

X.—*The Physical Constants of Nicotine. Part I.*
Specific Rotatory Power of Nicotine in Aqueous Solution.

By HARRY JEPHCOTT.

NICOTINE has been purified and its constants have been recorded by Landolt ("Optical Rotation of Organic Substances"), Nasini and Pezzolato (*Zeitsch. physikal. Chem.*, 1893, **12**, 501), Gennari (*ibid.*, 1896, **19**, 130), Hein (*Diss.*, Berlin, 1896), Příbram and Glücksmann (*Monatsh.*, 1897, **18**, 303), Ratz (*ibid.*, 1905, **26**, 1241), and Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 563). All, with the exception of Ratz, relied on the distillation in hydrogen of anhydrous nicotine. Ratz utilised two methods, namely, fractional distillation in a vacuum and the formation of nicotine zinc chloride followed by distillation. Their results for the specific rotation, which show considerable variation, are as follows:

	$[\alpha]_D^{20}$.	D_4^{20} .
Landolt	161.55	1.01101
Nasini and Pezzolato	161.29	—
Gennari	162.84	1.01071
Hein	164.18	1.01049
Příbram and Glücksmann	164.91	1.0095
Ratz (by fractional distillation)	166.77	—
„ (from double salt)	169.0 to 169.54	1.00925
Winther	163.85	—

It appeared probable that the variation was due to the presence of the alkaloids nicotine, nicotelline, and nicotimine, which occur with nicotine, and it was decided to purify nicotine by the method utilised by Pictet and Rotschy (*Ber.*, 1901, **34**, 696) when isolating these alkaloids. Nicotine which had been prepared from tobacco by steam distillation was dissolved in a slight excess of hydrochloric acid and treated with sodium nitrite at low temperature. The nicotine was subsequently liberated by alkali, dehydrated, and fractionally distilled under diminished pressure. Considerable loss of nicotine occurred owing to the formation of oxidation products during the treatment with nitrite.

A quantity, about 2500 grams in all, of commercial nicotine was also converted into nicotine zinc chloride, twice recrystallised, and the nicotine liberated, dehydrated, and fractionally distilled under diminished pressure in a manner similar to that of Ratz (*loc. cit.*).

The distillation was a source of much trouble. In the cold, nicotine readily forms highly-coloured oxidation products on exposure to the air. When hot, this oxidation is extremely rapid, and water is also absorbed. At the temperature of distillation, the vapour readily attacks cork or rubber used for connexions. Well-fitting ground-glass joints are essential, but there proved to be no necessity to flood the apparatus with hydrogen if a sufficiently high vacuum were maintained (20—40 mm. pressure).

The nicotine prepared in this way was colourless and almost without odour in the cold. When kept in bottles filled to the stopper and away from the light, nicotine remains colourless, only the slightest yellow tint being noticed after six months and no change in rotatory power (compare Pribram, *loc. cit.*, p. 303).

For pure nicotine, the density and rotatory power were found to be as follows:

	D_4^{20} .	$[\alpha]_D^{20}$.
Purified through nitroso-compound	1.00920	168.52
Purified through double chloride (1) ...	1.00925	168.61
" " " " (2) ...	1.00925	168.40
" " " " (3) ...	1.00925	168.66

The three sets of figures for the double chloride method refer to three separate and distinct preparations of pure nicotine in that way.

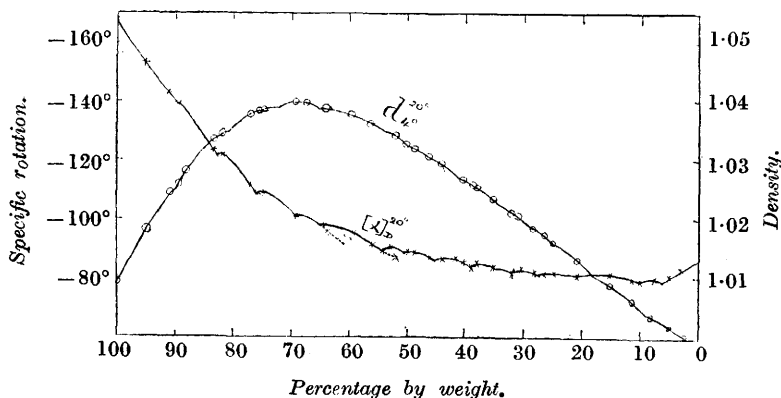
Many dilutions of this nicotine with water were prepared, and the specific gravity and specific rotatory power for them observed. The rotations were measured with a Schmidt and Haensch half-shade polarimeter, using a tube having a length of 100.04 mm.

