograms using solvents made by shaking butanol with 2 *N* aqueous acid.

appear could be attributed to differences in concentration (Table II) were it is not noticed that HBr ($R_F = 0.75$) takes a position below nitric acid ($R_F = 0.79$) although the concentrations would suggest that they should be placed in the opposite order. No clear reason for this has been established.

There is a marked difference between the behaviour of the solutions containing tartaric acid and those made with acetic acid. The tartaric acid solution, of a concentration comparable with the strong acids, shows from two to three times the adsorption by the paper. This resulted in all the tartaric acid being removed by an R_F value less than 0.5, compared with the 0.7–1.0 of the other acids.

TABLE II
 R_F VALUES FOR SEVERAL ACIDS

Acid	Concn. acid in solvent (<i>N</i>)	R_F
HCl	0.689	0.72
HNO ₃	0.813	0.79
HBr	0.831	0.75
HClO ₄	0.892	0.85
Acetic acid	1.091	1.00
Tartaric acid	0.893	0.47

Acetic acid solutions on the other hand gave R_F values of 1.0 even when the concentration of acid was reduced to 0.25 *M* in the original solvent.

In aqueous solution tartaric acid is dissociated about 150 times as strongly as

acetic acid. This does not appear to be the case in the butanol-water mixtures where the difference in equivalent conductance is small, 0.4 compared with 0.06. The equivalent conductance for hydrochloric acid is 350 in butanol-water solution under the same conditions. It is concluded that the difference between the acetic and tartaric acids lies not in differences of dissociation, but in the mode of their adsorption, the tartaric acid being adsorbed by hydrogen bonding through one of its hydroxyl groups, while acetic acid, possibly hydrogen bonded internally, is only very weakly adsorbed.

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SUMMARY

The distribution of hydrochloric acid, water and butan-1-ol on paper chromatograms is described for solvents made by saturating the butanol with aqueous acid and by adding dry HCl to solvents of fixed butanol-water ratios. It is shown that the hydronium ion is adsorbed onto the cellulose, probably by hydrogen bonding, thus giving rise to the adsorption fronts. The adsorption process may be described by the Langmuir isotherm. The variation to be found between a number of both weak and strong acids is also described.

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