

plants. Tulloch⁷ believes that alcohols can be used as a taxonomic criterion and it is clear from these six plants that each has its own characteristic distribution. The two *Carapa* species are distinguishable by the large amounts of branched chain components whilst the *E. agallocha* has a branched C₁₇ alcohol as the major component. This latter alcohol is a major component of the alcohols from the three members of the Myrtiflorae.

It appears that the waxes of plants grown in the mangrove areas of the Sundarban contain a number of unusual components which may be due to the plants habitat. It is clear that each plant wax is a distinct fingerprint for that species and could be used as taxonomic criteria. It is hoped later to compare these waxes with the waxes of plants from the same genera which grow under more normal conditions but it was felt necessary to examine first the waxes of mangrove plants to see if they had any unusual features.

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Bromatometric Determination of Some Aromatic Sulphones

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KOPPESCHAAR'S method¹ in which an acidified solution of the organic compound is treated with an excess of a standard solution of bromate-bromide and the excess bromine determined iodometrically using starch as indicator was used for the determination of several organic compounds². These include aromatic compounds with ring substituents which strongly influence *ortho* and/or *para* bromination. Pence³, while determining resorcinol by the above method, allowed the reaction mixture to stand for 5 min after the addition of potassium iodide and titrated the liberated iodine with standard thiosulphate. Redman, Weith and Brock⁴ studied the application of the method to phenol. In the case of *meta*-cresol Fox and Barker⁵ allowed the reaction mixture to stand for 30 min after the addition of potassium iodide. Callin and Henderson⁶ tested for free bromine in the reaction mixture using starch-potassium iodide paper. Francis and Hill⁷ carried out extensive investigations on the estimation of the *meta* isomers among several disubstituted derivatives of benzene and reported that the directive influence of hydroxyl and amino groups are so great in comparison to those of other groups that in aqueous solution when one of them is present in the benzene ring, all available *ortho* and *para* positions are substituted quantitatively with bromine. Day and Taggart⁸ used the excess method for the analysis of twenty-five phenols and aromatic amines and claimed good results.

Recently, we reported the bromatometric determination of hydroxy carbonyl compounds^{9,10}, amino carbonyl compounds¹¹, *p*-aminosalicylic acid¹² and some phenols and alkyl phenols¹³. In the present investigation we report the results obtained in determining the aromatic sulphones bromatometrically, since there seems to be no report in the literature on the bromatometric determination of these compounds.

Experimental

The aromatic sulphones used were synthesised by the literature methods. Hydroxy sulphones were prepared by subjecting the respective arenesulphonates to the Fries rearrangements. The arenesulphonates were prepared by treating phenols with sulphenyl chlorides by the usual Schotten-Baumann method. The amino sulphones were prepared by the reduction of the corresponding nitro derivatives.

Known weights of the compounds were dissolved in 20% (v/v) aqueous acetic acid and made up to required volume with distilled water. Aliquots of

TABLE 1—MODES OF BROMINATION OF SOME AROMATIC SULPHONES

Sl. No.	Compound	Direct method	Koppeschaar's method
1.	2-Hydroxyphenyl methyl sulphone	Monobromination (F)* Dibromination (M)**	Tribromination
2.	4-Hydroxyphenyl methyl sulphone	Monobromination (F) Dibromination (M)	Tribromination
3.	2-Aminophenyl methyl sulphone	Monobromination (F) Dibromination (M)	Tribromination
4.	4-Aminophenyl methyl sulphone	Monobromination (F) Dibromination (M)	Tribromination
5.	2-Hydroxydiphenyl sulphone	Dibromination (F/M)	Dibromination
6.	4-Hydroxydiphenyl sulphone	Dibromination (F/M)	Dibromination
7.	2-Hydroxy-2-methyldiphenyl sulphone	Dibromination (F/M)	Dibromination
8.	2-Hydroxy-3'-methyldiphenyl sulphone	Dibromination (F/M)	Dibromination
9.	2-Hydroxy-4'-methyldiphenyl sulphone	Dibromination (F/M)	Dibromination
10.	2-Hydroxy-5-methyldiphenyl sulphone	Monobromination (F/M)	Dibromination
11.	2-Hydroxy-5-methyl-2'-methyldiphenyl sulphone	Monobromination (F/M)	Monobromination
12.	2-Hydroxy-6-methyl-3'-methyldiphenyl sulphone	Monobromination (F/M)	Monobromination
13.	2-Hydroxy-5-methyl-4'-methyldiphenyl sulphone	Monobromination (F/M)	Monobromination
14.	2-Hydroxy-3,6-dimethyldiphenyl sulphone	Monobromination (F/M)	Monobromination
15.	4-Hydroxy-2,5-dimethyldiphenyl sulphone	Monobromination (F/M)	Monobromination

