

XXIV.—*Note on the use of Pyridine for Molecular Weight Determinations by the Ebullioscopic Method.*

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PYRIDINE has a very remarkable solvent power for both organic and inorganic compounds; many substances which are insoluble, or only sparingly soluble in the organic solvents in general use, dissolve readily in pyridine.

An organic liquid in which so many substances are soluble should be very valuable in the investigation of the physical properties of solutions, as a large number of comparable results can be obtained. For such a purpose, it is important to know whether the molecular weights of dissolved substances are normal in this solvent.

As is well known, substances containing hydroxyl groups generally give abnormally high molecular weights both by the freezing and boiling point methods, when hydrocarbons such as benzene, naphthalene, and phenanthrene are used as solvents. The molecular weight is found to increase with the concentration, and is usually nearly normal in dilute solution.

Von Laszczynski and von Gorski (*Zeit. Elektrochem.*, 1897, 4, 299) have shown that pyridine solutions of a number of inorganic salts have marked electrical conductivity, and deduce from this that the salts are ionised to a considerable extent. If this is the case, pyridine should give normal molecular weights with organic hydroxy-compounds, as an ionising solvent does not favour the formation of polymerised molecules.

Werner (*Zeit. anorg. Chem.*, 1897, 15, 1) has determined the molecular weight of a number of inorganic salts in pyridine. The concentrations used were small (about 0.5 to 3 percent.). The molecular weights found were constant within the limits of experimental error for the various concentrations and agreed closely with those calculated from the formulæ, in some cases being a few units above, in others slightly below the normal. The only substances which gave values much

below the normal were mercuric iodide and cyanide. Both these substances are ionised to an unusually small extent in aqueous solution.

There is therefore no evidence of ionisation in pyridine to be drawn from the molecular weights of dissolved salts.* Consequently there was a possibility that pyridine might give abnormal results with organic hydroxy-compounds.

As the author wished to examine in a polymerising solvent, substances which are soluble in pyridine, but insoluble in all the solvents known to have this action, the following determinations were carried out to test this point.

The method described by Jones (*Zeit. physikal. Chem.*, 1899, **31**, 114) was tried; the boiling tube was somewhat smaller than that used by him, but otherwise the apparatus was the same.

The boiling point of the pyridine was not of satisfactory constancy. It varied considerably with changes in the gas pressure, and draughts affected it very much. This may, no doubt, be ascribed to the direct manner of heating recommended by Jones, and to the absence of a vapour jacket.

A determination of the constancy of the boiling point was therefore made in an ordinary Beckmann apparatus, using a platinum cylinder in the way described by Jones. The result was very satisfactory.

A glass vapour mantle was used, and a plain glass boiling tube without a platinum rod fused into the bottom.

It was found that pyridine acted rapidly on cork, leaving a shrivelled, hard, wood-like residue; the condenser tube was therefore fused directly to the boiling tube and the boiling tube made longer than usual above the condenser. The cork holding the thermometer was covered with tinfoil. Hardly any pyridine vapour came into contact with it, owing to the length of the tube.

The platinum cylinder was 7.5 cm. long, 1.9 cm. in diameter, and made conical at the top so as to fit the thermometer closely.

The boiling tube was filled to a height of about 2.5 cm. with glass beads of the usual size, the platinum cylinder slipped down, and very fine beads poured in to occupy about 1 cm. The cylinder was then brought into the middle of the tube by tapping, and some pieces of platinum foil placed in it. The small beads hold the cylinder more firmly than the large ones, and mix the vapour and liquid more thoroughly.

* Jones has suggested (*Zeit. physikal. Chem.*, 1899, **31**, 114) that the apparent absence of ionisation indicated by osmotic methods in this and similar cases may perhaps be accounted for by combination of the dissolved substance with the solvent. It is evident, however, that combination with the solvent should lower, not raise, the apparent molecular weight. The number of molecules of dissolved substance would be the same, but the amount of solvent would be smaller than that used in the calculation.

The pyridine used was Kahlbaum's "gereinigt"; it was dried over solid potassium hydroxide and fractionated, a dephlegmating column being used. The fraction boiling at $115.2-115.5^{\circ}$ was taken for the experiments.

Two series of determinations were made with Kahlbaum's "pure" pyridine; the constant obtained agreed perfectly with that given by the much cheaper specimen.

A Jena glass Beckmann thermometer with a very small bulb was employed. A constant temperature was only obtained after the liquid had been boiling for several hours.

The following readings show the apparent variation of the boiling point due to changes in the thermometer:

Liquid began to boil at 11.30.

Time.	Reading.	Time.	Reading.
11.45	2.45	3.25	2.990
12.15	2.59	3.40	2.990
12.30	2.740	4.0	3.060
2.10	2.835	4.25	3.070
3.0	2.885	4.35	3.070
3.7	2.940		

By leaving the liquid boiling all night, a boiling point of satisfactory constancy was obtained.

Time.	Reading.	Time.	Reading.
5.10 P.M.	3.130	10.50 A.M.	3.272
6.10 „	3.148	1.5 P.M.	3.270
10.20 A.M.	3.278		

During both these determinations the atmospheric pressure varied very little.

In the experiments, of which the results are given, the pyridine was left boiling all night, the boiling point observed several times during an hour in the morning, and if it did not vary more than 0.01° the determinations were then carried out. A regulator was used to keep the gas pressure constant.

