Solubility of Benzene in Water

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For the determination of individual mass transfer coefficients for the benzene-water system, the mutual solubility of the components is required. This paper deals with the solubility of benzene in water. The interpretation by Seidell (*23*) of the then-available portion of the present (*1, 3-5, 7-19, 21-23, 25, 26*) data on the solubility of benzene in water indicated a relationship that continually increased with temperature in a manner similar to his other interpretations on the solubility of hydrocarbons in water. The more recent data of Bohon and Claussen (*4*) were the first to indicate a minimum in the solubility curve for benzene (and other aromatic compounds), although Hill (*13*) suspected one. Taken as a whole, the available data might have been considered discordant. As a precise analytical technique for the analysis of benzene in water was needed for mass transfer studies, it was decided to demonstrate and prove the technique by a redetermination of the solubility relationship.

Ultraviolet spectrophotometry was selected as the analytical tool. Study and experience indicated that the analytical technique had to be developed with great care to avoid errors due to excessive volatility, such as found by Saylor, Stuckey, and Gross (*22*), to improper calibration, to temperature-induced hazes, and perhaps to wall adsorption effects.

EXPERIMENTAL

Equipment. The spectrophotometer was a Beckman Model DU unit equipped with a hydrogen lamp for use in the ultraviolet region. The wave length scale was calibrated with a standard mercury-vapor lamp. The instrument was operated with a slit width of 1.20 mm., and set for the ultraviolet wave length of 254 mμ. The sample containers were 1.00-cm. silica absorption cells. Reference and test cells matched in transmittance with distilled water were selected.

Materials. The benzene used was one of the best commercial grades obtainable, supplied by the Barrett Division of Allied Chemical and Dye Corp. under the designation of thiophene-free, 1° benzene. It was water washed and distilled, and at that stage was in the condition for which the solubility data were desired. For a few results, this benzene was purified by three, slow, successive crystallizations, discarding about 30% of the material each time.

The water used was distilled water prepared from a Barnstead still, collected in a tin-coated receiver, and in part stored in a stainless steel drum. Several measurements of electrical conductivity confirmed its high quality.

Standard Solutions. Calibration data were obtained from standard benzene-in-water solutions. The preparation of these standard (benzene-in-water) solutions turned out to be a difficult problem because of the small percentages of benzene, the slow rate of solution, the problem of dissolved air, and the care necessary in handling the resulting highly volatile solutions. A procedure was devised to minimize these problems in the preparation of the standards, and was perfected in many details until the precision of measurement was about 1% for a single averaged value.

This procedure consisted essentially in adding a known amount of benzene to a known volume of vacuum-deaerated, distilled water in an inverted carboy in such a manner as to avoid entrapment of air (*2*). The carboy was allowed to stand at room temperature (with a mercury expansion seal to allow for room-temperature changes) for several months until all of the benzene was dissolved and uniformly mixed. The daily temperature fluctuations caused a slow mixing. Then, the carboy was righted and sampled from near the bottom, as for the saturated sample. All samples from a given standard solution had to be taken within an hour to avoid measurable evaporation losses to the air admitted over the solution during sampling, even though samples were taken from near the bottom. The calibration data were obtained from two standard solutions, and are shown in Figure 1.

Preparation of Saturated Solutions. The saturated solutions were prepared in a three-necked, 3-liter, round-bottom borosilicate glass flask submerged in a constant temperature bath controlled to within ±0.05°C. At higher temperatures, the bath water was covered with mineral oil to reduce evaporation losses. Inside the flask were 3 to 5 inches of distilled water plus 0.5 to 1 inch of benzene. The temperature of the equilibrium flask was measured with a calibrated, mercury-in-glass thermometer graduated at 0.1°C. intervals. The bath temperature was recorded continuously on a Brown recorder. When the desired saturation temperature was below the room temperature, the entire apparatus and the spectrophotometer were assembled and operated in a refrigerated room.

