

$$\frac{c c_R}{c_R - c} = \frac{K_2 F_2 w}{K_1 F_1 r} \cdot \frac{c_0 c_R}{c_0 - c_R} + \frac{w c_0}{K_1 F_1 r} \quad (4)$$

where  $c_0$ ,  $c_R$  and  $c$  represent the concentration of unprotonated *p*-nitroaniline determined spectrophotometrically in aqueous solution without added acid and alcohol, with added acid and alcohol and with added acid only, respectively:  $w = [\text{H}_2\text{O}]$  before addition of alcohol,  $r =$  the total added alcohol concentration,  $F_2 = f_{\text{N}} f_{\text{R}} \bar{O}_{\text{H}_2} / f_{\text{NH}} f_{\text{ROH}}$  and  $F_1 = f_{\text{N}} f_{\text{H}_2\text{O}} / f_{\text{NH}} f_{\text{H}_2\text{O}}$ . In dilute solutions of alcohol a plot of  $c c_R / (c_R - c)$  against  $c_R / (c_0 - c_R)$  should give a straight line. Such plots are found to be linear, and examples obtained at an ionic strength  $\mu = 1.0$  are given in Fig. 1. For these plots,  $K_b' = c_0 w / r w_R \times$  slope, where  $w_R = [\text{H}_2\text{O}]$  with the alcohol added. Table 1 shows that, except for sulphuric acid, reasonable agreement is obtained among the acids for a particular concentration of alcohol. Table 2 shows that little variation is observed among the acids in the range 2–10 per cent v/v isopropanol, except for sulphuric acid. Only a slight variation of  $K_b'$  with ionic strength has been observed: ionic strength was adjusted by adding the sodium salt of the acid (sodium sulphate with sulphuric acid).

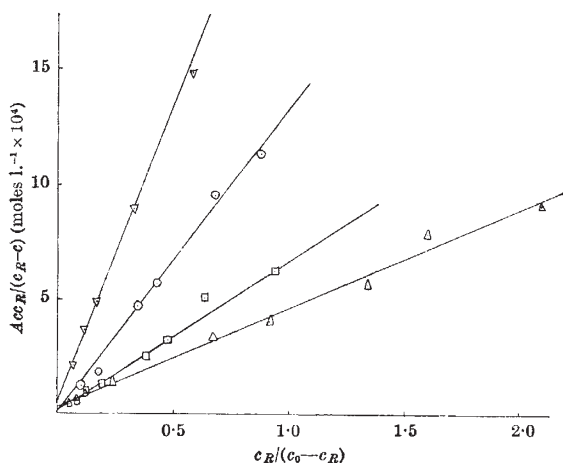


Fig. 1. Plots of  $Acc_R / (c_R - c)$  against  $c_R / (c_0 - c_R)$  at  $\mu = 1.0$  with 5 per cent v/v alcohol.  $\circ$ , Methanol + HCl,  $A = 1.0$ ;  $\square$ , isopropanol + HCl,  $A = 1.0$ ;  $\triangle$ , isopropanol +  $\text{H}_2\text{SO}_4$ ,  $A = 1.0$ ;  $\nabla$ , isopropanol +  $\text{HClO}_4$ ,  $A = 0.2$

Although, in these conditions, isopropanol and methanol are more basic than water, it is apparent that solutions of sulphuric acid behave in a different way to the other acids quoted in Tables 1 and 2. Moreover, values for  $K_b'$  for all the acids in Tables 1 and 2 differ from those found in sulphuric acid in the oxidation experiments<sup>4</sup>. However,  $K_b'$  can be calculated by a less direct method. Using equation (4), values of  $K_2 F_2$  can be calculated from the slopes and intercepts of lines similar to those in Fig. 1: from equilibria (1) and (3) values of  $K_b'$  can then be calculated. For all the acids and all the concentrations of isopropanol and methanol used in these dilute solutions, the apparent value of  $K_b'$  calculated in this way is independent of acidity, except for sulphuric acid, where  $K_b'$  increases with increasing acidity. This is illustrated in Table 3 for hydrochloric and sulphuric acids with 5 per cent v/v isopropanol. The values of  $K_b'$  in solutions of hydrochloric, nitric and perchloric acids agree with those determined directly from the slopes of Fig. 1, and the values of  $K_b'$  in sulphuric acid solution tend at low acidities to the values

Table 1.  $K_b'$  FOR 5 PER CENT v/v ALCOHOL AT  $\mu = 1.0$  AND 25° C

Acid	Isopropanol	Methanol
$\text{H}_2\text{SO}_4$	0.54	0.18
HCl	0.36	0.093
$\text{HClO}_4$	0.45	0.10
$\text{HNO}_3$	0.29	—

Table 2.  $K_b'$  AT  $\mu = 1.0$  AND 25° C

per cent v/v isopropanol	HCl	$\text{HClO}_4$	$\text{HNO}_3$	$\text{H}_2\text{SO}_4$
2	0.21	0.46	—	0.42
5	0.36	0.45	0.29	0.54
10	0.37	0.38	0.34	0.67

Table 3. APPARENT  $K_b'$  IN 5 PER CENT v/v ISOPROPANOL AT  $\mu = 1.0$  AND 25° C

[Acid]M	$\text{H}_2\text{SO}_4$	HCl
0.08	0.53	0.35
0.12	0.56	0.35
0.16	0.62	0.35
0.20	0.71	0.34
0.40	1.13	0.35
0.60	1.46	0.35
0.80	1.67	—
1.00	1.86	0.33

obtained directly from the slopes. One explanation of this is that  $F_2$  and  $F_1$  vary with  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  ions, but not with  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{Cl}^-$  ions: this variation would cancel out for the determination of  $K_b'$  direct from the slopes in Fig. 1, allowing straight lines with sulphuric acid as with the other acids. This would account for the differences of the values of  $K_b'$  in sulphuric acid solutions from those in solutions of hydrochloric, nitric and perchloric acids in Tables 1 and 2. Moreover, the values of  $K_b'$  in sulphuric acid solution in Table 3 are comparable in the same region of  $[\text{H}_2\text{SO}_4]$  with  $K_b' = 1.7$  at 25° C for isopropanol using picric acid and the rate of oxidation<sup>4</sup>.

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### Detection of Diols on Paper Chromatograms

Boric acid forms complexes with compounds having adjacent OH groups in the *cis* position. The  $pK'$  values of the complexes are lower than that of free boric acid, so that in the presence of diols it behaves as a stronger acid. This property has been used to detect *cis* diols on paper chromatograms. Spraying the dried paper with a 0.1 per cent solution of bromocresol purple in 0.5 per cent sodium carbonate solution which has been adjusted to pH 6.8 with hydrochloric acid reveals all acidic substances as yellow spots on a purple background.

These spots are marked and the wet paper is lightly sprayed with near-saturated borax solution adjusted to pH 6.9 with hydrochloric acid. Any freshly appearing yellow spots are due to *cis* diols. This method, in its rapidity and non-destructive effect on the compounds present, has some advantages over the more sensitive but cumbersome method of revealing diols devised by Baddiley *et al.*<sup>1</sup>. Preliminary work has shown that diols may be titrated in the presence of borax in an analogous manner to that in which formol titrations are performed.

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