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Solubility Measurements of Benzene and the Alkylbenzenes in Water by Making Use of Solute Vapor

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Aqueous solubilities of benzene and of alkylbenzenes, toluene, ethylbenzene, propyl- and isopropylbenzene, (*o*-, *m*-, and *p*-) xylene, and (1,2,3-, 1,2,4-, and 1,3,5-) trimethylbenzene, have been measured. An apparatus is described which provides a convenient means of obtaining aqueous solutions saturated with solute vapor. The method involves introducing solute vapor, which is in equilibrium with a liquid solute, into water and circulating it in a closed system. This method has three principal advantages: (1) The solubility equilibrium can be attained within 3 min, (2) it can be determined whether the solubility obeys Henry's law, and (3) based on Henry's law, solutions of any desired concentrations of solute at a given temperature of water can be easily prepared.

The solubilities of slightly soluble organic compounds in water have been studied by many reseachers. The solubility measurement generally consists of two steps; the first is a preparation of aqueous solution saturated with solute and the second is a measurement of solute concentration in the solution. The latter step has been markedly improved in sensitivity and selectivity by advances in instruments such as spectrophotometer and gas-liquid chromatography, whereas the former step seems to have remained unchanged for a long time. The former step is still the more important, since it often influences the precission and accuracy of the results. At the present time, it is true to say that the reproducibility of the solubility data mainly depends on this step.

Most of the earlier investigators prepared the saturated solutions by adding an excess quantity of a solute to a water and shaking the mixture mechanically for at least 24 h. The solutions thus prepared were usually allowed to stand for at least another 24 h or centrifuged to ensure removal of any organic droplets entrained in suspension, and then the solute concentrations were determined. Particular attention should be paid to the possible inclusion of a suspended micro-emulsion which may arise when liquid solute has been dispersed by vigorous shaking, and also to the extreme volatility and the strong adsorption on the container walls which are both characteristic of organic solutes in water. Instead of this conventional method, some attempts have recently been made to attain the solubility equilibrium. Sutton and Calder estimated solubilities of alkylbenzenes by equilibrating water with solute vapor in a closed vessel where water and liquid solute were separately placed.[1] Brown and Wasik used an apparatus which made it possible to measure the equilibrium distribution of a hydrocarbon between a gas phase and a liquid phase.[2] Mackay *et al.* estimated Henry's law constants for some liquid and solid hydrocarbons by measuring solute concentrations in aqueous solution while being stripped from solution at a known gas flow rate.[3]

This paper will describe a simple and useful technique that allows a rapid preparation of aqueous solutions of desired solute concentrations at a given temperature of water by making use of solute vapor.

Experimental

Materials. Materials used as solute were analytical reagent grade (Wako Pure Chemical Industries Ltd.) except 1,2,3- and 1,2,4-trimethylbenzene. The stated minimum purities (mass %) were: benzene; 99.5, toluene; 99.0, ethylbenzene, (*o*-, *m*-, and *p*-)xylene, and isopropylbenzene; 98.0, 1,3,5-trimethylbenzene; 97.0, 1,2,4-trimethylbenzene; 95.0, propylbenzene; no description. All these solutes were used without further purification. Redistilled water was used as solvent. Analytical reagent grade chloroform (minimum purity 99.8%) was used for solvent extraction and preparation of standard solution of solute.

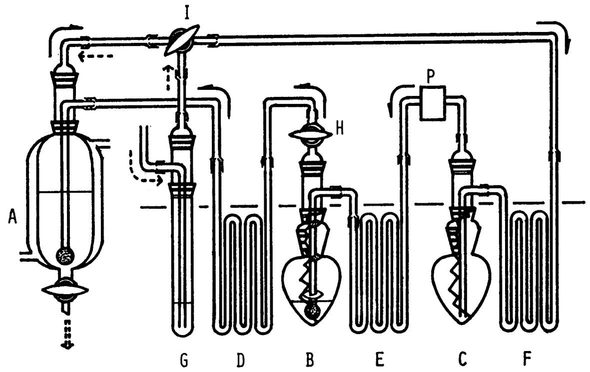

Fig. 1. Solubility apparatus.
The solid and the dotted arrows indicate, respectively, the direction of circulation and the sampling system.

Apparatus and Procedures. The apparatus used is shown in Fig. 1, which is essentially similar to that previously reported,[4] but with some modifications. It is composed of a separatory funnel (300 cm^3), A, two pear-shaped flasks (each 50 cm^3) B, and C, three triplicated-U-shape glass pipes (ϕ 8 mm, each 20 cm^3), D, E, and F, a glass test tube (30 cm^3), G, and a Viton diaphragm pump (Iwaki Type AP-32 Z), P. We will hereafter call A and B by the name "solubility flask" and "solute reservoir," respectively. Gas inlet-type adapters were mounted in A, B, C, and G. Teflon tubes (ϕ 8 mm), a stopcock, H, and a three-way cock, I, were used for connection. The U-shape glass pipes and the flask C serve as traps of water or liquid solute. The test tube, in which was placed some 5 cm^3 of the same liquid solute as the one being measured, was included in the system to facilitate withdrawing sample solution from the solubility flask. In order to prevent liquid solute from being carried over from the solute reservoir by bubbling air, three sheets of Teflon disks, each of which was bored in the center to fit the glass pipe, were attached to the gas inlet-type adapter inserted in the solute reservoir. Of these three disks, two were made with about 20 pinholes and they were tightly fitted to the lower parts of the ground glass joints and the other was set just above liquid solute phase. The temperature of the solubility flask was held constant by circulating water through a surrounding jacket from a thermostat, and the temperature of the solute reservoir was maintained constant by immersing in another thermostat, in which the other glass wares were also immersed as shown in Fig. 1. These thermostats were controlled within 0.01 °C (in some cases 0.1 °C). The assembled apparatus was placed in a draft chamber, the temperature of which was always kept higher than that of the solute reservoir.