*F = Fluorescein

**M = Methyl orange

the solution, strongly acidified with sulphuric acid, were used for titrations. A standard solution of potassium bromate (*ca* 0.1 N) containing 3 g per litre was prepared and its strength was verified with standard dichromate iodometrically to the starch end point. An approximately decinormal solution of sodium thiosulphate was prepared and standardised iodometrically against the two standard solutions. The standard solutions were diluted to the required concentration wherever necessary.

Direct method: A measured volume of the sulphone solution was strongly acidified with conc. sulphuric acid and fluorescein (sodium salt) or methyl orange indicator added and slowly titrated at 30-35° with the standard bromate-bromide mixture until the colour changed from yellow to reddish brown in the case of the former or until the colour was discharged in the case of the latter.

Koppeschaar's method: A measured volume of the sulphone solution acidified with an excess of conc. sulphuric acid was treated with a measured volume (in large excess) of the bromate-bromide mixture at 30° and left overnight. A 10% aqueous solution of potassium iodide was added and the liberated iodine was titrated with standard thio-sulphate using starch as indicator.

Results and Discussion

The phenolic and amino groups are *ortho-para* orienting while the sulphonyl group is *meta*-orienting. The vacant sites *ortho* or *para* to the phenolic group and *meta* to sulphonyl group are easily brominated. In the direct method, all the compounds under study are brominated according to the above

rule. The bromatometric determination of all the sulphones by titration with bromate-bromide mixture in the presence of internal indicator was undertaken. Some of the compounds could be titrated to the mono or dibromo stages by proper choice of the indicator though there is a possibility of tribromination. The mode of bromination and the accuracy claimed for the determination of the sulphones are given in Tables 1 and 2, respectively.

In the excess method, all the sulphones except 2- and 4-hydroxyphenyl methyl sulphones and 2- and 4-aminophenyl methyl sulphones gave good results. The hydroxy and aminophenyl methyl sulphones are overbrominated (tribromination). The overbromination by Koppeschaar's method¹ can be explained as due to the oxidation and destruction of the organic compound, which can be avoided by cooling at 0° and the displacement of the sulphonyl group thereby yielding tribromophenol or tribromoaniline. This type of displacement of groups is not uncommon. The carboxyl was eliminated as carbon dioxide, the sulphonic acid as sulphuric acid⁶ and the aldehyde as carbon monoxide⁷. The hydroxy-methyl group was eliminated as formaldehyde^{1,4}. Our study at 0° also shows that the hydroxy and aminophenyl methyl sulphones are tribrominated. The overbromination due to oxidation and destruction of the sample is ruled out. If the assumption that the tribromination is due to the replacement of sulphonyl group is valid, the product obtained should have been either tribromophenol or tribromoaniline. But the product analysis shows negative test for tribromophenol and tribromoaniline.