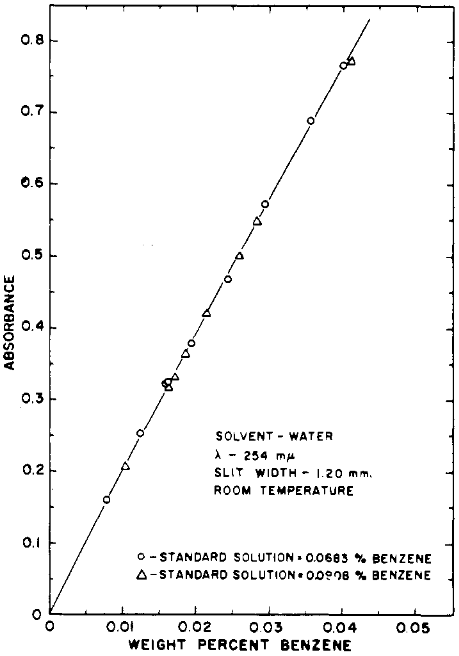

Figure 1. Calibration curve for benzene-in-water solutions

In the preparation of a given saturated solution, the temperature was selected and the stirrer was set to operate in the water phase at a very slow speed to avoid dispersing any benzene droplets in the aqueous phase. The equipment was left operating for several days as experience indicated. The continuous temperature recorder warned when any upset occurred. Then the stirrer was turned off and the flask was left quiescent for several hours before a sample was taken and analyzed. Only when samples on

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successive days indicated no change in benzene concentration was the solution considered saturated.

Sampling Technique. The sampling technique was critical, requiring speed and meticulous attention to details. The problems were to sample a known quantity, dilute that sample quantitatively to a concentration more suitable for analysis, then to transfer the diluted sample into the spectrophotometer cuvette and analyze, without incurring noticeable evaporation losses along the way. The technique was continually improved until reproducible results were obtained by each worker and by different workers.

For the saturated solutions, the sample line reached into about the center of the aqueous phase. The sampling lines were relatively small, of about 2.5-mm. bore (4 mm. in outside diameter) borosilicate glass tubing and extended out of the containers in such a manner as to provide a straight and vertical length about 8 inches long at the discharge end. This straight section was so positioned that the dilution test tube could be brought up to it rapidly and freely from below.

To sample, a slight air pressure was placed on the solution container, causing solution to flow out the sample line. The first portions, for 5 to 10 seconds, were used to flush the line, and condition its walls to some extent with the solution. This flow was discarded. Without stopping the flow, the dilution tube containing water was brought into position in a fraction of a second, so that the sample tube discharged aqueous benzene solution underneath the water surface of the dilution tube, near the bottom. The flow was continued until the total volume reached a mark near the top of the sample tube leaving the proper space for the stopper. The timing for this transfer required a little practice. The amount of added sample was usually 8 to 10 grams. At the proper time, the dilution tube was removed in a fraction of a second by a quick downward and outward motion, the sample line still flowing. Immediately, the stopper was inserted.

With practice, this operation was carried out swiftly and smoothly. However, each time the dilution tube was taken away, a small amount of liquid adhered to the outside of the sample line. Through auxiliary trials, the weight of this amount was found to be 0.1 to 0.2 gram usually, averaging 0.14 gram. A small correction was made for this loss, assuming it to be pure water. The correction was about 1% of the sample weight.

Dilution Technique. Dilution was necessary to avoid measurable evaporation losses and also to have the concentration in an appropriate range for spectrophotometric analysis. Dilution was accomplished in a 29 x 200-mm. test tube containing three glass marbles for mixing. Distilled water, amounting to about 70 grams, was placed in the test tube and weighed to the nearest 0.1 gram. Then the sample was introduced far underneath the surface by the technique described. Quickly, a cork stopper covered with thin Teflon film, paired with a hypodermic needle, was inserted in such a way as to remove all of the air from the tube with a minimum of disturbance of the liquid in the tube. Then the hypodermic needle was withdrawn, the dilution tube was reweighed to the nearest 0.1 gram, and the dilution was calculated. The object was to have the final absorbance in the range of 0.2 to 0.6, where the precision was adequate. Bohon and Claussen (*4*), with this identical problem, attempted for each analysis to adjust the concentration to give an absorbance of 0.40.

The contents of the dilution tube were then mixed by gently inverting the tube a number of times, allowing the marbles to run from end to end. A small air bubble and a small amount of mercury had been tried previously, but neither was satisfactory. The air bubble resulted in a loss of benzene, while the mercury did not provide adequate mixing.