A redistilled water of 100 to 200 cm^3 and a liquid solute of 10 to 20 cm^3 were placed in the solubility flask and in the solute reservoir, respectively. When the conditions of temperature were attained, the pump was started, and the solute vapor, which was generated by bubbling air through the liquid solute *via* a sintered glass ball, was introduced into the water *via* another sintered ball, and circulated as indicated in Fig. 1. The circulation rate, which can be changed by means of a Variac and had been calibrated in advance by a flow meter, was set at 2 dm^3/min in most instances. After the solubility equilibrium was attained, the stopcock (H) was closed and the three-way cock (I) was turned left through 90° so as to connect the system with the test tube (G) as indicated in Fig. 1. Then, by opening a stopcock attached to the bottom of the solubility flask, about 30 cm^3 was first discarded and 10 cm^3 portions were transferred successively into five cylindrical separatory funnels of 50 cm^3 capacity, to which each 10 cm^3 volume of chloroform had previously placed. Each separatory funnel had been calibrated in advance and the volume of aqueous solution poured into it was read off. The mixtures in the separatory funnels were hand shaken and allowed to stand for 30 min, then after dehydrating the chloroform phase with anhydrous sodium sulfate, UV-absorptions were measured using a Hitachi Model 100-50 spectrophotometer against the blank extract as a reference. In the case of benzene, the extracts were further diluted with chloroform. Wavelengths used for the measurements and the molar absorptivities were: benzene; 260.8 nm (126 dm^3 mol^{-1} cm^{-1}), toluene; 262.0 (275), ethylbenzene; 261.2 (257), *o*-xylene; 263.0 (324), *m*-xylene; 265.0 (302), *p*-xylene; 268.0 (562), propylbenzene; 261.4 (257), isopropylbenzene; 260.2 (234), 1,2,3-trimethylbenzene; 262.4 (234), 1,2,4-trimethylbenzene; 267.7 (537), 1,3,5-trimethylbenzene; 265.8 (229). Standard solutions were prepared by weighing out suitable quantities of the liquid solutes, followed by dilution with chloroform in volumetric flasks. Calibration curves were made as follows: into separatory funnels aliquots of less than 10 cm^3 of the standard solution were pipetted in succession, diluted with chloroform to 10 cm^3, and then 10 cm^3 portions of redistilled water were added, and the chloroform extracts were measured in the same way as the sample solution. The molar absorptivities described above were thus determined. Values of equilibrium solubilities were the average of at least five determinations.

When the apparatus was used in an open method, the system was modified to remove I, G, P, C, and F from the apparatus. A round-bottom flask of 300 cm^3 capacity was used as the solute reservoir instead of B and the liquid solute of 100 cm^3 was placed in it. Nitrogen gas was allowed to flow continuously through the solute reservoir and to escape through the solubility flask to the atmosphere.

Results

Factors Affecting the Solubility Measurement. When the circulation rate was set at 2 dm^3/min, the solubility equilibrium can be attained after 3 min for each solute. The typical results are shown in Fig. 2. With decreasing the circulation rate, the curve of solubility plotted against time appeared to level off after a somewhat prolonged time, but the solubilities were not affected. In the present method, it is essential to carry out under such experimental conditions that temperature of

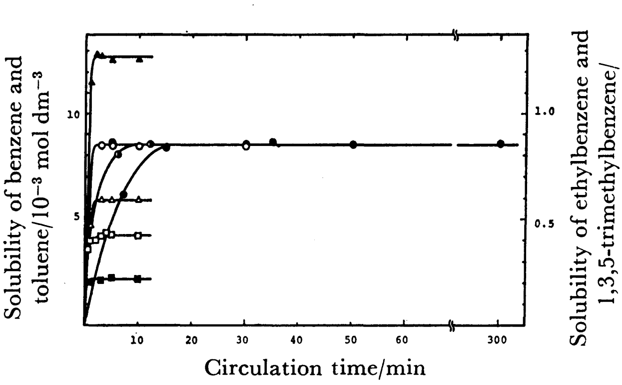

Fig. 2. The effect of circulation rate on the solubilities of benzene, toluene, ethylbenzene, and 1,3,5-trimethylbenzene.

Benzene (○, ◑, ●, ▲), toluene (△), ethylbenzene (□), 1,3,5-trimethylbenzene (■). Circulation rate: 2.0 (○, ▲, △, □, ■), 1.0 (◑), 0.2 dm^3/min (●). Temperature of solubility flask: 35.0 (○, ◑, ●, ▲, □, ■), 25.0 °C (△). Temperature of solute reservoir: 25.0 (△), 21.7 (■), 21.0 (▲), 15.0 (○, ◑, ●), 10.0 °C (□).

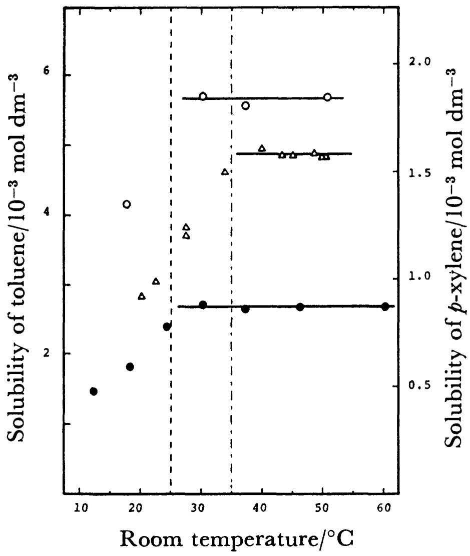

Fig. 3. The effect of room temperature on the solubilities of toluene and *p*-xylene.

