NITRILES AS SOLVENTS IN MOLECULAR WEIGHT DETERMINATIONS

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Nitriles have rarely been used as solvents in making molecular weight determinations. In 1897 Werner[1] determined the molecular weight of mercuric chloride, mercuric iodide and silver nitrate in benzonitrile by the ebullioscopic method, and this was the only case that I could find in the literature where a nitrile had been used as solvent. Werner determined the so-called molecular elevation of the boiling-point for this solvent empirically by using diphenylamine as solute and assuming its molecular weight to be that computed from its formula. In this way he obtained 36.5 as the constant for benzonitrile. According to the Trouton-Schiff rule, Werner calculated the constant to be 45.79; he states clearly that he is unable to explain the discrepancy. Recently the latent heat of evaporation of benzonitrile has been carefully measured by Louguinine[2] and also by myself.[3] The results of these investigations are practically identical, the value found being 87.7. From this value the molecular elevation of the boiling-point, when calculated according to the Arrhenius-Beckmann formula, becomes $K = \dfrac{0.02(189 + 273)^2}{87.7}$

or 48.67, which is the constant that ought to be used in computing the molecular weights. In Table I. are given the results of Werner, recalculated, using this constant. In the table, s represents the amount of solute, l the quantity of solvent, Δ the observed rise of the boiling-point, and m the molecular weight calculated according to the usual formula.

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[1] Zeit. anorg. Chem. **15**, 31 (1897).
[3] Archiv. des Sciences Naturelles de Genève, **9**, 5–26 (1899).
[3] Jour. Phys. Chem. **5**, 230 (1891).

TABLE I.

(Solvent benzonitrile)

Diphenylamine $((C_6H_5)_2NH$, mol. wt. $= 169)$

s	l	Δ	m
0.1298	20.11	0.135	233
0.2357	20.11	0.250	228
0.1104	14.45	0.169	220

Mercuric chloride $(HgCl_2$, mol. wt. $= 271)$

0.2123	19.45	0.126	421
0.5446	19.45	0.358	380
0.3738	21.68	0.280	300
0.8710	21.68	0.585	335

Mercuric iodide $(HgI_2$, mol. wt. $= 454)$

0.1737	23.92	0.061	580
0.5135	23.92	0.153	684

Silver nitrate $(AgNO_3$, mol. wt. $= 170)$

0.3534	23.74	0.345	220
0.8336	23.74	0.750	239
0.1874	23.50	0.160	243
0.4326	23.50	0.380	236

Table II. gives a series of determinations of my own. The sample of benzonitrile used was the same as that employed in making the measurement of the latent heat of evaporation.

TABLE II.

(Solvent benzonitrile)

Silver nitrate $(AgNO_3$, mol. wt. $= 170)$

s	l	Δ	m
0.1098	16.61	0.130	248
0.3352	16.61	0.381	258
0.5208	16.61	0.590	259

In the case of acetonitrile I found the latent heat of evaporation to be 173.6. The value obtained by Louguinine is 170.68. According to the former value the boiling-point constant becomes $\dfrac{0.02(80.5 + 273)^2}{173.6}$, or 14.39; while according to the

latter value it equals 14.63. In making the computations in Table III., the constant 14.39 was used. The sample of aceto-nitrile employed was the same as that used in making the deter-mination of the latent heat of evaporation. The solutes used were, with the exception of the silver nitrate, of Kahlbaum's manufacture. They were naphthalene, melting-point 80°; di-phenyl, melting-point 69–69.5°; and diphenylamine, melting-point 54°. The silver nitrate was obtained from Baker & Adam-son, and was thoroughly dried. The symbols in Table III. have the same significance as those in the preceding tables.

TABLE III.

