[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Solubility Studies. IV. The Solubilities of Certain Slightly Soluble Organic Compounds in Water[1]

BY PAUL M. GROSS, JOHN H. SAYLOR AND MARY A. GORMAN

In continuing a general program of research on the solubility in water and aqueous salt solutions of organic compounds in relation to their polar character,[2] the solubilities of an additional number of slightly soluble organic compounds in water have been measured. Since solubilities for most of these compounds are not in the literature, the value for the solubilities we have found are published now. The theoretical significance of these and other experimental values will be considered in a later paper.

Method.—The saturated solutions of the substances were prepared in thin-walled cylindrical flasks in a large water thermostat. The thermostat was kept at 30 ± 0.02°. The saturated solutions were analyzed by means of a Zeiss combination liquid and gas interferometer. The procedure has been previously described in detail.[2a]

Materials

Purification of Materials.—All of the organic chemicals were Eastman Kodak Company best grade with the exception of the cinnamic acid, which was a sample prepared in this Laboratory by Mr. William Miller, Jr. Solids were further purified by repeated recrystallization from an appropriate solvent until the melting points from two successive recrystallizations were the same. Liquids were purified by fractional distillation using for fractionations at atmospheric pressure a 25-cm. all-glass Widmer still and a small all-glass still with a 105-cm. column of the type previously described.[3] A Hickman still, designed for a moderate vacuum with a barostat operated by a vacuum tube relay was used for distillations under reduced pressure. The thermometers used were a set of small two-tenth degree thermometers with a fifty degree range, calibrated by the Bureau of Standards; a set of fiftieth degree Goetze thermometers with a twelve degree range, calibrated by the Physikalische Technische Reichsanstalt; and for 1,3-dibromopropane, an uncalibrated tenth degree thermometer of good quality. Melting points down to −10° were determined with a tenth degree thermometer calibrated by the Bureau of Standards. For lower temperatures a pentane-filled degree thermometer with a range of 0 to −200°, calibrated by the Physikalische Technische Reichsanstalt was used. For distillations at atmospheric pressure the boiling points were corrected to 760 mm. by means of Craft's rule, whenever the value of dT/dp could not be found in the literature. Distilled water of good quality from the laboratory supply was used for the solubility determinations.

Table I summarizes the boiling point and melting point data for the samples used for the solubility determinations. The pressures during the vacuum distillations were maintained by the barostat within ±0.5 mm. of the values listed in column three.

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[1] Based upon a thesis submitted by Mary A. Gorman in partial fulfilment of the requirements for the M.A. degree at Duke University.

[2] (a) Gross and Saylor, THIS JOURNAL, **53**, 1744 (1931); (b) Gross, *ibid.*, **51**, 2362 (1929); (c) Gross, *Z. physik. Chem.*, **B6**, 215–220 (1929).

[3] Gross and Wright, *J. Ind. Eng. Chem.*, **13**, 701 (1921).

TABLE I

DATA AND CONSTANTS FOR THE COMPOUNDS AND SOLUBILITIES IN WATER AT 30°

Substances	B. p. range, °C.	Pressure, mm.	M. p., °C.	Previously observed B. p., °C.	Previously observed M. p., °C.	Ref.	Grams per 1000 g. of water	Moles per 1000 g. of water	Estimated error, %
Diethyl ketone	101.64–101.82			101.7		6	46.9	0.545	1.0
1-Chloro-2-bromoethane	106.62–106.71			106.7		4b	6.88	.0479	1.0
1,3-Dichloropropane	120.5–120.6					5	2.87	.0254	1.0
Ethyl adipate	129.0–129.4	13	−22	127	−21	4d	4.26	.0211	0.5
Fluorobenzene	84.55–84.63			85.14	(86)	8, 6	1.54	.0160	1.5
o-Nitroanisole			9.2		9.4	6	1.69	.0111	0.5
o-Nitroaniline			71.45		71.5	6	1.47	.0106	1.5
m-Nitroaniline			111.7		111.8	6	1.21	.00877	1.0
1,3-Dibromopropane	166.64–166.86			166.95		4a	1.68	.00830	0.5
o-Nitrotoluene		9.4			9.55	4e	0.652	.00479	2.0
Cinnamic acid			133.1	133.0		6	.604	.00408	1.0
p-Nitroanisole			53.9		54	6	.589	.00385	1.0
m-Nitrotoluene	118.0	20	15.44	118.5	(15.55)	9, 6	.498	.00364	3.0
p-Nitrotoluene			51.4		51.3	6	.442	.00322	0.5
s-Tetrabromethane	124.6–125.0	19	−1.0	123.7	0.13	4c	.651	.00188	2.0
Iodobenzene	79.6–79.8	20		78.4		7	.34	.0017	4.0

Results

The solubilities of all of the substances measured and the estimated percentage errors are also given in Table I. The error was estimated from the concordance of duplicate determinations.