Toluene (○, ●), *p*-xylene (△). Temperature of solubility flask: 25.0 (○), 35.0 (△), 45.0 °C (●). Temperature of solute reservoir: 25.0 (○, ●), 35.0 °C (△).

TABLE 1. SOLUBILITIES OF BENZENE AND THE ALKYLBENZENES AS A FUNCTION OF SOLUTE VAPOR PRESSURE

Temperature of liquid solute °C	Vapor pressure of solute 10^3 Pa	Solubility 10^{-3} mol dm^{-3}
Benzene		
Temperature of water 5.00 °C		
5.00	4.682	20.7
Temperature of water 15.00 °C		
0.50	3.672	9.25
2.00	3.985	10.4
5.00	4.682	12.1
6.72	5.126	13.3
10.52	6.241	16.2
15.00	7.818	20.0
Temperature of water 25.00 °C		
0.40	3.652	5.91
5.50	4.808	7.92
5.99	4.934	8.15
10.88	6.357	10.6
15.20	7.895	13.1
19.20	9.595	15.9
25.00	12.61	20.5,20.6,20.7a)
Temperature of water 35.00 °C		
5.50	4.808	5.63
6.00	4.936	5.44
12.40	6.866	8.00
15.30	7.935	8.92
20.90	10.41	11.5
27.80	14.35	15.9
35.00	19.73	21.5
Temperature of water 45.00 °C		
5.50	4.808	3.85
14.12	7.483	5.80
17.80	8.969	6.87
20.40	10.16	8.08
22.90	11.44	8.92
24.10	12.10	9.25
30.59	16.25	12.5
33.30	18.32	14.1
40.92	25.37	19.1
45.00	30.04	22.2,22.5a)
Toluene		
Temperature of water 15.00 °C		
−6.18	0.5955	1.55
1.60	0.9925	2.57
9.60	1.619	4.11
15.00	2.210	5.52
Temperature of water 25.00 °C		
2.35	1.041	1.61
11.32	1.790	2.80
17.70	2.568	3.89
25.00	3.793	5.61
Temperature of water 35.00 °C		
8.70	1.535	1.52
17.14	2.490	2.37
17.15	2.491	2.42
19.72	2.868	2.80
29.90	4.864	4.65
35.00	6.239	5.73
Temperature of water 45.00 °C		
18.45	2.676	1.75
31.64	5.301	3.40
40.02	7.894	5.04
45.00	9.883	6.23
Ethylbenzene		
Temperature of water 15.00 °C		
−3.70	0.1923	0.455
2.62	0.3041	0.696
8.30	0.4490	0.988
15.00	0.6934	1.47
Temperature of water 25.00 °C		
1.50	0.2809	0.374
9.50	0.4863	0.626
16.32	0.7532	0.949
25.00	1.268	1.59
Temperature of water 35.00 °C		
8.59	0.4577	0.362
15.47	0.7142	0.549
27.31	1.447	1.10
35.00	2.208	1.62
Temperature of water 45.00 °C		
15.39	0.7106	0.341
29.72	1.656	0.837
37.80	2.558	1.27
45.00	3.682	1.83
o-Xylene		
Temperature of water 15.0 °C		
4.9	0.2384	0.858
7.9	0.2942	1.04
15.0	0.4735	1.50
Temperature of water 25.0 °C		
11.7	0.3810	0.756
19.2	0.6189	1.22
23.7	0.8159	1.49
25.0	0.8820	1.68
Temperature of water 35.0 °C		
14.6	0.4613	0.555
22.9	0.7774	0.919
29.9	1.174	1.39
35.0	1.563	1.84
Temperature of water 45.0 °C		
24.5	0.8561	0.646
30.5	1.215	0.904
38.5	1.889	1.43
45.0	2.649	2.00
m-Xylene		
Temperature of water 15.0 °C		
6.2	0.3361	0.870
9.3	0.4148	1.04
15.0	0.6015	1.46,1.47a)
Temperature of water 25.0 °C		
6.2	0.3361	0.473
13.4	0.5429	0.783
19.6	0.8012	1.10
22.6	0.9602	1.35
25.0	1.106	1.45
Temperature of water 35.0 °C		
11.2	0.4704	0.417

Table 1. (Continued)

