

classical dissociation constant. At that time a comparison will be made of the activity coefficients of benzoic acid and those of other acids.

Summary

The hydrogen-ion concentrations of benzoic acid-benzoate buffers saturated with benzoic acid in potassium chloride solutions have been determined by two independent methods.

The results obtained by the catalytic method are in agreement with those determined by the quinhydrone electrode.

In both cases "electrolyte effects" have been considered.

The mean activity coefficients of the ions of benzoic acid have been determined in potassium and sodium chloride solutions.

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THE SOLUBILITIES OF CERTAIN SLIGHTLY SOLUBLE ORGANIC COMPOUNDS IN WATER¹

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As part of a general investigation of solubility in relation to polar character, the solubilities of a number of slightly soluble organic compounds in water have been determined. Since the final interpretation of the data from this standpoint must await the completion of certain supplementary measurements now under way, it seemed advisable to publish the solubility data at this time since no reliable values for the solubilities of these substances are available in the literature.

Experimental

Method.—The saturated solutions of the substances were prepared by shaking in a thermostat and were analyzed by means of an interferometer. The instrument used was a combination liquid and gas interferometer made by Zeiss.

The procedure was a modification of that of Adams² and of Gross.³ The standard or reference solutions were made by dissolving weighed amounts of the substance under investigation in approximately 1000 g. of water. In the case of liquids, a vial containing a weighed amount of the substance was dropped into the weighed sample of water contained in a glass stoppered bottle. During the weighing, the vial was closed with a cork stopper and care was taken that the liquid did not come in contact with the stopper. The stopper of the vial was removed, the vial quickly

¹ Based upon a thesis submitted by John H. Saylor in partial fulfillment of the requirements for the Ph.D. degree at Duke University.

² Adams, *THIS JOURNAL*, **37**, 1181 (1915).

³ Gross, *ibid.*, **51**, 2362 (1929).

dropped into the water and the bottle immediately stoppered. Solids were weighed out on a watch glass and quantitatively transferred to the bottle containing the water. The free space above the solutions was kept small enough to render negligible the error due to vapor losses. In most cases, this space was not more than 10 cc. per 1000 g. of solution. In the case of the less volatile liquids and solids, the vapor space was made somewhat larger in order to shorten the time of shaking necessary for complete solution. The bottles were placed in a shaker and shaken until all of the substance was dissolved. Inspection showed whether all of the drops of a liquid or particles of a solid had disappeared. The method, by which the proper concentrations to use for the standards were chosen, will be described below.

Three standard solutions, A, B and C were used whose concentrations were so chosen that the reading of the weakest against the strongest was not more than two hundred drum divisions. The concentrations of the standard solutions were usually about 0.25 or 0.3 that of the saturated solution. $\Delta C/\Delta R$, the value of a drum division in grams per 1000 g. of solution, was calculated from the difference between the concentrations of A and B and from the interferometer reading of A against B. $\Delta C/\Delta R$ obtained in the same fashion from A and C served as a check on the value obtained. In some cases B was also read against C. This gave not only an additional check on the value of $\Delta C/\Delta R$ but also checked the accuracy with which the solutions were prepared. An average value of $\Delta C/\Delta R$ was then used in the solubility measurements. Dry pipets were used for sampling the solutions. The interferometer chamber was dried after every determination by a stream of warm air.

The concentration difference between A and C was so chosen as to give a reading of not more than two hundred scale divisions, because for larger differences the drum reading is not a linear function of the concentration except in special cases.⁴ In the present work the linearity of drum reading against concentration over the range of two hundred divisions was checked directly by plotting the readings of A against B and A against C against the corresponding concentrations. Within the limits of accuracy necessary, a straight line was obtained in all cases. Concordant values of $\Delta C/\Delta R$ also gave a direct test of the linear relationship.

