CCCXXXIX.—*The Solubility of Certain Anilides in Water–Acetic Acid Mixtures.*

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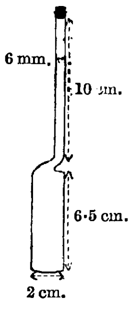

In connexion with the examination of the relative reactivities of anilides towards chlorine (Orton and Bradfield, J., 1927, 986; Bradfield and Jones, J., 1928, 3073), some knowledge of the solubilities of anilides in aqueous acetic acid was required. Owing to the paucity of data in the literature, a series of determinations of the solubility of acetanilide, propanilide, benzanilide, toluenesulphonanilide, *N*-methylacetanilide, and *N*-methyltoluenesulphonanilide in water and in acetic acid–water mixtures up to 99% acetic acid over the temperature range 20—35° was undertaken.

The "synthetic method" was employed, *i.e.*, known weights of solvent and solute were gradually heated with constant shaking, and the temperature was noted at which the last trace of solid disappeared (compare Kuriloff, *Z. physikal. Chem.*, 1897, **23**, 547; Hartley and Thomas, J., 1906, **89**, 1013; Sidgwick and collaborators, J., 1921, **119**, 983, 1003, 1016). Solvent and solute were introduced into a specially designed bottle (see fig.), which was attached by rubber bands to a standardised thermometer graduated in 0·1°, and almost completely submerged in a large beaker of water, heated by a hand-adjusted microburner. The shape of the neck permitted vigorous agitation of the bottle without splashing of the liquid to the upper part of the neck. A rough determination of the temperature at which the solid just dissolved was first made. The saturated solution was then cooled and shaken so that solid separated as a cloud of fine crystals. The bottle was re-immersed in the bath, which had cooled to about 2° below the solution point, and the temperature was raised at the rate of about 1° in 30—45 minutes. The temperature at which the cloud disappeared was taken as the solution temperature. Usually one or two small particles, representing a weight of anilide negligibly small compared with the total anilide, remained still undissolved, and only passed into solution after a long time. Repeated determinations gave values agreeing within 0·1°. A further quantity of solvent was then introduced and the solution temperature for the more dilute solution determined.

About eight or nine determinations over the range 15—40° were made, the points plotted, and the solubilities at 20°, 25°, 30°, and 35° read from the curve. The following figures illustrate the experimental results :

Acetanilide in 99% acetic acid.

G. solute in 100 g. solvent ...	44·7	46·3	50·0	55·7	56·4	58·3	64·0	69·1	75·6
Solution temp.	18·7°	20·1°	22·9°	26·6°	27·7°	28·4°	31·5°	34·2°	37·1°

A curve through these points gives the solubilities at 20°, 25°, 30°, and 35° as 46·2, 52·9, 60·9, and 70·7 g. of solute per 100 g. of solvent.

The method described above did not prove suitable when the solubility to be measured was small. In these cases, *viz.*, those of benzanilide, and the sulphonanilides in dilute acetic acid, and of propanilide in water, determinations were limited to the single temperature of 20° and the following method was employed. Tubes of about 20 c.c. capacity, containing various quantities of anilide and solvent, were sealed, placed in a thermostat, and left for a week, being shaken at intervals. After a few trials it was possible to obtain two tubes containing weights of anilide differing by 1—2% such that one gave a clear solution, while particles remained undissolved in the other. The mean concentration was taken as the solubility at that temperature. There is no danger of hydrolysis of benzanilide or the sulphonanilides by this prolonged contact with acetic acid, since these anilides are only hydrolysed with difficulty by boiling mineral acids. Propanilide is rather more readily hydrolysed, but we obtained no indication of appreciable hydrolysis, and consequent increase in solubility, under these conditions.

Little comparison of our measurements with existing data is possible. Seidell (*J. Amer. Chem. Soc.*, 1907, **29**, 1088) gives the solubility of acetanilide in 99·5% acetic acid as 49·7 g. in 100 g. of solvent at 21·5°, whereas we obtain the value 48·1 g. in 100 g. of 99·0% acetic acid at this temperature. Our values for the solubility of acetanilide in water (g./100 g. of solvent) are here compared with those of other workers :

Temp.	15°	20°	25°	30°	35°	40°
Others	0·501*	0·462†	0·563‡ 0·543*	0·533† 0·634*	— —	0·654† 0·867*
Authors	—	0·504	0·563	0·665	0·808	—

* Schoorl and Weerd, *Rec. trav. chim.*, 1922, **41**, 15.
† Pawlewski, *Ber.*, 1899, **32**, 1425. ‡ Seidell, *loc. cit.*

The number of grams of solute dissolved in 100 g. of a solvent containing x g. of acetic acid (for water, $x = 0$) are tabulated below.

x.	Temp.	I.	II.	III.	IV.	V.	VI.
99	20°	46·2	35·5	158	1·73	22·0	9·0
	25	52·9	40·8	170	2·09	26·1	11·2
	30	60·9	48·7	186	2·54	32·5	14·3
	35	70·7	61·6	204	3·10	42·1	19·2
91·3	20	45·4	33·5	158	1·60	15·9	5·6
	25	52·5	41·0	172	1·92	19·4	6·9
	30	61·2	50·0	188	2·31	24·6	8·9
	35	71·6	61·4	204	2·77	31·7	11·8
85	20	40·4	26·6	158	1·11	11·0	3·6
	25	47·6	32·5	172	1·37	13·2	4·4
	30	56·7	40·9	189	1·69	16·7	5·7
	35	67·9	51·7	207	2·07	21·6	7·4
76·8	20	31·5	18·0	153	0·61	6·2	1·83
	25	38·2	21·5	168	0·79	7·5	2·36
	30	46·6	28·6	186	1·00	9·7	3·05
	35	56·9	37·4	206	1·22	12·6	3·94
52·4	20	9·82	4·15	119	0·13	0·88	0·18
	25	12·2	5·10	136	—	1·02	—
	30	15·3	6·36	156	—	1·24	—
	35	19·2	8·05	181	—	1·60	—
26·9	20	2·23	0·87	45	Almost insoluble.	0·09	0·02
	25	2·70	1·05	59		—	—
	30	3·28	1·26	78		—	—
	35	4·05	1·52	104		—	—
0	20	0·504	0·18	2·25		Almost insoluble.	Almost insoluble.
	25	0·563	—	2·56			
	30	0·665	—	2·93			
	35	0·808	—	3·34			

I = Acetanilide.
II = Propanilide.
III = *N*-Methylacetanilide.
IV = Benzanilide.
V = *p*-Toluenesulphonanilide.
VI = *N*-Methyl-*p*-toluenesulphonanilide.

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