

CXVI.—*The Affinity Constants of Aminosulphonic Acids as Determined by the Aid of Methyl-Orange.*

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IN former papers (*Zeitsch. physikal. Chem.*, 1906, 57, 147, and *Trans.*, 1907, 91, 153) it was shown that (i) the affinity constants as determined by the above method conform either to a logarithmic type ($\log y = \log k + x \log a$) or to a straight-line type $y = kx$, and (ii) in the particular case of the naphthylaminesulphonic acids the positions 2 and, to a less extent, 7 afford cases of steric "furtherance," whilst the position 8 affords a case of steric "hindrance." It was thought worthy of interest to pursue the latter subject with reference to the aminonaphtholsulphonic acids, more especially as regards the effect produced by the introduction of the hydroxyl group in different

* For this experiment we are indebted to Miss F. M. G. Micklethwait, who conducted it in connexion with other acridine work a few years ago.

relative positions to the sulphonic acid group. So far as I am aware, no results have been obtained by the electric conductivity method for the aminonaphtholsulphonic acids, mainly owing to the experimental difficulties of obtaining these compounds in a reasonable degree of purity, and their sparing solubility.

Ostwald (*Zeitsch. physikal. Chem.*, 1889, 3, 170 *et seq.*) has shown that the effect produced by the introduction of the hydroxyl group on the benzenoid carboxylic acids varies greatly according to the position taken up by the hydroxyl.

While my former papers were in the press, an investigation on various indicators was published by Salm (*Zeitsch. physikal. Chem.*, 1906, 57, 471); certain results were obtained by the tintometer method with methyl-orange. Although the form of experiment used was not identical with that adopted by me, yet the same practical conclusions follow as a consequence of both lines of research, namely, that "it is necessary in volumetric analysis to titrate to one constant tint, which corresponds to a known concentration of hydrogen ions," more especially in the cases of two-coloured indicators.

It is again my pleasant duty to express my obligations to the Directors of the Badische Anilin- und Soda-Fabrik for supplying me with the necessary materials.

Aminonaphtholsulphonic Acids.

It was not found practicable to purify these acids by recrystallisation, partly owing to their sparing solubility, and partly to the tendency of carbonaceous matters to separate out when the solutions were evaporated under the ordinary pressure. The following method was therefore adopted; molecular equivalents of the several acids in centigrams were suspended in 25 c.c. of water, then a quantity of *N*-sodium carbonate solution added in slight excess of that required to neutralise the acid. The mixture was warmed until the acid had passed into solution and all the carbon dioxide was apparently displaced. It was observed that the rapidity with which the several acids decomposed the sodium carbonate differed widely under approximately similar conditions, but the problem of the relative affinities of the sodium ion for the aminonaphtholsulphonic and the carbonic ions, although interesting in itself, was beyond the sphere of this investigation.

The solutions obtained in this way were filtered, and then *N*-sulphuric acid added in a quantity slightly less than that of the *N*-sodium carbonate originally taken. The acids were thus reprecipitated as amorphous powders, which were washed, and dried at 25°; they were thus obtained as powders either white or of a pale pink or

green tint. Solutions were made up of $N/400$, $N/200$ or $N/100$ concentrations according to circumstances, and these were in some cases slightly above or below the saturation point at the ordinary temperature. It may be worth remarking incidentally that the introduction of the hydroxyl group in the naphthylaminesulphonic acids almost completely extinguishes their remarkable fluorescence. The methods of working and of calculating the results are identical with those of my former papers on the same subject.

5-Amino-1-naphthol-3-sulphonic acid,* obtained in pale pink solution, was kept slightly warm to prevent recrystallisation.

TABLE I.

$V = 8 \times 10^4$.		$V = 4 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0.4	0.55	1.0	1.25
1.1	1.1	2.4	2.5
2.2	2.2	5.0	5.0
—	—	9.9	10.0

The values in the second and fourth columns are calculated from the expression $\log y = \log k + x \log a$ ($k = 0.55$ and 1.25 , $a = 2$ respectively).

The above values are identical within the limit of experimental error with those obtained for the 1-naphthylamine-7-sulphonic acid, thus showing that the introduction of the hydroxyl group in a meta-position relative to the sulphonic acid group produces no alteration in the affinity constant. This result is precisely analogous to that found by Ostwald for *m*-hydroxybenzoic acid as compared with benzoic acid. 8-Amino-1-naphthol-4-sulphonic acid was obtained as a pale violet solution.

TABLE II.

$V = 4 \times 10^4$.	
y (found).	y (calc.).
0.3	0.35
0.8	0.7
1.6	1.4
2.8	2.8

On comparison of the above results with those obtained for the 1-naphthylamine-5-sulphonic acid, it appears that the introduction of the hydroxyl group in the 8-position reduces the affinity constant to

* In order to make the arguments intelligible, it will be understood that in my former paper the naphthylaminesulphonic acids were considered as derived from α - and β -naphthylamine; in the present paper, the aminonaphtholsulphonic acids are considered as derived from α - and β -naphthol. The numbering of the groupings is thereby altered, but not their relative positions.

about one-third of its value (actually 1.12 to 0.35). This result appears to afford a case of steric hindrance caused by the introduction of the hydroxyl group in the 8-position; it is also analogous with the results obtained both by Ostwald and myself, which show that the introduction of the hydroxyl group in the 4-position relative to the carboxyl produces a considerable diminution (50—60 per cent.) in the affinity constant.