Table I. Averaged Solubility Data for Benzene in Water

Temp., °C.	Average Wt. % Benzene[a]	Number in Average	Standard Deviation
Solid, Gaseous Benzene Plus Water and Air			
0.4	0.168	8	0.0040
3.0	0.170	8	0.0028
3.9	0.176	5	0.0021
4.5	0.172	14	0.0024
Solid, Liquid, Gaseous Benzene Plus Water and Air			
4.9	0.177	14	0.0034
Liquid, Gaseous Benzene Plus Water and Air			
5.0	0.174	11	0.0024
6.7	0.174	10	0.0019
9.0	0.173	15	0.0031
12.5	0.172	4	0.0002
15.0	0.173	11	0.0026
20.0	0.171	9	0.0021
20.6	0.172	10	0.0020
24.8	0.171	10	0.0034
24.9	0.174	10	0.0024
27.3	0.174	9	0.0023
30.0	0.177	11	0.0019
35.0	0.182	24	0.0023
39.9	0.188	7	0.0015
45.0	0.197	5	0.0002
49.8	0.204	5	0.0022
54.5	0.215	13	0.0040
59.8	0.226	10	0.0027
64.8	0.241	10	0.0051
69.0	0.260	10	0.0021
30.0	0.176[b]	7	0.0023
45.0	0.196[b]	5	0.0018

[a] Grams of benzene per 100 grams of solution.
[b] This benzene was thrice-crystallized. For the other benzene, see text.

Analytical Technique. The analysis was performed shortly after dilution. The transfer from dilution tube to cuvette was accomplished as follows: A hypodermic needle was inserted alongside the Teflon covering of the stopper, and the stopper was slowly pulled out of the tube. Without the use of the hollow needle, a flashing of benzene was found to occur on removal of the stopper. Even so, presumably the top layers of the benzene solution start to lose benzene by evaporation. Quickly an "automatic" pipet (Schaar Co. No. AR1770, 5-ml.) with the glass tip drawn out, was inserted into the bottom of the dilution tube, and a sample was drawn gently from the bottom. The minimum amount of air was allowed in the pipet, and this was kept saturated with benzene-water vapor. When this step was too rapid, benzene was lost from solution as a result of the vacuum created. Two absorption cells were each rinsed twice with the solution from the automatic pipet, then filled and capped; each cell was filled from a separate portion of the diluted sample. The drawn-out tip was placed at the bottom of each cell for the filling. The pipet held considerably more sample than was required to fill the cell. This technique plus the conditioning of the pipet by two preliminary flushes minimized the evaporation errors in this step. The absorbance of the sample was read with the spectrophotometer, using a matched reference cell filled with distilled water. Auxiliary experiments demonstrated that evaporation losses did occur from the capped cells, but that the analyses could readily be carried out before the losses were significant.

OBSERVATIONS AND RESULTS

Accuracy. With solutions as selectively volatile as indicated by Saylor, Stuckey, and Gross (*22*) for benzene-in-water solutions, any technique that exposes the solutions to air, however briefly, must be somewhat suspect. Unfortunately, the use of the Model DU Beckman spectrophotometer precluded an entirely closed system. As the calibration and the analyses were carried out by the same technique, any systematic evaporation errors would tend to be self-compensating. Analytical results were initially erratic. It required a number of months and many auxiliary experiments to locate and correct sensitive points of technique. However, in the end each worker readily obtained results agreeing within about 1%, and different workers, with their individual variations in technique, also agreed within the same limit.

Calibration. The calibration data were obtained at room temperature using various dilutions from two standard benzene-in-water solutions. A plot of the calibration results is presented in Figure 1, showing clearly a slight curvature. By the method of least squares, the best-fitting second degree equation passing through the origin was:

$$A = 20.3820W - 32.8650W^2$$

where A = absorbance and W = weight % benzene in solution.

A statistical analysis indicated the standard deviation to be 0.0044; the probable error, 0.0030 unit of absorbance. For a given absorbance in the range of a typical diluted solution, about 0.015 weight % benzene, the probable error in benzene concentration was about 0.00015 weight % or 1% of the total.

In view of the extreme volatility of the solutions of benzene in water, the slight curvature of the calibration curve might be due to progressive losses of benzene.

