CHEMISTRY LETTERS, pp. 225-228, 1981.

SOLUBILITIES OF BENZENE AND THE ALKYLBENZENES IN WATER —— METHOD FOR OBTAINING AQUEOUS SOLUTIONS SATURATED WITH VAPOURS IN EQUILIBRIUM WITH ORGANIC LIQUIDS ——

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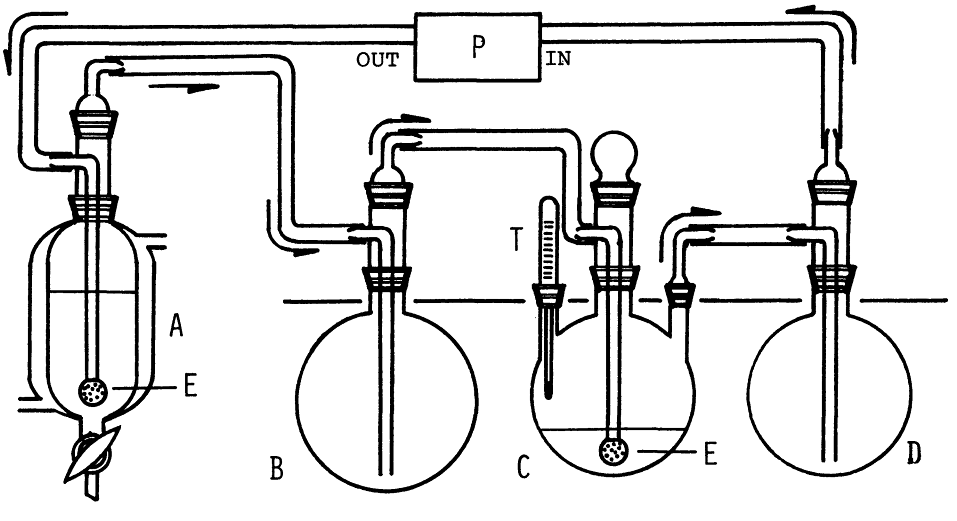
A method is presented which is simple and useful in attaining solubility equilibria of organic liquids in water. The solute vapour, which is in equilibrium with the liquid solute, is introduced into water and circulated in a closed system. It has been confirmed that Henry's law applies to aqueous solubilities of benzene and the alkylbenzenes used.

The solubilities of slightly soluble organic compounds in water have been studied by many workers. Most of the earlier investigators prepared saturated solutions by adding an excess quantity of the solute to water and shaking the mixture, then they analysed the dissolved solute after the saturated solutions had been allowed to stand for at least 24 h. Recently, some investigators have made use of the solute vapour instead of the liquid solute.[1,2] The present letter is concerned with a simple technique for attaining solubility equilibrium within a short time. Solubilities were determined based on Henry's law constants. In order to evaluate the utility of the technique, benzene and the alkylbenzenes were chosen as solutes, since there are abundant data concerning their solubilities.

The apparatus used is shown in Fig. 1, which is essentially similar to that previously used in the solubility measurement of mercury vapour,[3] but some modifications were made. It is composed of a separatory funnel A with a jacket, three flasks, B, C, and D, a Viton diaphragm pump P, and Tefron tubes (8 mm i.d.) to connect them. Gas inlet-type adapter were mounted in the vessels. The three flasks were immersed in a thermostat, of these, B and D were used as traps for water and liquid solute droplets, respectively. The temperature of the separatory funnel was held constant by circulating water through the jacket from another thermostat. A liquid solute (ca. 100 cm^3) and redistilled water (100 to 200 cm^3) were placed in the vessel C and the funnel A,



A; separatory funnel (300 cm^3)
B; flask (2 dm^3)
C; three-necked flask (300 cm^3)
D; flask (500 cm^3)
E; sintered glass ball
P; pump (Iwaki, Type AP-32 Z)
T; thermometer

Fig. 1. Solubility apparatus

respectively. The solute vapour, generated by bubbling air through the liquid solute via a sintered glass ball, was introduced into A via another sintered glass ball, and circulated by means of the pump. The circulation rate, which can be changed by a Variac, was 2 dm^3/min in most instances. After the solubility equilibrium was attained, a ground glass joint, which was connected to B through Tefron tube, was removed from the gas inlet-type adapter mounted on A. Then by opening a stopcock attached to the bottom of A portions (ca. 10 cm^3) of the aqueous solution were transferred successively into five calibrated cylindrical separatory funnels of 50 cm^3 capacity, to which each 10 cm^3 volume of chloroform had previously been added. Experimental procedures involved in spectrophotometric measuring the chloroform extracts and preparing standard solutions will be reported elsewhere. Benzene and the alkylbenzenes were of analytical reagent grade and were used as purchased. The temperature of the room where the apparatus was placed was always kept higher than that of the solute reservoir. The pressure in the closed system was kept under atmospheric pressure.