Temperature of liquid solute / °C	Vapor pressure of solute / 10^3 Pa	Solubility / 10^{-3} mol dm^{-3}
19.8	0.8111	0.728
27.7	1.293	1.11
35.0	1.938	1.53,1.54a)
Temperature of water 45.0 °C		
22.6	0.9602	0.550
31.6	1.610	0.885
38.3	2.309	1.264
45.0	3.252	1.69
p-Xylene		
Temperature of water 15.00 °C		
2.62	b)	0.523
5.20	b)	0.701
7.60	b)	0.845
10.36	b)	1.06
15.00	0.6377	1.48,1.48a)
Temperature of water 25.0 °C		
14.0	0.5985	0.811
15.1	0.6417	0.879
20.0	0.8683	1.16
25.0	1.167	1.44,1.55a)
Temperature of water 35.0 °C		
13.6	0.5834	0.478
19.4	0.8373	0.682
25.5	1.202	0.990
35.0	2.036	1.55
Temperature of water 45.0 °C		
19.5	0.8424	0.426
28.4	1.418	0.718
34.4	1.972	1.00
45.0	3.403	1.63
Propylbenzene		
Temperature of water 15.0 °C		
6.4	0.1238	0.215
11.3	0.1775	0.290
12.9	0.1990	0.322
15.0	0.2307	0.400
Temperature of water 25.0 °C		
12.1	0.1880	0.179
18.1	0.2854	0.258
21.1	0.3487	0.337
25.0	0.4489	0.421
Temperature of water 35.0 °C		
15.7	0.2422	0.135
24.5	0.4348	0.245
28.8	0.5697	0.308
30.1	0.6170	0.344
35.0	0.8270	0.450
Temperature of water 45.0 °C		
18.4	0.2912	0.113
30.6	0.6361	0.240
36.6	0.9077	0.331
39.7	1.083	0.395
45.0	1.451	0.521
Isopropylbenzene		
Temperature of water 15.00 °C		
6.76	0.1775	0.302
9.45	0.2141	0.327
10.12	0.2242	0.372
15.00	0.3122	0.477
Temperature of water 25.00 °C		
9.03	0.2080	0.212
12.82	0.2697	0.239
18.78	0.4004	0.338
22.40	0.5050	0.414
25.00	0.5946	0.513
Temperature of water 35.00 °C		
17.82	0.3761	0.204
26.80	0.6646	0.368
30.48	0.8311	0.423
31.43	0.8798	0.479
35.00	1.086	0.552
Temperature of water 45.00 °C		
19.20	0.4114	0.146
26.72	0.6614	0.232
33.30	0.9828	0.344
39.62	1.416	0.473
45.00	1.909	0.630
1,2,3-Trimethylbenzene		
Temperature of water 15.00 °C		
6.00	0.06438	0.281
7.76	0.07295	0.314
10.10	0.08594	0.349
15.00	0.1201	0.488
Temperature of water 25.00 °C		
7.58	0.07203	0.165
10.72	0.08973	0.205
16.62	0.1339	0.321
22.82	0.2001	0.414
25.00	0.2297	0.538
Temperature of water 35.00 °C		
5.80	0.06346	0.0792
20.18	0.1689	0.245
23.90	0.2144	0.302
31.13	0.3348	0.469
35.00	0.4213	0.601
Temperature of water 45.00 °C		
12.70	0.09798	0.0932
25.30	0.2341	0.210
33.38	0.3829	0.368
38.08	0.5038	0.474
45.00	0.7438	0.702
1,2,4-Trimethylbenzene		
Temperature of water 15.00 °C		
5.96	0.08054	0.238
12.62	0.1287	0.363
15.00	0.1513	0.463
Temperature of water 25.00 °C		
5.56	0.07825	0.130
11.30	0.1175	0.191
15.73	0.1591	0.256
19.98	0.2108	0.337
25.00	0.2929	0.472
Temperature of water 35.00 °C		
7.12	0.08753	0.0840

TABLE 1. (Continued)

Temperature of liquid solute °C	Vapor pressure of solute 10^3 Pa	Solubility 10^{-3} mol dm^{-3}
16.86	0.1715	0.166
25.26	0.2957	0.305
29.62	0.3878	0.374
35.00	0.5360	0.499
Temperature of water 45.00 °C		
13.40	0.1357	0.0795
24.50	0.2818	0.171
32.70	0.4674	0.279
40.60	0.7419	0.446
45.00	0.9503	0.569
1,3,5-Trimethylbenzene		
Temperature of water 15.0 °C		
0.3	0.07081	0.147
5.6	0.1034	0.211
9.1	0.1318	0.256
15.0	0.1957	0.375
Temperature of water 25.0 °C		
0.4	0.07133	0.0865
5.6	0.1034	0.126
12.5	0.1658	0.202
19.7	0.2650	0.295
25.0	0.3689	0.406
Temperature of water 35.0 °C		
5.6	0.1034	0.0701
12.5	0.1658	0.106
21.7	0.3007	0.221
28.6	0.4587	0.316
35.0	0.6675	0.446
Temperature of water 45.0 °C		
7.0	0.1140	0.0507
20.5	0.2788	0.129
31.4	0.5416	0.244
31.8	0.5544	0.257
38.5	0.8141	0.340
45.0	1.163	0.461

a) Determinations were repeated on another days. b) Vapor pressure data are not available.

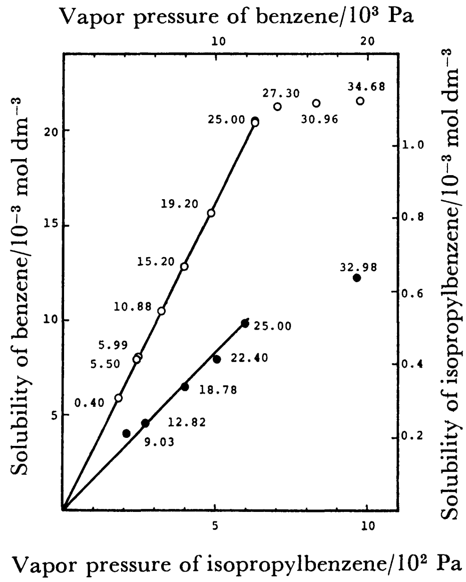

Fig. 4. The effect of temperature of solute reservoir at constant temperature of solubility flask on the solubilities of benzene and isopropylbenzene.
Benzene (○), isopropylbenzene (●). Temperature of solubility flask: 25.00 °C. The figure near each circle indicates the temperature of solute reservoir.

water≥temperature of liquid solute<room temperature. In fact, when the temperature of room was lower than that of the solute reservior, the measured solubilities were lowered correlatively depending on the former temperature. The results are shown in Fig. 3. On the other hand, when the temperature of the solute reservoir was higher than that of the solubility flask, the solute vapor condensed and separated in the solubility flask to form two immiscible phases. Under such conditions, solubilities were found to be considerably higher than those at the same temperature of water and solute. The results are shown in Fig. 4.