The saturated solutions of a substance under investigation were prepared by shaking an excess of the liquid or solid with about 500 g. of water in thin-walled cylindrical flasks in a large water thermostat. The thermostat was regulated at $30 \pm 0.01^\circ$ and at $15 \pm 0.02^\circ$. In all cases the flasks were shaken for at least twelve hours, and in most instances they were shaken for a longer period of time. Samples were then withdrawn from two or three different saturation flasks and read against water in the interferom-

⁴ Adams, *THIS JOURNAL*, 37, 1181 (1915); Gans and Bose, *Z. Instrumentenk.*, 36, 137 (1916).

eter. Equilibrium was usually reached in less than twelve hours, as shown by the constancy of the readings of the saturated solutions at different time intervals. It was possible in most cases to reproduce the readings of the saturated solutions within two or three scale divisions of the interferometer drum. The values of $\Delta C/\Delta R$ were of the same order of magnitude for all aliphatic compounds. Also the values of $\Delta C/\Delta R$ were of the same order of magnitude for all aromatic compounds.

The value of $\Delta C/\Delta R$ in the case of a given aromatic compound could be employed to calculate approximately the amounts of substances necessary to make up the standard solutions of all other aromatic compounds. Likewise, the value of $\Delta C/\Delta R$ in the case of a given aliphatic compound could be used to calculate the amounts of substances needed to make up the standard solutions of all aliphatic compounds. The only other quantities needed were the readings of the saturated solutions of the substances in question. These readings when multiplied by $\Delta C/\Delta R$ would give the approximate concentrations of the saturated solutions. Then the amounts of substances which would give standard solutions of the desired concentrations could be calculated.

From the reading of the saturated solution and the average value of $\Delta C/\Delta R$, it was possible to calculate the extent to which the saturated solution would have to be diluted in order to give a reading of less than two hundred divisions when read against one of the standard solutions as a reference. Usually this difference was made about one hundred rather than two hundred divisions. The weight of water necessary for the dilution was put in a 500-cc. glass-stoppered volumetric flask. A two-holed rubber stopper carrying a glass siphon fitted with a stopcock was then placed in the saturating flask in the thermostat. The siphon was started by gently blowing into the flask. Enough of the saturated solution was allowed to siphon over and discarded to insure thorough rinsing of the siphon. Then a sample large enough to fill the volumetric flask to the mark was run into it. The sample was run in beneath the surface of the water in the volumetric flask in order to prevent loss by evaporation. The volumetric flask was immediately stoppered and weighed, thus giving the weight of the saturated solution added. The dilution of the saturated solution could then be calculated. A sample of this diluted solution was read in the interferometer against a sample of the standard solution. The standard solution chosen was usually the one whose concentration was between the standard with the lowest and the standard with the highest concentration, as the bottle containing this intermediate standard had had fewer samples removed from it. The concentration of the saturated solution was calculated from the reading of the dilution against the standard, the concentration of the standard, the value of $\Delta C/\Delta R$ and the dilution of the saturated solution.

In the case of some substances whose saturated solutions did not give a reading of over five or six hundred scale divisions against water, the values of $\Delta C/\Delta R$ were obtained by reading the standards directly against water. The saturated solutions were then diluted so as to give a reading of less than two hundred when read against water.

In all cases, duplicate determinations were run on samples from at least two different saturated solutions of the same substance. The 80-mm. chamber of the interferometer was used throughout except for the saturated solutions of some of the more soluble substances. In those cases, the 40-mm. chamber was employed.

The method used has several advantages. As mentioned above, it is not necessary to correct for the non-linearity of drum reading as a function of concentration since no reading exceeds two hundred divisions. Also, errors in dilution, reading of the interferometer, etc., will have a small effect on the precision of the final result since the reading is a difference measurement between the dilution and the reference solution. The reference solution can be prepared with a high degree of precision.

The method as used has the further advantage that it affords a check on the purity of the organic substances. Since varying amounts of the same substance were used in preparing different saturated solutions of the substance, if any soluble impurities were present, the interferometer readings for these saturated solutions would not agree with each other.

Materials

The chloroform, carbon tetrachloride and toluene were Baker's c. p. analyzed grade. All of the other organic substances were Eastman Kodak Co. best grade. The substances were purified by fractional distillation unless otherwise stated. For this purpose, two all-glass stills of the type described by Gross and Wright⁵ were so designed that the thermometers were totally immersed in the vapor, eliminating exposed thread corrections. The large still had a capacity of one liter and had a fractionating column a meter long. The small still had a capacity of 250 cc. and had a column 0.5 meter long. Pressures were read on an accurate barometer. Temperatures below 105° were read on thermometers calibrated by the Bureau of Standards. For higher temperatures, a set of Anschütz thermometers of good quality were used. Boiling points were corrected to 760 mm. by means of Craft's rule when dT/dP was not given in the literature. Unless otherwise stated, melting points were taken in open tubes on 5- or 10-g. samples.