The conversion of O-H to O-Br and NH₂ to NHB₂ could not be considered since under the

TABLE 2—DIRECT METHOD

Sl. No.	Amount taken mg	Amount found mg	Error %
1.	5.15	5.13 (5.12)*	-0.39 +0.58
2.	6.18	6.20 (6.20)	+0.32 +0.32
3.	2.17	2.19 (2.16)	+0.90 -0.46
4.	3.95	3.99 (3.88)	+1.01 -1.77
5.	4.72	4.75 (4.71)	+0.63 -0.21
6.	4.50	4.53 (4.52)	+0.67 +0.44
7.	3.76	3.72 (3.75)	-1.06 -0.26
8.	4.21	4.24 (4.20)	+0.71 -0.24
9.	4.93	4.95 (4.94)	+0.40 +0.20
10.	4.16	4.19 (4.17)	+0.72 +0.24
11.	3.11	3.13 (3.12)	+0.64 +0.32
12.	5.85	5.82 (5.83)	-0.51 -0.34
13.	3.73	3.75 (3.74)	+0.54 +0.27
14.	4.25	4.23 (4.26)	-0.47 +0.23
15.	3.92	3.90 (3.91)	-0.51 -0.25

* Values within paranthesis are obtained using methyl orange as indicator and the others with fluorescein.

experimental conditions, the hydroiodic acid formed reduces the O-Br and -NHBr groups quantitatively to O-H and -NH₂, respectively liberating an equivalent quantity of iodine. Therefore, the only other possibility for tribromination is the substitution at the ω-position, yielding SO₂CH₂Br. Earlier, we noticed such a ω-substitution in the case of ketones.

Though Koppeschaar's method gives more accurate results compared with indicator method for all the sulphones, some complications arise in the case of 4-aminophenyl methyl sulphone. The determination of this compound is quantitative only when there is a small excess of bromate-bromide mixture as required on theoretical grounds. As the excess of brominating mixture increases, the error in the determination also increases showing that the extent of bromination is a function of time and the excess bromine used. This type of abnormal behaviour has already been reported by us while carrying out the determination of *p*-aminosalicylic acid with bromate-bromide mixture at room temp. Wells has also found that the bromination of *p*-aminobenzoic acid was quantitative only when 140% excess of bromine was added, 2 hr allowed for the reaction to reach completion and the time required varied inversely with the excess of bromine used.

To overcome this difficulty and for the accurate determination of 4-aminophenyl methyl sulphone, the Koppeschaar's method is modified as follows.

Several determinations have been made by varying the amount of excess bromate-bromide mixture and in each case the volume of hypo consumed has been plotted (Fig. 1) against the excess volume of brominating mixture. Extrapolation of the volume of

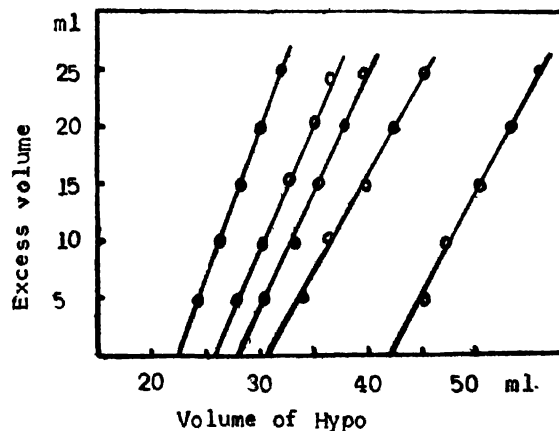


Fig. 1. Plot of excess volume vs volume of hypo consumed.

hypo consumed to the zero excess gives the actual volume of hypo required. The analytical data obtained by this method are shown in Table 3. This

TABLE 3—KOPPESCHAAR'S METHOD

Sl. No.	Amount taken mg	Amount found mg	Error %
1.	4.62	4.61	-0.22
2.	4.79	4.80	+0.21
3.	5.12	5.10	-0.39
4.	4.08	4.17	+2.20
	3.10	3.15	+1.61
	2.92	2.96	+1.37
	2.71	2.75	+1.48
	2.43	2.45	+0.82
5.	5.00	4.96	-0.80
6.	4.55	4.55	0.00
7.	2.18	2.20	+0.92
8.	3.97	3.99	+0.50
9.	6.08	6.12	+0.66
10.	3.14	3.13	-0.32
11.	5.07	5.11	+0.79
12.	3.96	3.95	-0.25
13.	3.35	3.38	+0.89
14.	3.52	3.50	-0.57
15.	4.01	4.02	+0.25

result also shows that the -SO₂CH₃ group is not at all replaced by bromine but substitution occurs in the ω-position with the replacement of one, two or even three hydrogen atoms of the methyl group thereby consuming varying amounts of bromine. This trend has not been observed in the case of 2-aminophenyl methyl sulphone and this may be due to steric factors.