Solubility and Vapor Pressure. Solubility runs were made under conditions such that the temperature of the solute reservoir was made to vary while that of the solubility flask was maintained at a constant temperature. The experimental results for all the solutes used here are listed in Table 1. Vapor pressures for pure luquid solutes have been estimated by reference to published tabulations.[5] In this paper, the vapor pressure of liquid solute was taken to be that of pure solute, neglecting the effects of water dissolution in the solute phase and of solute-solvent interaction in the water phase. It can be seen from Table 1 that the concentrations of each solute in aqueous solutions increase linearly with the solute vapor pressure at a constant temperature of water. That is, solubilities obey Henry's law

$$P = K_H X_2, \tag{1}$$

where P is the partial pressure of solute vapor in Pa, X_2 is the mole fraction of the dissolved solute, and K_H is Henry's law constant. Henry's law constants thus determined are given in Table 2. We estimated the solubilities when the temperature of solute was the same as that of water from K_H and P using Eq. 1, since the experimental values under such conditions were somewhat poor in precision. The results are listed in Table 2. To compare the present results with the literature, the reported values, most of which are available only at 25 °C, are summarized in Table 3. In Table 4 are also given some available data of Henry's law constant. Our results are in accord with the literature values except for benzene and propylbenzene. With respect to the latter, the literature value would be overestimated when considered the relationship between the number of methyl group and the solubility.

TABLE 2. HENRY'S LAW CONSTANTS AND THE ESTIMATED SOLUBILITIES OF BENZENE AND THE ALKYLBENZENES

Solute	Temperature of water a) °C	Henry's law constant 10^7 Pa	γ b)	Solubility 10^{-3} mol dm^{-3}
Benzene	5.00	1.25c)		20.7
	15.00	2.15±0.03	0.999	20.2 ±0.3
	25.00	3.38±0.04	0.999	20.7 ±0.1
	35.00	5.03±0.14	0.999	21.8 ±0.6
	45.00	7.34±0.17	0.999	22.8 ±0.5
Toluene	15.00	2.20±0.04	0.999	5.58 ±0.11
	25.00	3.69±0.09	0.999	5.71 ±0.14
	35.00	5.89±0.16	0.999	5.88 ±0.16
	45.00	8.73±0.13	0.999	6.28 ±0.10
Ethylbenzene	15.00	2.55±0.12	0.999	1.51 ±0.08
	25.00	4.43±0.14	0.999	1.59 ±0.05
	35.00	7.44±0.22	0.999	1.65 ±0.05
	45.00	11.2 ±0.3	0.999	1.83 ±0.05
o-Xylene	15.0	1.66±0.11	0.999	1.58 ±0.11
	25.0	2.92±0.11	0.995	1.68 ±0.06
	35.0	4.69±0.04	0.999	1.85 ±0.02
	45.0	7.35±0.06	0.999	2.00 ±0.02
m-Xylene	15.0	2.25±0.06	0.999	1.49 ±0.04
	25.0	4.06±0.15	0.996	1.52 ±0.06
	35.0	6.83±0.41	0.998	1.57 ±0.10
	45.0	10.4 ±0.4	0.999	1.73 ±0.08
p-Xylene	15.00	2.39c)		1.48
	25.0	4.24±0.17	0.993	1.53 ±0.07
	35.0	7.03±0.33	0.998	1.61 ±0.08
	45.0	11.4 ±0.3	0.999	1.66 ±0.05
Propylbenzene	15.0	3.30±0.12	0.988	0.388±0.015
	25.0	5.90±0.17	0.997	0.423±0.012
	35.0	10.1 ±0.2	0.999	0.455±0.007
	45.0	15.3 ±0.5	0.999	0.528±0.017
Isopropylbenzene	15.00	3.50±0.19	0.985	0.495±0.028
	25.00	6.47±0.52	0.994	0.510±0.045
	35.00	10.6 ±0.4	0.994	0.568±0.022
	45.00	16.6 ±0.6	0.999	0.638±0.024
1,2,3-Trimethylbenzene	15.00	1.34±0.05	0.998	0.498±0.019
	25.00	2.45±0.14	0.989	0.520±0.032
	35.00	3.92±0.25	0.999	0.597±0.041
	45.00	5.88±0.16	0.999	0.702±0.019
1,2,4-Trimethylbenzene	15.00	1.93±0.05	0.998	0.435±0.012
	25.00	3.44±0.05	0.999	0.469±0.007
	35.00	5.79±0.22	0.997	0.514±0.020
	45.00	9.24±0.12	0.999	0.571±0.007
1,3,5-Trimethylbenzene	15.0	2.84±0.11	0.999	0.383±0.015
	25.0	4.93±0.24	0.999	0.415±0.022
	35.0	8.14±0.40	0.998	0.455±0.023
	45.0	13.3±0.8	0.996	0.485±0.032

a) In the course of this study, the thermostats were replaced by new ones, temperature of which could be controlled within 0.01 °C. b) Correlation coefficient of the equation, $X=P/K_H$ (the symbols are described in the text). c) Estimated under the conditions where the temperatures of water and liquid solute were the same.

