

# POTENTIOMETRIC STUDIES IN DIAZOTISATION, DETERMINATION OF AROMATIC AMINES.

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A number of amines in presence of hydrochloric acid were titrated potentiometrically (Pt-electrode calomel electrode in amine) against a sodium nitrite solution. E. M. F. was found to rise steadily with the addition of standard sodium nitrite till the equivalence point. At the equivalence point there was a sharp jump in potential in each case.

Aromatic amines are quantitatively converted into diazo-compounds by nitrous acid, *i.e.*, by nitrite in acid medium. The end-point of the diazotisation is reached with the first slight excess of nitrous acid that is stable for some time, and may be detected with potassium iodide-starch as indicator. This indicator is by no means to be added directly to the reaction mixture because it responds instantaneously to nitrous acid and, since the diazotisation requires a certain time, it would, change much too soon. The course of the reaction is followed by spotting tests on potassium iodide-starch paper. The reaction is complete when on stirring after each addition, and testing with the iodide-starch paper, a distinct blue colour is obtained at once. A drop of the solution is removed on a glass rod at intervals and placed on the iodide-starch paper. Whenever the blue colour is obtained, and this colour persists when another test is made after a few minutes, the reaction is complete. To obviate the difficulty of finding the end-point by this visual method, the titrations were conducted potentiometrically.

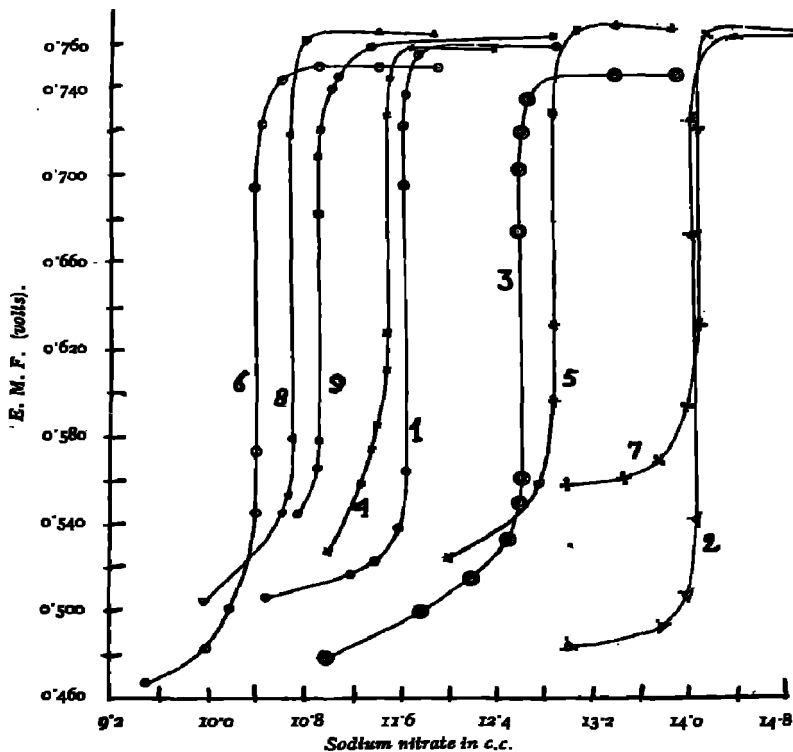
When the solution of an aromatic amine is diazotised free nitrous acid is formed at the completion of the reaction. A solution of nitrous acid in contact with a platinum electrode, gives a definite potential. E. Muller and E. Dachselt (*Z. Elektrochem.*, 1925, 31, 662) studied the titration of aniline, xylidine, toluidine and amino-azobenzene disulphonic acid. They found that there is a jump in potential at the equivalence-point of the titration of the acid solution of the aromatic amine with sodium nitrite. The potential requires some time to become steady during the titration. Attempts were made to accelerate the reaction by using higher temperatures. It was found that side-reactions occur, causing errors; 3% at 60°; 0.5% at 30°. At 20° or below the results are very accurate. It is not necessary, therefore, to cool the mixture in ice during the titration.

A systematic study of the application of the potentiometric method to diazotisation has been taken up during the course of this investigation.

## EXPERIMENTAL.

A bright platinum electrode immersed in a solution of the amine to be titrated, was coupled with a saturated calomel electrode. The cell was placed in a water bath, the temperature of which was maintained at 10°. The E.M.F. of the cell was read on a potentiometer scale.

FIG. 1



Curves 1-9 refer respectively to *o*-, *m*-, and *p*-nitroanilines, *o*- and *p*-aminobenzoic acids, sulphanilic acid, *p*-chloroaniline, 3-nitro-4-aminophenol and 2-amino-4-nitrophenol.