The effect of room temperature on the solubility measurements were investigated with toluene as solute. The results are shown in Fig. 2. So far as the temperature of room was kept above that of solute reservoir, the solubilities were independent of the former over the temperature range investigated. This can be accounted for by considering that, since experiments are carried out under atmospheric pressure, the vapour pressure of solute introduced into the aqueous phase can be equated to that in equilibrium with the liquid solute, partial pressure of the solute remaining constant regardless of the room temperature in this range. Moreover, we assume, though the data are lacking, that, when the solute vapour was bubbled into the solvent through the sintered ball and bubbles were in contact with the solvent, the temperature of interface of each bubble can be equated to that of the bulk solvent almost immediately.

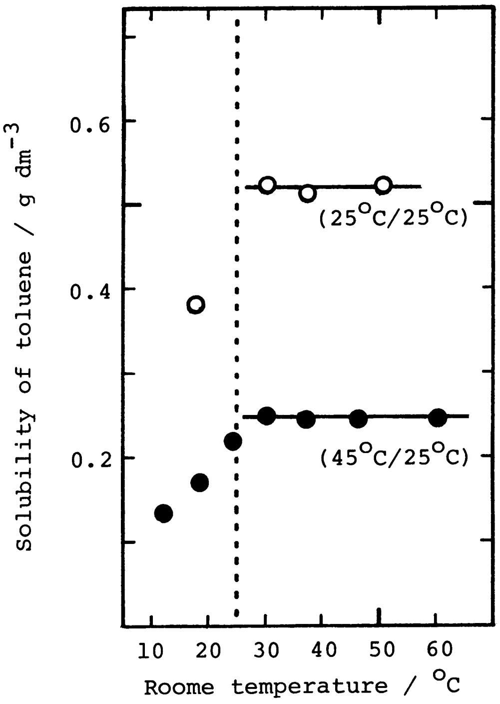


Fig. 2. Effect of room temperature on solubility of toluene (Temp. of water / Temp. of solute)

Solubility equilibria can be attained within 5 min as will be seen in Fig. 3. The time required to attain equilibrium increases with decreasing circulation rate, but the solubilities are not affected. The solubility runs were made under conditions such that the temperature of solute reservoir was made to vary while that of solvent phase was held constant. In Fig. 4, the solubilities of toluene, as an example, are plotted against its vapour pressure. The vapour pressure data for solutes were taken from the literature.[4] It can be seen from Fig. 4 that the solubility obeys Henry's law at constant solvent temperature. The law also applies to the other solutes used. Henry's law constants and the calculated solubilities are given in Table 1. The solubilities obtained in this work are in good agreement with literature values except

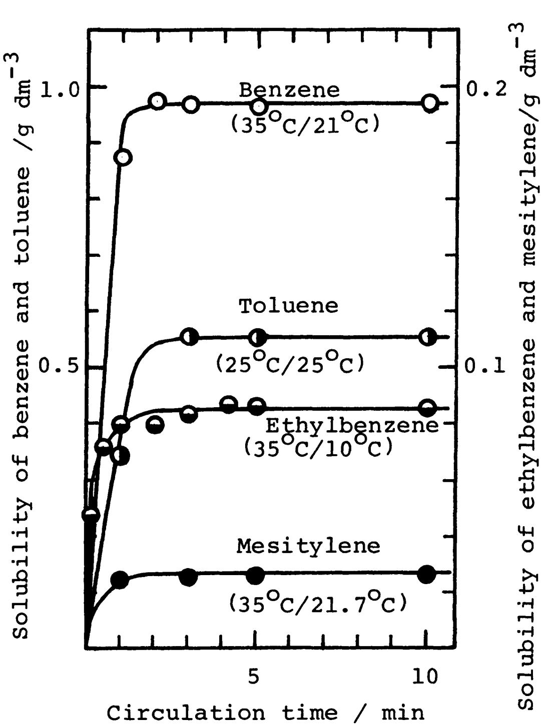


Fig. 3. Concentration vs. circulation time (Temp. of water / Temp. of solute)