Solubility in an Open Method. An alterative method may be applicable to attain the solubility equilibrium between the water phase and the saturated solute vapor phase. Thus, solubility runs were undertaken in an open method as described in the experimental section. In the open method, it seems to be natural that the flow rate of nitrogen gas should affect the solubility results to a large extent. The results are shown in Fig. 5. Contrary to our expectation, the nitrogen gas flow rate up to 1.2 dm^3/min had no effect on the solubility and the steady solubility was reached within a relatively short time. The solute vapor generated by bubbling through the liquid solute phase is considered to be sufficient to saturate the nitrogen gas in the wide range of its flow rate. Solubilities of benzene and toluene plotted against vapor pressures are shown in Figs. 6

TABLE 3. SOLUBILITIES OF BENZENE AND THE ALKYLBENZENES AT 25 °C REPORTED IN THE LITERATURE

Solute	Solubility/10^{-3} mol dm^{-3}
Benzene	22.3,$^{a,d)}$ 22.9,$^{b)}$ 23.0,$^{c)}$ 22.79,$^{e)}$ 22,$^{f)}$ 27.8,$^{g)}$ 22.47,$^{h)}$ 22.782,$^{i)}$ 23.3—24.7,$^{k)}$ 23.8$^{p)}$
Toluene	5.8,$^{a)}$ 6.81,$^{b)}$ 5.599,$^{e)}$ 6.22,$^{h)}$ 5.639,$^{i)}$ 5.805,$^{j)}$ 7.16—7.27,$^{k)}$ 6.01,$^{n)}$ 5.4$^{p)}$
Ethylbenzene	1.58,$^{a)}$ 1.96,$^{b)}$ 1.43,$^{e)}$ 1.67,$^{h)}$ 1.518,$^{j)}$ 1.32,$^{l)}$ 1.55,$^{m)}$ 1.23,$^{n)}$ 1.65$^{p)}$
o-Xylene	1.92,$^{a)}$ 1.65,$^{e)}$ 2.01$^{h)}$ 1.606,$^{j)}$ 1.57$^{n)}$
m-Xylene	1.63,$^{a)}$ 1.85,$^{b)}$ 1.53,$^{h)}$ 1.375,$^{j)}$ 1.26,$^{n)}$ 1.48$^{o)}$
p-Xylene	1.88,$^{a)}$ 1.87,$^{b)}$ 1.74,$^{h)}$ 1.469,$^{j)}$ 1.48,$^{n)}$ 1.54$^{o)}$
Propylbenzene	0.998$^{p)}$
Isopropylbenzene	0.61,$^{a)}$ 0.42,$^{e)}$ 0.543,$^{j)}$ 0.402$^{n)}$
1,2,3-Trimethylbenzene	0.626$^{j)}$
1,2,4-Trimethylbenzene	0.47,$^{e)}$ 0.491$^{j)}$
1,3,5-Trimethylbenzene	0.401$^{j)}$

a) L. J. Andrew and R. M. Keefer, *J. Am. Chem. Soc.*, **71**, 3644 (1949). b) R. L. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, **73**, 1571 (1951). c) H. Hayashi and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **29**, 857 (1956). d) D. S. Arnold *et al.*, *Chem. Eng. Data. Ser.*, **3**, 253 (1958). e) C. McAuliffe, *J. Phys. Chem.*, **70**, 1267 (1966). f) A. A. Taha *et al.*, *J. Chem. Educ.*, **43**, 432 (1966). g) J. D. Worley, *Can. J. Chem.*, **45**, 2465 (1967). h) J. Polak and B. C. Y. Lu, *Can. J. Chem.*, **51**, 4018 (1973). i) Ref. 10. j) Ref. 1. k) F. P. Schwarz, *Anal. Chem.*, **52**, 10 (1980). l) H. Fühner, *Chem. Ber.*, **57**, 510 (1924). m) T. J. Morrison and F. J. Billett, *J. Chem. Soc.*, **1952**, 3819. n) L. C. Price, Ph. D. disertation, University of California, Riverside, Calif. (1973). o) R. B. Hermann, *J. Phys. Chem.*, **76**, 2754 (1972). p) H. B. Klevens, *J. Phys. Colloid. Chem.*, **54**, 283 (1950).

TABLE 4. HENRY'S LAW CONSTANTS REPORTED IN THE LITERATURE

Solute	Temperature/°C	Henry's law constant/10^7 Pa			
		I$^{a)}$	II$^{b)}$	III$^{c)}$	IV$^{d)}$
Benzene	10	1.46			
	15	1.87,1.89			
	20	2.39			
	25	3.06	3.2		3.13
	30	3.82,3.61			
	35			4.702—4.522	
Toluene	25				3.75
Ethylbenzene	25				4.76

a) W. J. Green and H. S. Frank, *J. Solut. Chem.*, **8**, 187 (1979). b) A. A. Taha *et al.*, *J. Chem. Educ.*, **43**, 432 (1966). c) E. E. Tucker and S. D. Christian, *J. Phys. Chem.*, **83**, 427 (1979). d) Ref. 3.