We have included ethyl adipate in the list of compounds measured, as a paper by Sobotka and Kahn[10] has recently appeared describing a rapid and simple solubility method applicable to certain liquids in which the solubilities of ethyl adipate and similar compounds were given. Our value at 30° of 4.26 g. per 1000 g. of water is in good agreement with the value found by the above authors which is 4.23 g. per 1000 cc. of water at 20°. Our results confirm the accuracy of their method.

Values for the solubilities of four of the compounds we have measured are given in the literature as follows, the temperature in all cases being 25° instead of 30°.

Cinnamic acid, 0.546 g. per 1000 g. of water,[11] 1,3-dichloropropane, 2.73 g. per 1000 g. of water,[2b] *o*-nitroaniline, 1.212 g. per 1000 g. of water, *m*-nitroaniline, 0.910 g. per 1000 g. of water.[12]

Allowing for the difference in the temperature of 5° our results are in

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(4) (a) Timmermans, *Bull. Soc. chim. Belg.*, **28**, 392 (1919); (b) *ibid.*, **25**, 300 (1912); (c) *ibid.*, **27**, 334 (1914); (d) *ibid.*, **36**, 507 (1927); (e) *ibid.*, **31**, 389 (1922).

(5) A sample previously purified by one of us. See Gross, THIS JOURNAL, **51**, 2362 (1929).

(6) "International Critical Tables."

(7) Young, *J. Chem. Soc.*, **55**, 490 (1889). Attempts to fractionate iodobenzene under reduced pressure in carbon dioxide at atmospheric pressure resulted in some decomposition. By using the Hickman still and pressure regulator under a carbon dioxide atmosphere this was eliminated.

(8) Rechenberg, "Einfache und fractionierte Destillation in Theorie und Praxis," Schimmel and Company, 1923, p. 239.

(9) Neubeck, *Z. physik. Chem.*, **1**, 649 (1887).

(10) Sobotka and Kahn, THIS JOURNAL, **53**, 2935 (1931).

(11) Meyer, *Z. Electrochem.*, **17**, 978 (1911).

(12) Collett and Johnson, *J. Phys. Chem.*, **30**, 70–82 (1926).

good agreement with those for cinnamic acid and 1,3-dichloropropane. The discrepancy in the case of the nitroanilines is, however, larger than would be expected.

Summary

The solubilities in water of sixteen slightly soluble organic substances have been determined by means of an analytical method employing an interferometer.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Dissociation Constant of Acetic Acid from 0 to 60° Centigrade[1]

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In a recent communication,[2] we showed that it was possible to determine the dissociation constant of a weak acid with very high accuracy from electromotive force measurements of the cells

$$H_2 \mid HAc\ (m_1),\ NaAc\ (m_2),\ NaCl\ (m_3) \mid AgCl \mid Ag$$

Values of the dissociation constants were determined from 0 to 35° inclusive at 5° intervals. More recently, we have obtained data from which this important constant may be obtained from 0 to 60° at 5° intervals. This determination involves values of the normal potential of the silver-silver chloride electrode through this temperature range. The values of this quantity which we shall employ have been revised slightly by us between 0 and 35° and determined between 35 and 60°.[3]

The method of calculation of K is described fully in our earlier contribution and was adhered to in all its detail. The equation for the electromotive force, E, of the cell is

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{HAc} m_{Cl}}{m_{Ac}} = -\frac{RT}{F} \ln \frac{\gamma_H \gamma_{Cl} \gamma_{HAc}}{\gamma_H \gamma_{Ac}} - \frac{RT}{F} \ln K \qquad (1)$$

E_0 is the normal potential of the cell, K, the dissociation constant, and the "m's" and "γ's" are the molalities and activity coefficients of the species denoted by subscripts. m_{HAc} and m_{Ac} were evaluated as previously described. As before, we let the right side of the equation equal $-RT/F \ln K'$, and then plot this quantity against μ. At zero μ, K' equals K. The extrapolation is easily carried out accurately as indicated by Fig. 1 of the former investigation. The value of K at 35° was redetermined and the

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(1) This contribution contains material which constituted a part of a Thesis presented to the Graduate School by Russell W. Ehlers in partial fulfilment of the requirements of the degree of Doctor of Philosophy, June, 1932.

(2) Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932).

(3) The considerations and new data which have led to the review of the normal elctrode potential, E_0, will be published in another contribution.