(Solvent acetonitrile)

Naphthalene ($C_{10}H_8$, mol. wt. $= 128$

s	l	Δ	m
0.3103	11.04	0.280	144
0.5153	11.04	0.469	143
0.7910	11.04	0.717	144
0.9952	11.04	0.905	143

Diphenyl ($C_{12}H_{10}$, mol. wt. $= 154$)

0.2208	11.25	0.165	171
0.3246	11.25	0.242	172
0.5494	11.25	0.421	167
0.8374	11.25	0.673	159

Diphenylamine ($(C_6H_5)_2NH$, mol. wt. $= 169$)

0.1641	11.29	0.168	125
0.5314	11.29	0.549	124
0.6838	11.29	0.679	128
0.8735	11.29	0.833	133

Silver nitrate ($AgNO_3$, mol. wt. $= 170$)

0.1856	10.99	0.180	135
0.3050	10.99	0.298	134
0.5397	10.99	0.510	138
0.7977	10.99	0.760	138
1.0350	10.99	0.939	144

If the constant calculated from Louguinine's value for the latent heat of vaporization had been used, the molecular weights

in Table III. would have been 1.8 percent higher. As the boil-
ing-point constant of acetonitrile is nearly 2.8 times that of
water, the molecular weights in the former solvent are more
readily determined with accuracy.

The attempt was made to use propionitrile as a solvent for
molecular weight determinations, but it was unsuccessful, inas-
much as in spite of all exertions, it was found impossible to
secure a sample of the substance that had a sufficiently constant
boiling-point. The same difficulty was met in trying to employ
butyronitrile and valeronitrile.

From Tables I. and II. it appears that the molecular
weights of the solutes in benzonitrile are all considerably higher
than the theoretical values, without, however, reaching a figure
corresponding to a double molecule. The mercuric chloride,
mercuric iodide and silver nitrate solutions in benzonitrile are
fairly good electrolytes; while the solution of diphenylamine in
this solvent is a non-electrolyte. From the boiling-point results
in the tables one could clearly not have foretold these facts.

Turning now to Table III. we see that naphthalene and di-
phenyl yield molecular weights higher than the theoretical.
The solutions of these substances in acetonitrile are non-electro-
lytes. Again, diphenylamine, which is also a non-electrolyte
when dissolved in acetonitrile, yields an abnormally low molec-
ular weight.[1] In fact the molecular weight of this solute is
lower than that of silver nitrate, although the latter substance
when dissolved in acetonitrile is an electrolyte par excellence.

A comparison of the results obtained with diphenylamine
and silver nitrate is of special interest, because these two sub-
stances have practically the same theoretical molecular weight.
Though the solutions of diphenylamine in both benzonitrile and
acetonitrile are non-electrolytes, and the solutions of silver ni-
trates in these solvents are good electrolytes, yet in both solvents
these solutes behave practically alike. This then is a striking
illustration that there is no such simple relation between the

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[1] Reference has been made to this fact on a previous occasion. Compare
Jour. Phys. Chem. **5,** 344 (1901).

boiling-points of solutions and their electrical conductivity as the theory of Arrhenius claims.[1]

At any given pressure, the boiling-point of a solution is determined by the concentration and by the chemical character of the solvent and solute, which determines the mutual attraction existing between them. This mutual attraction is the essence of the so-called osmotic pressure and is the cause of the process of solution. In applying the gas laws to solutions, we do at times get molecular weights for the solute that are equal to the theoretical within the limit of error of experiment; but more frequently we do not, and this regardless as to whether the solutions are electrolytes or not, as is well shown by the solutions in these nitriles.

It is probable that the high molecular weights in benzonitrile are partly, if not largely, due to the relatively high boiling-point of the solvent (189°). In acetonitrile the molecular weights are much lower. Its boiling-point is 80.5°. Examples of this kind are not uncommon ; and I hope to recur to this point ere long in the course of a more general consideration of the subject of solutions.

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Dec. 5, 1901.

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[1] In the case of silver nitrate when dissolved in acetonitrile, the so-called degree of electrolytic dissociation corresponding to the molecular weight 135 (Compare Table III.) is 26 percent; from the conductivity determinations of Dutoit and Friderich (Bull. Soc. Chim. Paris, (3) **19**, 327 (1898)) it is about 34 percent for approximately the same concentration. To be sure, this comparison is not quite fair, as we are not comparing the solutions at the same temperature ; but the discrepancy would very likely not disappear even if the comparison were made at the same temperature. Compare Jour. Phys. Chem. **5**, 339 (1901).