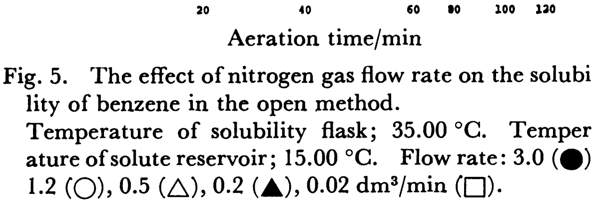

Fig. 5. The effect of nitrogen gas flow rate on the solubility of benzene in the open method.
Temperature of solubility flask; 35.00 °C. Temperature of solute reservoir; 15.00 °C. Flow rate: 3.0 (●), 1.2 (○), 0.5 (△), 0.2 (▲), 0.02 dm^3/min (□).

and 7, respectively, where those obtained in the closed method are also given for the sake of comparison. Similarly Henry's law was applied in the open method to these solutes, but the reproducibility was somewhat poor. However, the open method has an advantage that the liquid solute phase is free from contamination with water vapor.

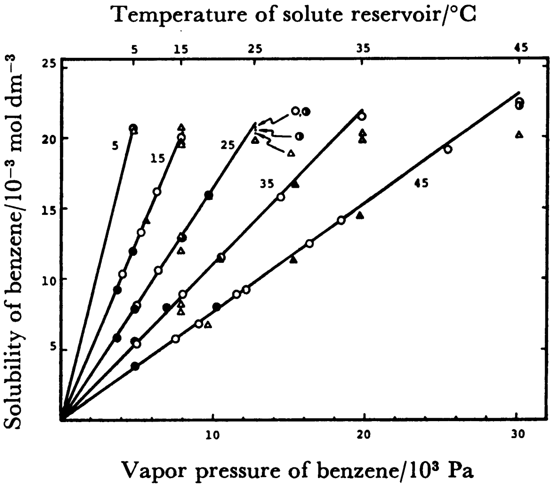

Fig. 6. The solubility of benzene plotted against vapor pressure.
The closed method: circulation rate; 2 dm^3/min, time; 5 min, measured on Oct. 26—28 (1980) (●) Dec. 14—16 (1980) (◑) July 25—30 (1981) (○). The open method: nitrogen gas flow rate; 0.2 dm^3/min, time; 60 min, measured on May 6—28 (1981) (△) Aug. 3—10 (1981) (▲). The figure near each solid line indicates the temperature of solubility flask in °C.

Discussion

The Evaluation of the Present Method. The present method is essentially the same as that previously employed in determining the solubility of metallic mercury in water.[6] In writing this paper, we have searched the literature for the one most similar to the present method and found a paper published by Joris and Taylor.[7] They made use of a similar closed circulatory system

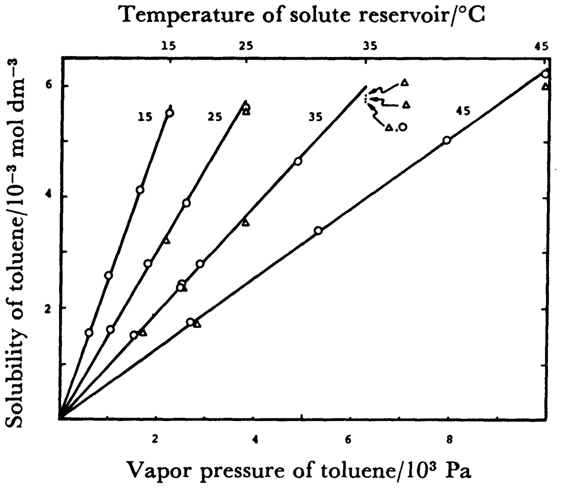

Fig. 7. The solubility of toluene plotted against vapor pressure.

The closed method (○), circulation rate; 2 dm^3/min, time; 5 min. The open method (△), nitrogen gas flow rate; 0.2 dm^3/min, time; 60 min. The figure near each solid line indicates the temperature of solubility flask in °C.

in determining the solubility of water in organic solvent, which is just the opposite situation to the present study. In their method, temperatures of solvent and solute are nearly equal to each other, while the whole circulatory system is kept at a higher temperature than either.

It is a thermodynamic requirement that the solubility measurement should be done under the same temperature of solvent and solute. From this standpoint, two basic questions arise concerning the validity of the present method; the first is that the temperature of the solute reservoir differs from that of the solubility flask and the second is that the partial pressure of the solute vapor may be affected by the temperature change in a different part of the closed system. The temperature of the solute vapor just before entering the solubility flask certainly differs from that in the solubility flask; the former is higher than that of the solute reservoir owing to the room temperature. However, the solubilities were found to be independent of the room temperature so far as being kept above the temperature of the solute reservoir (Fig. 3). We have assumed that when the solute vapor is bubbled into the water phase through the sintered ball and bubbles come into contact with the water, the temperature of the interface of each bubble can be equated to that of bulk water almost immediately. The temperature change in the bulk water was examined in the preliminary experiment by introducing solute vapor at 2 dm^3/min into the solubility flask in which a thermometer was inserted. A slight decrease in the temperature of the bulk water was observed, probably due to the vaporization of water. We have concluded that such temperature change is negligibly small in the solubility measurement.

On the other hand, the second question is more substantial, since the total pressure undoubtedly relates to the temperature of system. In the closed system, however, it seems likely that the different temperature inside the apparatus (solute, solvent, and room) dose not cause the pressure change, but contributes to the flow rate of the gas phase in the corresponding parts of the system. That is, the flow rate of the circulating gas is faster in places of higher temperature. Thus, the total pressure remains constant at atomospheric pressure over the temperature range investigated. This situation may be more easily understood by referring to the open method, where the nitrogen gas carrying the solute vapor is always open to the atmosphere after having been introduced into the water phase. We suppose from the following observation that the total pressure in the closed system is also kept under atmospheric pressure: when the three-way cock was turned prior to sampling so as to connect the system to the test tube as indicated in Fig. 1, only a small change was observed in the liquid solute level inside the glass pipe in the test tube.