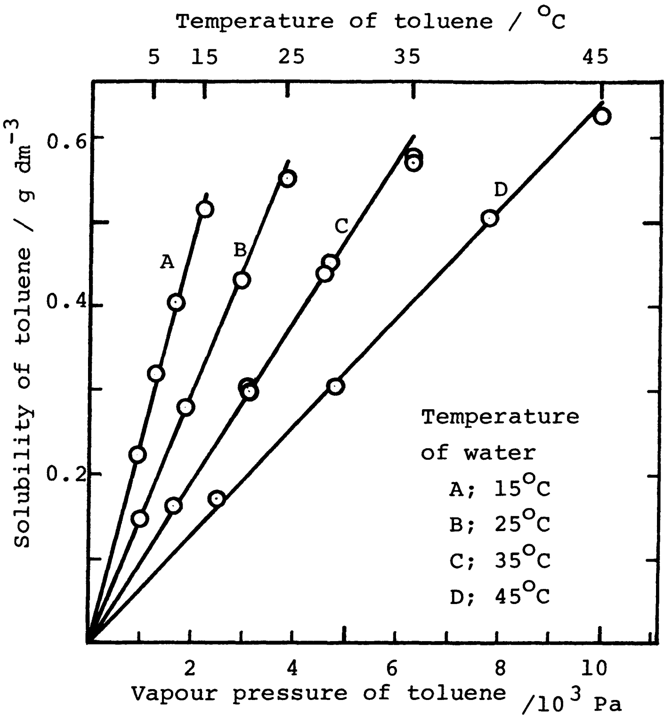


Fig. 4. Solubility vs. vapour pressure of toluene

Table 1. Henry's law constants, K_H, and solubilities, [S], calculated from K_H (K_H / 10^7 Pa, [S] / g dm^{-3}. Values in paranthese are correlation coefficients of the equation, $X = P / K_H$, where X and P denote the mole fraction of dissolved solute and the vapour pressure of solute, respectively.)

Solute		Temperature / °C			
		15.0	25.0	35.0	45.0
Benzene	: K_H	2.20 ± 0.05	3.39 ± 0.17	4.87 ± 0.17	7.04 ± 0.38
		(0.997)	(0.999)	(0.998)	(0.993)
	[s]	[1.54 ± 0.04]	[1.61 ± 0.09]	[1.76 ± 0.06]	[1.85 ± 0.11]
Toluene	: K_H	2.12 ± 0.07	3.49 ± 0.04	5.44 ± 0.15	7.98 ± 0.23
		(0.999)	(0.999)	(0.998)	(0.999)
	[s]	[0.533 ± 0.017]	[0.557 ± 0.007]	[0.587 ± 0.015]	[0.635 ± 0.019]
Ethylbenzene	: K_H	2.32 ± 0.13	4.13 ± 0.14	6.73 ± 0.14	10.1 ± 0.2
		(0.990)	(0.999)	(0.999)	(0.999)
	[s]	[0.176 ± 0.009]	[0.181 ± 0.006]	[0.194 ± 0.006]	[0.215 ± 0.004]
Mesitylene	: K_H	3.04 ± 0.07	5.16 ± 0.16	8.34 ± 0.53	13.7 ± 0.8
		(0.999)	(0.999)	(0.998)	(0.996)
	[S]	[0.0456 ± 0.0010]	[0.0495 ± 0.0015]	[0.0542 ± 0.0033]	[0.0565 ± 0.0031]

Literature values at 25°C (solubilities expressed in g dm^{-3})

Benzene : 1.74a,d), 1.79b), 1.80c), 1.780e), 1.7f), 2.17g), 1.7795i), 1.82 - 1.93k)
Toluene : 0.53a), 0.627b), 0.5158e), 0.573h), 0.5195i), 0.5348j), 0.660 - 0.670k)
Ethylbenzene : 0.208b), 0.152e), 0.177h), 0.1612j)
Mesitylene : 0.0482j)

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) Ref. 5. 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) D.Mackay and W.Y.Shiu, *Can. J. Chem. Eng.*, 53, 239(1975). j) Ref. 2. k) F.P.Schwarz, *Anal. Chem.*, 52, 10(1980).

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for benzene, which show serious disagreements (ca. 10 % lower than most values).

From the standpoint of "hydrophobic interaction", particular attention has been paid to the problem of whether the solubility of benzene obeys Henry's law.4-6) Our present results seem to indicate the validity of the law. In order to substantiate this point more clearly and also to explain the observed disagreements between the present results and literature values, we are now carring out experiments in which modification is made to avoid contaminating the liquid benzene phase in the reservoir with water vapour. It is preferred in the modified runs to reduce the vapour pressure of benzene to such an extent that the solute vapour may be taken as an ideal gas.

The present method has three principal advantages: (1) the solubility equilibrium can be attained within a quite short time, (2) it can be confirmed whether the solubility obeys Henry's law, and (3) based on Henry's law we can easily prepare solutions of any desired concentrations of solute, which are below the saturation, at the constant solvent temperature.

REFERENCES AND NOTES

1) R. L. Brown and S. P. Wasik, *J. Res. Natl. Bur. Stand. Sec. A*, 78, 453(1974).
2) C. Sutton and J. A. Calder, *J. Chem. Eng. Data*, 20, 320(1975).
3) I. Sanemasa, *Bull. Chem. Soc. Jpn.*, 48, 1795(1975).
4) For benzene, vapour pressures were estimated from "International Critical Tables," Vol. III, McGraw-Hill (1928), p. 208 and p. 221. For the alkylbenzenes, estimated from "Kagaku Binran, Kiso-Hen II," ed by The Chemical Socity of Japan, published by Maruzen, Tokyo (1975), pp. 710 - 731.
5) A. A. Taha, R. D. Grigsby, J. R. Johonson, S. D. Christian, and H. E. Affsprung, *J. Chem. Educ.*, 43, 432(1966).
6) W. J. Green and H. S. Frank, *J. Solution Chem.*, 8, 187(1979).
7) E. E. Tucker and S. D. Christian, *J. Phys. Chem.*, 83, 426(1979).

(Received November 22, 1980)