8-Amino-1-naphthol-5-sulphonic acid gave an almost colourless solution, which was kept warm to prevent crystallisation :

TABLE III

$V = 8 \times 10^4$.		$V = 4 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
1	0.9	1.8	2.05
2.2	1.8	4.0	4.1
3.8	3.6	7.8	8.2
7.0	7.2	16.6	16.4

The values in the second and fourth columns are calculated from the expression $\log y = \log k + x \log a$ ($k = 0.9$ and 2.05 , $a = 2$ respectively).

In this case no comparison is possible with the 1-naphthylamine-4-sulphonic acid, which was found to be not sufficiently soluble for observations.

6-Amino-2-naphthol-4-sulphonic acid was obtained as a pale pink solution.

TABLE IV.

$V = 4 \times 10^4$.		$V = 2 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
2.2	2.2	4.1	4.3
4.2	4.4	8.4	8.6
6.2	6.6	12.8	12.9
8.6	8.8	17.4	17.2
10.8	11.0	22.0	21.5
13.6	13.2	—	—
16.4	15.4	—	—

The values in the second and fourth columns are calculated from the straight-line formula $y = kx$ ($k = 2.2$ and 4.3 respectively), but it will be observed that although the differences $y^1 - y$ are at first constant, there is a tendency for this difference to increase, as previously observed in the cases of salicylic and oxanilic acids, &c.

The introduction of the hydroxyl group in the 6-position increases the affinity constant, as the 2-naphthylamine-8-sulphonic acid was found to be inert.

This result is not in accordance with those obtained for the 1-naphthylamine-7-sulphonic acid and 5-amino-1-naphthol-3-sulphonic acid (p. 1248), and it would thus appear that in the case of naphthalene

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the positions 5:7 and 6:8 are not the same relative to 1 and 2 or to one another. It is further remarkable, on comparing 2-naphthylamine-6:8-disulphonic acid and 6-amino-2-naphthol-4-sulphonic acid, that the substitution of the sulphonic group in the former by the hydroxyl group should increase the affinity constant from *nil* to a considerable value. There does not appear to be any data of analogous cases available for the purpose of comparison, so further speculation in the present state of knowledge seems undesirable.

6-Amino-1-naphthol-3-sulphonic acid was obtained in nearly colourless solution, and kept slightly above the ordinary temperature for the purpose of observation.

TABLE V.

$V = 4 \times 10^4.$	
y (found).	y (calc.).
1	1
2	2
3	3
4	4
4.9	5

These results are also in accordance with the straight-line formula $k=1$; on comparison with those obtained for 2-naphthylamine-7-sulphonic acid, it appears that the end point is nearly the same (4.6 and 4.9), although arrived at by different stages of the logarithmic and straight-line types.

The general net result is that the introduction of the hydroxyl group in the meta-position produces only a slight alteration in the affinity constant (see p. 1248 as to comparison of 1-naphthylamine-7-sulphonic acid and 5-amino-1-naphthol-3-sulphonic acid).

8-Amino-1-naphthol-3:6-disulphonic acid could not be purified by the method used for the mono-acids, so that it was examined directly, the solution being of a pink colour.

TABLE VI.

$V = 4 \times 10^4.$	
y (found).	y (calc.).
0.6	0.65
1.2	1.3
2.8	2.6
5.4	5.2

The value of $k=0.65$ and $\alpha=2$.

It is not possible to draw any conclusion as to the effect of the introduction of the hydroxyl group in the 8-position, as the 1-naphthylamine-3:6-disulphonic acid has not been examined.

Naphtholsulphonic Acids.

Attempts were made to obtain solutions of these acids, fit for investigation, by precipitating their sodium or potassium salts with basic lead acetate, and then decomposing the lead salts suspended in water by a current of hydrogen sulphide. The excess of dissolved gas in the filtered solution was driven off by warming partly at ordinary and partly at reduced pressure. But although the solutions obtained in this way contained abundance of acid as shown by titration with a *N*/10-soda solution, phenolphthalein being used as an indicator, it was not found possible to obtain satisfactory observations by the methyl-orange tintometer method, as the orange-red tint produced at first by addition of successive quantities of the acid solution disappeared more or less quickly, doubtless owing to some secondary change. The investigation of this series of acids was therefore reluctantly abandoned.

Summary.

(I) The affinity constants of the aminonaphtholsulphonic acids, as determined by the methyl-orange tintometer method, show, as regards the effect of the introduction of the hydroxyl group in the naphthylaminesulphonic acids, relationships similar to those observed by Ostwald by the electric conductivity method for the hydroxybenzoic acids as compared with benzoic acid.

(II) One possible case of steric hindrance induced by the introduction of the hydroxyl group in the 8-position is noted.

I desire to express my thanks to Mr. J. E. Marsh, F.R.S., for practical assistance and suggestions.