The absorbancy index calculated from the calibration curve (slit width = 1.20 mm.) is 1.974 l./(g.)(cm.) at an absorbance of 0.40, and 1.906 at 0.763. Bohon and Claussen (*4*) measured the absorbance of benzene in 95% ethyl alcohol, with a slit width of 1.00 mm., and obtained an absorbancy index of 1.90 l./(g.)(cm.). They used this value for determination of benzene in water, at absorbances closely adjusted to 0.400, on the basis that in the region of 250 mμ the solvent used makes very little difference.

Variation of Absorbance with Temperature. The effect of temperature upon the absorbance was studied by making calibration runs at various temperatures. For these tests the entire equipment, solutions, spectrophotometer, and auxiliaries were placed in a controlled-temperature refrigerated room. Absorbance readings were taken over the range of 3° to 25 °C. on dilutions of one given homogeneous solution. Within the same limits of reproducibility as evidenced in Figure 1, no differences could be distinguished.

Solubility Data. The experimental solubility data are given in Table I and in Figure 2. Each value is an average of a number of individual determinations. The temperature variation was obtained by carrying out all operations that involved data below 25 °C. in a controlled-temperature refrigerated room. Most of the runs were carried out on benzene as previously described, but two runs were made on benzene that had been purified by three crystallizations.

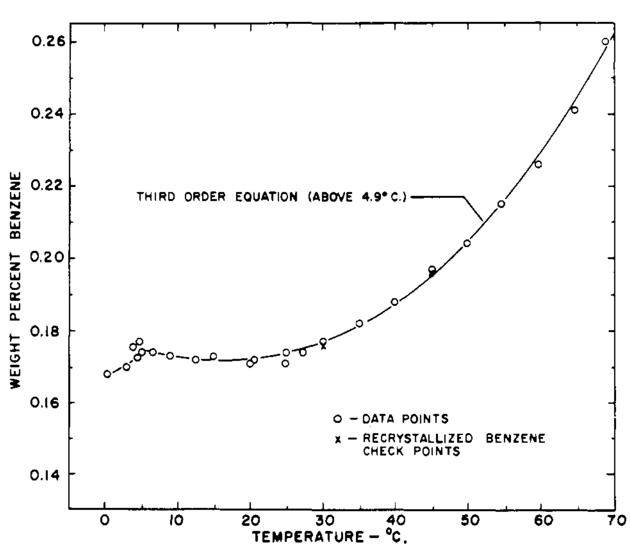

Figure 2. Benzene-in-water solubility results

The quadruple point for the benzene used was observed to be 4.9 °C., a value repeatedly obtained by approach from both temperature directions and once reached, was maintained for periods of days. The true quadruple point for benzene appears to be 5.40°, as found by Richards, Carver, and Schumb (*21*) in a careful study, and also by Hill (*13*). Groschuff (*7*) and Bohon and Claussen (*4*), while studying solubility, found their benzenes still to be liquid at 3.0° and 5.2 °C., respectively.

Over the range of 0.4° to 4.5 °C., there was definitely no liquid benzene present. In this region, equilibrium with the crystallized benzene was difficult to obtain, for, even with days allowed, the readings were more erratic than when liquid benzene was present.

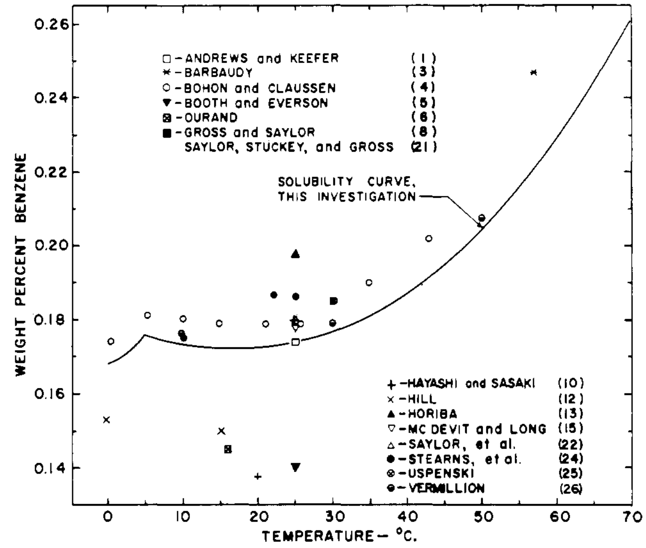

Figure 3. Comparison of solubility results with literature data

The agreement of the data on the purified benzene with the other data appears to indicate that the data in general applies to pure benzene. Mass transfer experiments, using this system, carried out over the past 4 years have consistently indicated the reliability of these data.