In calculating the results, 0.2 gram is deducted from the weight of solvent actually taken.

Rosenheim and Woge (*Zeit. anorg. Chem.*, 1897, 15, 315) used pyridine to determine the molecular weight of beryllium chloride. They state that, with ordinary German glass, constant results could not be obtained, as the pyridine attacked the glass. They found it necessary to use Jena glass. No effect of this sort had been noticed in my experiments.

Twenty grams of pyridine were heated for sixteen hours in the

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boiling tube, fitted up as if for a molecular weight determination. The pyridine was then evaporated to dryness in a weighed platinum dish. There was no residue, and the weight of the dish was the same to four places of decimals.

Determination of the molecular rise of boiling point for pyridine :

Wt. of solvent.	Wt. of subst.	Rise of b. p.	Grams subst. per 100 g. solvent.	Mols./100 per 100 g. solvent.	Constant.
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Benzophenone, $C_{13}H_{10}O = 182$.

15.72	0.2480	0.268°	1.60	0.88	30.5
„	0.5970	0.648	3.85	2.12	30.7
„	0.926	0.988	5.97	3.28	30.1
„	1.259	1.318	8.12	4.46	29.6

Phenanthrene, $C_{14}H_{10} = 178$.

18.59	0.1592	0.140°	0.87	0.49	28.8
„	0.4236	0.392	2.30	1.29	30.3
„	0.8406	0.740	4.57	2.57	28.8
„	1.450	1.240	7.88	4.43	28.0
„	2.063	1.758	11.21	6.30	27.9

Diphenylamine, $C_{12}H_{11}N = 169$.

18.40	0.2282	0.218°	1.23	0.73	29.0
„	0.5278	0.536	2.84	1.68	30.9
„	1.7008	1.596	9.34	5.53	28.5

The mean of all the determinations is 29.5.

The constant has been determined by Werner (*loc. cit.*) with diphenylamine in concentrations varying from 0.93 to 9.69 per cent. The mean value was 30.1, the numbers varying from 28.6 to 31.5.

The constant has also been determined by Rosenheim and Woge (*loc. cit.*), who used diphenyl, triphenylmethane, and *p*-toluidine as dissolved substances in concentrations of from 1.7 to 3.7 per cent. The mean was 30.7. The numbers obtained for the constant were very concordant, the greatest difference being only 1.3, but the determinations were nearly all carried out at about the same concentration, and the greatest differences of concentration were small.

Werner calculated the constant from the Trouton-Schiff rule $C = 0.00096T_m = 29.5$. This method only gives an approximate value in most cases. The constant may be calculated with considerable

accuracy by van't Hoff's formula $C = \frac{0.0198T^2}{L}$, which has been shown to apply to the boiling point by Arrhenius (*Zeit. physikal. Chem.*, 1889, 4, 550).

The heat of vaporisation of pyridine has been determined by Louguinine (*Compt. rend.*, 1899, 128, 366), who found it to be 101.39 at 115.5°. Introducing these values, we get

$$C = \frac{0.0198 \times (388.5)^2}{101.39} = 29.47;$$

29.5 is therefore taken as the constant for pyridine.

Molecular weight of hydroxy-compounds in pyridine:

Wt. of solvent.	Wt. of subst.	Rise of b. p.	Grams subst. per 100 g. solvent.	Mols./100 per 100 g. solvent.	Mol. wt.
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Succinic acid, $C_2H_4(CO_2H)_2 = 118$.

17.77	0.2104	0.278°	1.18	1.00	127
„	0.4316	0.575	2.43	2.06	126
„	0.8524	1.215	4.80	4.06	117
„	1.492	2.205	8.40	7.11	113

Tartaric acid, $C_2H_2(OH)_2(CO_2H)_2 = 150$.

19.60	0.3542	0.335°	1.81	1.20	160
„	1.1530	1.065	5.88	3.92	164
„	2.372	2.175	12.10	8.07	165

Salicylic acid, $C_6H_4(OH) \cdot CO_2H = 138$.

18.26	0.1782	0.188°	0.98	0.71	123
„	0.5021	0.615	2.75	1.99	133
„	1.1978	1.390	6.56	4.75	140
„	2.193	2.630	12.00	8.70	136

Resorcinol, $C_6H_4(OH)_2 = 110$.

16.89	0.0968	0.145°	0.57	0.53	124
„	0.3050	0.497	1.80	1.64	107
„	0.6968	1.153	4.17	3.99	105

Tartaric ditoluidide, $C_2H_2(OH)_2(CO \cdot NH \cdot C_6H_4 \cdot CH_3)_2 = 328$.

16.99	0.2094	0.110°	1.23	0.38	331
„	0.4112	0.218	2.42	0.74	330
„	0.6234	0.308	3.67	1.12	354

β-Naphthol, $C_{10}H_7 \cdot OH = 144$.

Wt. of solvent.	Wt. of subst.	Rise of b. p.	Grams subst. per 100 g. solvent.	Mols./100 per 100 g. solvent.	Mol. wt.
18.54	0.1734	0.176°	0.93	0.65	158
„	0.4284	0.465	2.31	1.60	148
„	0.9694	1.060	5.23	3.63	147
„	1.342	1.470	7.22	5.01	146
„	1.798	2.000	9.68	6.72	144

The molecular weights found are in every case near the normal, and there is no regular increase with concentration. Pyridine may therefore be used to find the normal molecular weight of hydroxy-compounds.

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