Concerning the evaluation of the present method, we have taken account of the serious disagreement of benzene with the literature; some 10% lower than most literature values. After presenting our short communication,[4] we have continued the solubility measurements by the modified apparatus employed here. However, the results always indicated the lower values. The reason is not explicable at present, but it is felt that the present method may give lower saturated solution for such solute exhibiting high vapor pressure as benzene. It can be seen from Figs. 6 and 7 that the solubilities of benzene obtained by the open method are a little lower than those by the closed method, especially at higher temperature of water, and that the agreements between the open and the closed methods are better for toluene than for benzene. It seems likely that an escape of solute vapor from aqueous solution occurs in preference to a dissolution into it in the open system. This escaping tendency may have likewise taken place even under the closed system owing to the extreme volatility of benzene in water. The solubility measured by the present method might be called "steady state solubility," that is, the solubility determined under such condition that the rate of escape of solute vapor from the aqueous phase is equal to the rate of dissolution of solute vapor into it. The balance for benzene may be changed in favor of escape.

Interpretation of the Solubility Results. As suggested by Amidon and Anik,[8] the solution process of liquid hydrocarbon can be divided into two steps; pure liquid to gas and gas to aqueous solution. The present study is concerned with the latter step, that is, the solvation process. The thermodynamic parameters estimated from the temperature dependence of Henry's law constant are tabulated in Table 5, in which are given the solvation enthalpies reported by the two groups. They estimated these values indirectly by subtracting the heat of vaporization to form ideal gas from the energy of solution. Our results are in fair agreement with them. It should be noticed, however, that the present results have been derived on the assumption of ΔH being temperature independent. Thermodynamic features of the solution process of benzene and the alkylbenzenes will be reported and discussed elsewhere.

It can be seen from Table 2 that the number of the methyl groups is predominant in determining the

TABLE 5. THERMODYNAMIC PARAMETERS OF SOLVATION OF SOLUTE VAPOR AT 25 °C DETERMINED FROM TEMPERATURE DEPENDENCE OF HENRY'S LAW CONSTANT[a)]

Solute	ΔG/kJ mol^{-1}	$-\Delta S$/J K^{-1} mol^{-1}	$-\Delta H$/kJ mol^{-1}		
			This work	Literature I[b)]	Literature II[c)]
Benzene	14.4±0.04	157±1	32.3±0.4	31.77±0.06	31.9
Toluene	14.6±0.08	167±1	35.1±0.3	36.26±0.06	36.2
Ethylbenzene	15.1±0.08	177±2	37.8±0.5	40.24±0.06	40.1
o-Xylene	14.0±0.13	173±1	37.7±0.2		
m-Xylene	14.9±0.08	181±2	39.2±0.6		40.0
p-Xylene	15.0±0.08	183±1	39.7±0.2		40.0
Propylbenzene	15.8±0.08	184±2	39.1±0.6	43.9 ±0.1	
Isopropylbenzene	16.0±0.17	186±3	39.6±0.7		41.5
1,2,3-Trimethylbenzene	13.6±0.17	171±3	37.5±0.8		
1,2,4-Trimethylbenzene	14.4±0.04	182±1	39.9±0.2		
1,3,5-Trimethylbenzene	15.4±0.08	183±1	39.2±0.1		

a) Thermodynamic parameters determined in this work were derived based on the assumption of ΔH being temperature independent. b) S. J. Gill, N. F. Nichols, and I. Wadsö, *J. Chem. Thermodyn.*, **8**, 445 (1976). c) R. D. Wauchope and R. Haque, *Can. J. Chem.*, **50**, 133 (1972).

solubility; the solubility decreases to *ca.* 1/3.6 with an increase of one methyl group. Moreover, as pointed out by Sutton and Calder,[1)] the positions of the substituents on the benzene ring are of secondary importance. The expression in terms of Henry's law constant seems to indicate more pronounced differences among the substituted isomers rather than the solubility proper. Henry's law constant might be predictable from the scaled particle theory,[9)] which requires many parameters for a single solute such as molecular diameter, energy parameter, polarizability, and dipole moment. Of these parameters, the last one appears to play an important role in the solubility characteristic of isomers; Henry's law constant decreases with increasing dipole moment of the solute. On the basis of the scaled particle theory, we have tried briefly to correlate Henry's law constants of a series of benzene and the alkylbenzenes with their molecular parameters. The results, however, were not satisfactory.

Applicability of the Present Method. The present method has three principal advantages. Firstly, the solubility equilibria can be attained in quite a short time such as 3 min, and they are easily reproducible. Secondly, it can be easily confirmed whether the solubility obeys Henry's law. Henry's law constant and its temperature dependence should help to clarify the solution process in more detail than the solubility itself. Finally, the apparatus is best suited for preparing aqueous solutions of any desired concentrations of solute, which are equal or below the saturation, at a given temperature of water.

Of these, the last one is the most remarkable feature of the present method and attractive from the practical point of view. For instance, certain specific interaction of a third component such as an electrolyte or another organic compound with organic liquid solutes can be substantiated experimentally by measuring the solubility change in the presence of the third component.

Recent workers have taken it as an advantage that their methods of solubility measurement do not necessarily require the preparation of truly saturated solutions.[2,3,10)] Nevertheless, it is still important and indispensable in some cases to prepare the truly saturated solutions.

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