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Studies on the pH and Sorption of Basic Dyes on Alumina in Relation to Chromatography. Pt—II*

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PRETREATMENT of alumina with an alkali like sodium hydroxide frequently enhances its cation exchange capacity¹. In view of the above, the cationic dye, Janus red (C. I. 26115), was taken up to investigate its adsorption-desorption behaviour on alumina of varying pH (7.0-11.3). Galbraith *et al*² found the adsorption of Janus red (JR) on graphite to be dependent on the surface charge. Giles *et al*³ measured adsorption of the dye on a variety of solids and proposed ion-exchange.

Experimental

Alumina samples of pH 7.0-11.3 were prepared as described earlier¹, and their surface area determined (BET method).

Janus red (Gurr) was purified by repeated crystallization from ethanol-water (1 : 1 v/v), and dried at 50° for 8 hr. Projection area of the dye-ion was

estimated to be 227 Å² from 'Stuart-Briegleb' model. To minimise the adsorption effect of glass, the apparatus were rinsed with cetyl-trimethyl-ammonium bromide soln (1 g/l) and washed with water before use.

2.5-100 ml solutions were withdrawn from the stock solution of the dye in water (0.2 g/l), diluted to 100 ml and estimated colorimetrically at 505 nm with 'Spekol' spectrophotometer.

Adsorption experiments were conducted on alumina (0.25 g) with aqueous dye solutions of known concentration in 25 ml volumetric flasks. The flasks were immersed in thermostat, shaken periodically, 2 ml aliquot withdrawn after a specified period, centrifuged and estimated.

Adsorption vs time and temperature : The extent of adsorption from water as a function of time (10 min-24 hr) was studied with the substrate of pH 8.6-11.3 at 25 ± 1°. For this, the initial concentration of the dye solutions was 200, 100 and 20 mg/l. The results indicate the process to be slow with higher concentrations of the dye and fast at lower concentrations. Thus, at pH 10.6 (10 min) about 30% (200 mg/l) and 65% (20 mg/l) of the dye is adsorbed. The equilibrium is almost attained in 24 hr, although it takes 72 hr for higher dye concentrations. Temperature variation studies show the phenomenon to be endothermic (30-60°, pH 8.6-11.3, 4 hr), and the isosteric heats of adsorption (Q) is calculated to be 11-24 k cal/mole.

Adsorption vs pH : The change in the nature of adsorption with pH (7.0-11.5) was observed. The affinity of the solute gradually increases with increase in pH of the substrate and drops to zero at pH 7.0. The isotherms are of L₂-type and develop linear nature at pH 11.3.

Desorption studies : The reversibility of the dye adsorbed (25 ± 1° 24 hr, pH 8.6-11.3) was investigated with a number of organic solvent-water mixtures, CTA⁺-water (0.1% w/v) and aqueous inorganic electrolytes (10⁻² M NaCl and MgCl₂), as described earlier¹.

The desorption data reveal that the adsorption process is quite reversible. Thus, quantitative desorption occurs with dioxane-water (1 : 1) and *n*-butanol-ethanol-water (1 : 1 : 2). However, pyridine-water (1 : 4) and ethanol-water (1 : 1) desorb the dye completely at pH 8.6-9.5 and 8.6, respectively. Glycerol-water (1 : 4) and aqueous CTA⁺ also desorb 90% of the adsorbed dye. The Na⁺ ions have no effect, whereas Mg²⁺ ions are effective in removing the dye from the substrates. Precipitation of magnesium hydroxide occurs at pH > 10.6.

Results and Discussion

The adsorption is presumed to be essentially the same as that for anionic dyes on acid-treated alumina i.e., ion-exchange of dye-cations (simple or aggregated) with Na⁺ ions on the surface of alumina powder.

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