In Figure 3 is a comparison with reported experimental values that fell within the region indicated. Recently Brady and Huff (*6*) determined the solubility to be 1.76 ± 0.03 grams of benzene per liter at 25 °C. The results of Bohon and Claussen (*4*) were consistently about 4% higher than the results reported here. In a similar measurement of the solubility of naphthalene and biphenyl, Bohon and Claussen (*4*) were also about 5% higher than Paul (*20*). Except for a point at 75 °C., which is above the solution boiling point, the data of Vermillion (*27*) average less than 1.5% higher than authors', an excellent agreement.

STATISTICAL TREATMENT

Excluding the results using recrystallized benzene, and those below 4.9 °C., the averaged values were treated by the method of least squares to derive the following two equations, using S to denote the benzene solubility in weight per cent, and T for Centigrade degrees.

$$S = 0.1806 - 0.001095\,T + 0.00003179\,T^2$$

$$S = 0.1784 - 0.0007436\,T + 0.00001906\,T^2 + 0.0000001217\,T^3$$

The two equations agree within 0.001 weight % over practically the entire experimental range of temperature. However, the third order equation gave a better (statistically significant) fit of the data. It was probable that the use of still higher terms also would have permitted a significantly better fit of the data.

The reproducibility of the analyses was such that the standard deviation of an average was 0.0028 weight % unit, the probable (50% confidence) error of a single value was 0.0019 weight % unit. For 95% confidence, the value was 0.0055 weight % unit. Based upon a solubility of 0.173 weight %, the value applicable from about 10° to 25°C., these figures represent, respectively, 1.1 and 3.2% for 50 and 95% confidence.

From the third-order equation, the minimum solubility is 0.172 weight % benzene at 16.80°C. From 10° to 25°C. the solubility is constant within 0.173 ± 0.001 weight %, or within ±0.6% of the average value.

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Distribution Coefficients of Fatty Acids between Water and Methyl Isobutyl Ketone

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It is often desirable to predict the distribution coefficient of organic compounds in a given immiscible water-organic solvent system. To do this it is helpful to know how members of a homologous series react in such a system. With such data it may be possible to develop generalized correlations to help predict these phenomena. Previous studies (*1–4*) have been made with formic and acetic acids in the water-methyl isobutyl ketone solvent system at 25.0°C. and some experimental distribution coefficient data have been obtained.

In this work additional experimental distribution data were obtained in the very dilute region for the above two acids in the same solvents and data were also obtained for the higher members—propionic, *n*-butyric, *n*-valeric, and *n*-caproic—of the fatty acid series. Data were obtained primarily in the dilute region to allow the distribution coefficient, *K*, at infinite dilution to be determined.

EXPERIMENTAL

The equilibrium determinations were performed in glass-stoppered flasks totally immersed in a constant temperature bath and agitated by magnetic stirrers. The flasks were sealed on the outside by rubber stalls. After agitation and settling, a sample of each phase was removed with a pipet and analyzed for acid content by titration with standard sodium hydroxide solution using phenolphthalein as an indicator. In the ketone phase, alcohol was added before titration to make the phases miscible. Each acid was equilibrated separately in the flask. The data are given in Table I. The source and purity of the acids used are: formic, reagent grade, > 99.6% purity, Baker's; acetic, reagent grade, > 99.7% purity, Eastman; propionic, boiling point 140-2°C., Eastman; *n*-butyric, boiling point 161-3°C., Matheson; *n*-valeric, boiling point 184-7°C., Eastman; *n*-caproic, boiling point 203-5°C., Matheson.

RESULTS AND DISCUSSION

To determine the distribution coefficient at infinite dilution for formic acid, the concentration in the water phase was plotted against the equilibrium concentration in the ketone phase, and a smooth curve was drawn through the data. Then the slope or *K* value was determined at the origin. As a check, the experimental *K* values were plotted against the concentration in the ketone phase and the extrapolated value at zero concentration was determined. This was done for each acid (Table I). The plots showed that the *K* val-

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