Chloroform.—Two kilos were shaken for one hour with sodium hydroxide solution, washed twice with distilled water, shaken three times with concd. sulfuric acid, twice with distilled water, once with mercury and finally washed with distilled water and dried over calcium chloride as recommended by Harris.⁶ The dried product was fractionated in the large still. A fraction of about 700 g. which boiled from 61.07–61.09° was used. Timmermans⁷ gives a boiling point of 61.09–61.21°.

Carbon Tetrachloride.—This was purified according to the method of Williams and

⁵ Gross and Wright, *J. Ind. Eng. Chem.*, **13**, 701 (1921).

⁶ Harris, *J. Chem. Soc.*, **127**, 1063 (1925).

⁷ Timmermans, *Bull. soc. chim. Belg.*, **24**, 244–269 (1910).

Krchma.⁸ One kilo was refluxed for eight hours over mercury, shaken twice with concd. sulfuric acid, shaken with dilute sodium hydroxide, washed with distilled water and dried over calcium chloride. It was then fractionated in the large still. A fraction of about 800 g. boiling at $76.74 \pm 0.02^\circ$ was used. Timmermans⁷ gives a boiling point of $76.74\text{--}76.76^\circ$.

Benzene.—This material was a sample of benzene purified for another purpose according to the method of Richards and Shipley.⁹ Baker's c. p. crystallizable benzene was shaken successively with sulfuric acid, water, sodium hydroxide solution, water and mercury; dried over calcium chloride and then over sodium, distilled through a long all-glass column and a fraction of about one liter boiling between $80.05\text{--}80.07^\circ$ collected. This was then recrystallized three times by freezing, resulting in a sample of about 700 cc. with m. p. 5.40° . This was dried over sodium in a glass-stoppered distilling flask for two years and was distilled directly from this flask into carefully dried bottles whose necks were sealed off after distilling the benzene into them.

Toluene.—The material was purified according to the method of Beal and Souther.¹⁰ A fraction of 600 g. all of which came over at $110.74 \pm 0.02^\circ$ was used. Timmermans¹¹ gives a boiling point of 110.7° . "International Critical Tables" gives a boiling point of 110.5° .

Monochlorobenzene.—A fraction of approximately 700 g. all of which came over at $131.83 \pm 0.02^\circ$ was used. Timmermans⁷ gives a boiling point of $131.99\text{--}132.01^\circ$.

Monobromobenzene.—A fraction of 700 g. boiling from 155.88 to 155.93° was used. Timmermans⁷ gives a boiling point of $156.14\text{--}156.16^\circ$.

Nitrobenzene.—A sample containing 700 g. of this material was distilled under reduced pressure using cork stoppers as recommended by Roberts and Bury.¹² The first and last portions were discarded. The distillate was fractionally frozen twice. A fraction of 400 g. melting at 5.7° was used. "International Critical Tables" gives a melting point of 5.7° .

Ethylene Bromide.—Two different samples were purified. The first sample, containing 250 g., was fractionally frozen five times according to the method of Biron.¹³ A fraction of 125 g. melting at 9.7° was used. The second sample had a slightly yellow color before it was purified. Four hundred grams of it was fractionated. A sample containing 250 g. boiling from $131.19\text{--}131.29^\circ$ was used. "International Critical Tables" gives a boiling point of 131.7° . This fraction melted at 9.7° . Biron¹³ gives a melting point of 10.012° .

Methylene Bromide.—Two samples were used. The first containing 100 g. was fractionated through a Hempel column. Nearly all distilled over at 97.2° . The second sample containing 300 g. was distilled in the small glass still. A fraction of 200 g. boiling from 97.13 to 97.23° was used. "International Critical Tables" gives a boiling point of 97.8° . Timmermans¹⁴ gives a boiling point of 96.5° .

Normal Butyl Bromide.—Two hundred grams of this material was fractionated three times through a Hempel column. A fraction containing about 75 g. boiling from 101.52 to 101.72° was used. "International Critical Tables" gives a boiling point of 101.6° .