*o*-Nitroaniline (m.p. 70°), *m*-nitroaniline (m.p. 114.2°), *p*-nitroaniline (m.p. 146.5°), *o*-aminobenzoic acid (m.p. 144.8°), *p*-aminobenzoic acid (m.p. 187.0°), sulphanilic acid (m.p. 172.5°), *p*-chloroaniline (m.p. 70.5°), 3-nitro-4-aminophenol (m.p. 112.0°) and 2-amino-4-nitro-

phenol (m.p. 142°) were quantitatively determined by titrating them against a standard solution of sodium nitrite in the presence of hydrochloric acid by the potentiometric method. On each addition of the titrant, the mixture was thoroughly stirred by means of a mechanical stirrer. The potentiometric readings were recorded two to five minutes after the addition of the reagent when the potential acquired a steady value. For an accurate determination a micro-burette was used to add the standard solution near the equivalence-point.

A series of potentiometric titrations were performed with different amounts of each substance. One titration, as typical of that set, is recorded in the following table.

TABLE I.

Titration of 0.3231 g. of *o*-nitroaniline mixed with 20 c.c. water and 25 c.c. conc. hydrochloric acid, against sodium nitrite (M/5).

NaNO <sub>2</sub>	E.M.F. (volts)	E/C. (m. volts/c.c.)	NaNO <sub>2</sub>	E.M.F. (volts)	E/C. (m. volts/c.c.)
11.200 c.c.	0.515		11.700 c.c.	0.694	
		30			1080
11.400	0.521		11.725	0.721	
		50			600
11.500	0.526		11.750	0.736	
		80			360
11.550	0.530		11.775	0.745	
		120			200
11.600	0.536		11.800	0.750	
		200			120
11.625	0.541		11.825	0.753	
		320			80
11.650	0.549		11.850	0.755	
		520			40
11.675	0.562		11.900	0.757	
		520 (maximum)			

The titrations, one for each substance, are represented by the curves given in Fig. I.

#### D I S C U S S I O N .

In these titrations, with the addition of the standard sodium nitrite, the E.M.F. rose steadily till the equivalence-point. At the equivalence-point there was a sharp jump in potential in each case. For the addition of 0.025 c.c. of the reagent the value of the inflection-potential was of the order of about 90 to 136 millivolts for the nitroanilines, 86 to 110 millivolts for the

aminobenzoic acids, 220 to 136 millivolts for sulphanic acid, 80 to 90 millivolts for *p*-chloroaniline, 130 to 140 millivolts for 3-nitroaminophenetole and 100 to 120 millivolts for 2-amino-4-nitrophenol.

After the equivalence-point there was again rise in the potential but with further addition of the reagent the potential assumed a constant value, followed by a steady fall. From the volume of the sodium nitrite required in each titration, corresponding to the equivalence-point, the amount of the amine was calculated. The values obtained are compared in the following table with the amount of the amine taken.

TABLE II.

Substance.			Amount	
			(taken) gms.	(found) gms.
1. <i>o</i> -Nitroaniline	...	...	0.3231	0.3227
			0.4260	0.4255
			0.5250	0.5246
			0.6894	0.6899
			0.8434	0.8428
		1.1016	1.1014	
2. <i>m</i> -Nitroaniline	...	...	0.3900	0.3895
			0.4504	0.4502
			0.6019	0.6022
			0.7212	0.7217
3. <i>p</i> -Nitroaniline	...	...	0.3490	0.3488
			0.4858	0.4854
			0.5642	0.5640
			0.6528	0.6517
4. <i>o</i> -Aminobenzoic acid	...	...	0.3173	0.3168
			0.4748	0.4744
			0.5044	0.5039
			0.6390	0.6388
5. <i>p</i> -Aminobenzoic acid	...	...	0.3552	0.3547
			0.3848	0.3846
			0.4864	0.4864
			0.5652	0.5653
			0.6572	0.6567

TABLE II (contd.).

Substance.	Amount	
	(taken) gms.	(found) gms.
6. Sulphanilic acid	0.1812	0.1810
	0.4046	0.4043
	0.5752	0.5752
	0.7654	0.7649
7. <i>p</i> -Chloraniline	0.3608	0.3607
	0.4212	0.4209
	0.5240	0.5237
	0.7620	0.7617
8. 3-Nitro-4-aminophenetole	0.3924	0.3922
	0.4118	0.4112
	0.5023	0.5021
	0.7010	0.7004
	0.8012	0.8007
9. 2-Amino-4-nitrophenol	0.3382	0.3380
	0.5552	0.5549
	0.6530	0.6527
	0.7382	0.7380

From the above results it is evident that the amines can be determined quantitatively by the potentiometric method, by titrating them against a standard solution of sodium nitrite.

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