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Per- centage by weight.	Grams in 100 c.c.	D_4^{20} .	$[\alpha]_D^{20}$.	Per- centage by weight.	Grams in 100 c.c.	D_4^{20} .	$[\alpha]_D^{20}$.
100	100.925	1.00925	168.61	44.004	45.296	1.02936	86.47
95.068	96.801	1.01823	153.06	41.718	42.882	1.02790	86.71
91.084	93.323	1.02458	141.65	40.237	41.308	1.02661	85.09
89.471	91.781	1.02583	138.73	38.798	39.804	1.02592	83.79
88.338	90.820	1.02810	134.11	38.065	39.025	1.02522	85.21
83.336	86.132	1.03356	123.21	37.986	38.950	1.02538	84.98
81.842	84.632	1.03439	121.48	35.098	35.920	1.02341	83.52
77.006	79.921	1.03784	111.47	34.877	35.696	1.02351	83.39
75.538	78.551	1.03836	108.39	32.141	32.810	1.02107	81.83
84.868	77.764	1.03839	108.69	30.973	31.607	1.02048	82.48
69.202	71.963	1.03990	100.47	30.637	31.253	1.02010	82.67
67.538	70.231	1.03988	—	30.291	30.915	1.02060	82.60
64.423	66.918	1.03890	97.82	28.151	28.664	1.01820	81.95
63.950	66.440	1.03894	95.63	26.473	26.930	1.01725	81.78
60.773	63.110	1.03846	94.02	24.975	25.369	1.01588	81.67
59.898	62.131	1.03728	93.69	20.963	21.235	1.01300	80.64
59.649	61.895	1.03765	95.12	20.726	20.995	1.01299	80.06
56.241	58.250	1.03614	91.27	15.023	15.156	1.00880	80.99
54.289	56.245	1.03603	89.27	12.963	13.027	1.00492	79.79
53.096	54.934	1.03463	90.12	11.508	11.579	1.00611	79.43
51.969	53.750	1.03428	86.91	10.012	10.061	1.00611	78.66
50.134	51.777	1.03278	89.03	9.921	9.971	1.00494	79.20
48.949	50.513	1.03194	88.19	7.417	7.441	1.00317	79.94
46.632	48.062	1.03065	86.23	6.604	6.622	1.00276	79.25
46.183	47.629	1.03131	—	4.998	5.006	1.00153	80.48
46.015	47.412	1.03037	86.79	2.505	2.504	0.99970	83.15

The effect of temperature on the density and rotatory power both of pure nicotine and certain of its aqueous solutions has also been observed. For this purpose, a jacketed polarimeter tube was

Nicotine in aqueous solution.



employed, a Sprengel tube being used for the densities. It was not convenient in every case to observe both density and angle at the same temperature, and the density at the temperature at

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which the rotatory power was observed was obtained from a graph constructed from the recorded densities.

Pure Nicotine.

Temperature.	20°.	21.1°.	40°.	60°.	80°.	97.7°.
D_4^{20}	1.00925	1.00865	0.99424	0.97799	0.96184	0.94534

Temperature.	D_4^t (from graph).	$[\alpha]_D^t$.
20°	1.00925	168.20°
29.5	1.0017	168.71
41.5	0.9924	169.09
52	0.9840	169.51
62	0.9760	169.74
69.6	0.9699	169.94
86.4	0.9567	169.73
92.0	0.9521	169.71

Owing to the so-called closed curve of solubility of nicotine in water, it is not possible to observe the rotatory power and density of solutions containing between 7 and 87 per cent. of nicotine at all temperatures up to 100°, since separation occurs at about 60°. Two solutions were therefore prepared which would fall outside this closed curve, and contained 6.638 per cent. and 88.338 per cent. of nicotine. For these, the following figures were found:

Temperature.	Percentage by weight.	Grams in 100 c.c.	D_4^t .	$[\alpha]_D^t$.
20°	6.638	6.682	1.00275	76.82
85	6.638	6.4188	0.96328	95.29
20	88.338	90.820	1.02810	134.16
90	88.338	86.936	0.98412	150.34

It will be observed that the change in rotatory power is marked.

On cooling to 20°, the 6 per cent. solution at once showed its original rotatory power, but the 88 per cent. solution did not revert to its former value for some days, although an immediate fall to about $[\alpha]_D^{20}$ 138.0 took place. Difficulty occurs in determining the rotatory power of pure nicotine and its more concentrated solutions, since, owing presumably to light absorption, it is necessary to match a greyish-pink against a grey when taking polarimetric readings. In the case of the more concentrated aqueous solutions, the difficulty is greatly increased owing to the very marked changes in density. In observing the angle of the 88 per cent. solution at 90°, even with a rapid stream of water circulating round the jacket, the change in density by cooling at the exposed surface of the end plates was so marked as to make it almost impossible to get light to pass through the tube, and the

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rotation recorded must be considered liable to an error of 1° . No such difficulties were experienced with the 6 per cent. solution.

The graphs for density and specific rotatory power of nicotine in aqueous solution both exhibit a series of maxima, and these agree with molecular proportions of nicotine and water. This indication of the formation of a series of hydrates is confirmed by an examination of the freezing points of nicotine solutions.

Between 40 and 80 per cent., the time taken for hydrate-formation is appreciable, and the abnormal points marked were found in cases of solutions when the rotation was observed immediately after mixing. A solution containing 69.2 per cent. of nicotine showed no change in rotation after keeping for twelve months.

The "Closed Curve of Solubility" for Nicotine.

The formation of hydrates of nicotine and their decomposition at higher temperatures shows the true nature of the "closed curve of solubility." Nicotine is only sparingly soluble in water, and water is only sparingly soluble in nicotine, but hydrates of nicotine are miscible with either, a state of balance existing at any given temperature between nicotine, its hydrates, and water.

When the temperature rises, the hydrate-formation reverses, and on the concentration of free nicotine becoming greater than the solubility of nicotine in water at that temperature, separation occurs. By choosing concentrations of nicotine and water such that the limit of solubility of the one in the other was not exceeded, it was possible, as shown above, to note the marked rise in rotatory power as the concentration of free nicotine increased with the rise in temperature, and it is to be expected that with convenience for observing the angle at a sufficiently high temperature, the true rotatory power of nicotine in water would be obtained.

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WEST HAM MUNICIPAL TECHNICAL INSTITUTE.

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