***p*-Dichlorobenzene.**—A sample melting at 52.7° was recrystallized twice from ethyl

⁸ Williams and Krchma, *THIS JOURNAL*, **48**, 1888 (1926).

⁹ Richards and Shipley, *ibid.*, **36**, 1828 (1914).

¹⁰ Beal and Souther, *ibid.*, **49**, 1994 (1927).

¹¹ Timmermans, *Bull. soc. chim. Belg.*, **25**, 300–27 (1911).

¹² Roberts and Bury, *J. Chem. Soc.*, **123**, 2038 (1923).

¹³ Biron, *Z. physik. Chem.*, **81**, 590 (1913).

¹⁴ Timmermans, *Bull. soc. chim. Belg.*, **28**, 392 (1919).

alcohol. The product melted at 52.84°. "International Critical Tables" gives a melting point of 52.9°.

Bromoform.—A sample containing 500 g. was partially frozen once as recommended by Cauwood and Turner.¹⁵ A fraction of about 350 g. melting at 7.7° was used. "International Critical Tables" gives a melting point of 7.7°.

Ethylene Chloride.—This was a portion of material previously purified.³

Ethyl Iodide.—The fraction used, which contained 125 g., boiled at 72.42°. Timmermans¹⁶ gives a boiling point of 72.30°.

Normal Propyl Bromide.—A fraction of about 300 g. boiling from 70.97–71.08° was used. Timmermans¹⁷ gives a boiling point of 71.0°.

Methylene Iodide.—A sample containing 300 g. of this material was shaken with sodium thiosulfate solution in order to decolorize it. It was then washed with distilled water, dried over potassium carbonate and fractionally frozen twice. A fraction of about 200 g. melting at 5.85° was used. "International Critical Tables" gives melting points of 5.2 and 5.7°.

Normal Propyl Iodide.—The sample of 200 g. was highly colored with iodine. It was decolorized by shaking with sodium thiosulfate solution. It was then washed twice with distilled water and dried for ten days over aluminum oxide. The dried substance was fractionated. A fraction of 100 g. boiling from 102.28 to 102.58° was used. Timmermans¹¹ gives a boiling point of 102.4°.

Carbon Tetrabromide.—This material was recrystallized once from ethyl alcohol and once from petroleum ether. It was found impossible to obtain a sharp melting point. Melting point determinations were carried out in an open tube using a 10-g. sample; in a capillary tube and in a sealed bulb. "International Critical Tables" gives a melting point of 91.1°. However, according to Biltz and Meinecke,¹⁸ it is impossible to obtain a sharp melting point in an open tube due to partial decomposition of the carbon tetrabromide. In a capillary tube, the above authors found that the melting point was 92.5°. Our experience in the present work indicates a slight decomposition at the melting point.

m-Dinitrobenzene.—This material was recrystallized three times from ethyl alcohol. The product used melted at 89.5°. "International Critical Tables" gives a melting point of 89.7°.

p-Nitroaniline.—This was recrystallized successively from ethyl alcohol, methyl alcohol, a mixture of ethyl and methyl alcohols, ethyl alcohol and finally from water. It was found to be impossible to obtain a sharp melting point. Melting points were taken in an open tube, a capillary tube and in a sealed bulb. In the capillary tube, all of the solid had disappeared at 147° but the sample did not melt sharply. The indications point to decomposition at the melting point. "International Critical Tables" gives 148° for the melting point. The value quoted in Beilstein and found in most of the literature is 147°.

Water.—Distilled water of good quality was obtained from the laboratory supply.

Results

The following substances were also purified with the intention of measuring their solubility: methyl iodide, trichloroethylene, ethylidene bromide, benzyl benzoate, isopropyl bromide, nitromethane and ethyl bromide. However, all of these substances were found to hydrolyze. The following

¹⁵ Cauwood and Turner, *J. Chem. Soc.*, 107, 280 (1915).

¹⁶ Timmermans, *J. chim. phys.*, 25, 418 (1928).

¹⁷ Timmermans, *ibid.*, 23, 776 (1926).

¹⁸ Biltz and Meinecke, *Z. anorg. allgem. Chem.*, 131, 14 (1923).

materials were available as Eastman Kodak Co. best grade: isopropyl iodide, tetrachloroethane, and tetrachloroethylene. These were found to hydrolyze. They were not further purified as from their nature and from the extent of hydrolysis it seemed likely that the existence of this hydrolysis was attributable not to impurities but to the substances themselves.

Hydrolysis was readily detected by the fact that constant interferometer readings of the saturated solutions could not be obtained, the readings continuing to increase over a period of time. Hydrolysis was confirmed in the case of the halogen compounds by appropriate tests for acid and halogen in the aqueous solutions. Nitromethane solutions showed increasing interferometer readings over a period of time. This was probably due to the formation of the pseudo acid as postulated by Hantzsch.¹⁹

TABLE I
SOLUBILITIES IN WATER AT 30°

Substance	G./1000 g. water	Moles/1000 g. water	% Estimated error
Ethylene chloride	9.00	0.0909	0.3
Methylene bromide	11.93	.0686	0.5
Chloroform	7.71	.0646	1.0
Ethyl iodide	4.04	.0259	0.5
Benzene	1.85	.0237	1.0
Ethylene bromide	4.31	.0229	0.5
<i>n</i> -Propyl bromide	2.31	.0188	1.0
Nitrobenzene	2.05	.0167	0.5
Bromoform	3.19	.0126	1.0
Toluene	0.57	.0062	2.0
<i>n</i> -Propyl iodide	1.04	.00613	3.0
Carbon tetrachloride	0.81	.0053	2.0
<i>p</i> -Nitroaniline	0.728	.00527	1.0
Methylene iodide	1.24	.00463	2.0
<i>n</i> -Butyl bromide	0.608	.00444	1.5
Monochlorobenzene	.488	.00433	1.0
<i>m</i> -Dinitrobenzene	.654	.00389	2.0
Monobromobenzene	.446	.00284	2.0
Carbon tetrabromide	.24	.00072	8.0
<i>p</i> -Dichlorobenzene	.077	.00052	5.0

TABLE II
SOLUBILITIES IN WATER AT 15°

Substance	G./1000 g. water	Moles/1000 g. water	% Estimated error
Ethylene chloride	8.72	0.0882	0.5
Chloroform	8.52	.0713	1.0
Methylene bromide	11.70	.0673	0.5
Ethylene bromide	3.92	.0209	1.0
Nitrobenzene	1.78	.0145	1.0
Bromoform	3.01	.0119	1.5
Carbon tetrachloride	0.77	.0051	2.5

¹⁹ Hantzsch and Schultze. *Ber.*, 29, 699, 2251 (1896).

The solubilities of all the substances measured and the estimated errors of all determinations are given in Tables I and II. The error was estimated from values of duplicate determinations.

Rex²⁰ gives values for the solubilities of several of the substances measured in this investigation. Most of his values are higher than those obtained in the present work. As previously suggested by one of us,³ this may be due to the possible loss of liquid in Rex's measurements. Also several of the compounds which he measured have been shown to hydrolyze in the present work, thus making the validity of his results doubtful in these cases. However, hydrolysis may not have introduced a significant error in his work if the determinations were completed in a sufficiently short interval of time.

Discussion

Attention may be drawn to a number of points of interest in connection with these data. The magnitude of some of the solubility values is surprisingly large for substances such as chloroform and ethylene chloride which are commonly thought of as "insoluble" in water. In view of this it would seem that water should at least be thought of when considering solvent media in which to carry out reactions involving such substances.

The existence of appreciable hydrolysis in the cases of a number of the compounds mentioned above, whose solubility we wished to determine, is of interest in connection with the statements found in the standard organic references that such hydrolysis does not occur. This indicates that the criteria commonly used to detect such hydrolysis are inadequate.

Lastly, this method of analysis or some modification of it would seem to have considerable promise as a method for studying reaction rates. We plan to investigate some of these hydrolyses from this point of view.

Summary

1. A modification of the existing methods for using the interferometer in the determination of the solubility of difficultly soluble liquids and solids in water and aqueous solutions is described.
2. The solubilities of a number of organic compounds in water at 30 and 15° are given.

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²⁰ Rex, *Z. physik. Chem.*, **55**, 355 (1906).