490. Determination of the Solubility of Water in Some Organic Liquids by Means of Tritium.

By J. R. Jones and C. B. Monk.

Tritiated water and liquid scintillation counting have been used to obtain the saturation solubilities of water in some aromatic hydrocarbons and halides at 25°, 30°, and 35°. The results are analysed in terms of Hildebrand's concepts of solubility parameters and various expressions for calculating entropies of mixing.

THE very low concentrations of water needed to saturate many liquids can be measured by using the tritiated form HTO. This was first shown by Joris and Taylor (ref. 1; cf. ref. 2) who effected saturation by bubbling air saturated with HTO and then found the count-rates of the liquid solvents with a gas-counter. Wing and Johnston[3,4] made similar studies but simplified the saturation process into simply shaking solvents with tritiated water; and Caddock and Davies,[5] although they reverted to the bubbling method to saturate benzene and toluene at 20°, used the simpler liquid scintillation-counting process that has been developed in recent years.

For the present studies, the two liquid phases were shaken together, the saturated solvent was separated and a known volume of it was shaken with a known volume of inactive water, and samples of this mixture were assayed by a liquid scintillation-counter. The two-stage process is necessary with many solvents owing to their quenching effects on the scintillator; this is particularly true when the solvents contain halogen. On the other hand, since liquid scintillator solutions often contain hydrocarbons such as toluene it should be possible to assay the saturated organic phase directly provided the reference solutions are made up with identical compositions. This was tested with benzene and toluene, and the answers by the two methods agreed well (±2%).

---

[1] Joris and Taylor, *J. Chem. Phys.*, 1948, **16**, 45.

[2] Black, Joris, and Taylor, *J. Chem. Phys.*, 1948, **16**, 537.

[3] Wing and Johnston, *Science*, 1955, **121**, 674.

[4] Wing and Johnston, *J. Amer. Chem. Soc.*, 1957, **79**, 864.

[5] Caddock and Davies, *Nature*, 1959, **184**, 2011.

Results and Discussion.—The measured solubilities are shown in Table 1, together with the results of others.[4,6] The average deviations ranged from ±1% for the higher figures to ±5% for the lower ones.

TABLE 1.

Solubility data: (ml. of water/ml. of solvent) × $10^4 = 10^4 s_2$.

Solvent	25°	30°	35°	Solvent	25°	30°	35°
Benzene	5·7 ($5{\cdot}5_4$[4], 5·7[6])	$6{\cdot}5_5$ (6·5[6])	7·5 ($7{\cdot}2_5$[6])	Chlorobenzene ...	3·4 (3·6[4])	$3{\cdot}9_5$	4·6
Toluene	4·0 ($3{\cdot}3_5$[4], 4·5[6])	4·8 (5·1[6])	5·9 ($5{\cdot}6_5$[6])	Bromobenzene ...	4·1 (4·2[4])	4·7	5·3
Ethylbenzene ...	3·7	4·3	5·3	Iodobenzene	4·9 (5·0[4])	5·6	$6{\cdot}3_5$
n-Butylbenzene	3·5	4·1	4·9	*o*-Dichlorobenzene	3·2 (3·1[4])	$3{\cdot}7_5$	$4{\cdot}2_5$

Hildebrand[7,8] has discussed solubility data in terms of activities a, volume fractions ϕ, molar volumes V of the pure components, mole fractions x, and solubility parameters δ. For a binary mixture, the entropy of mixing component 2, ΔS_2, with component 1 is calculated from the above terms by:

(*a*) Assuming $V^f{}_1/V^f{}_2 = V_1/V_2$ where V^f represents free volume (*i.e.*, space between molecules), then

$$\Delta S_2 = \boldsymbol{R}\{\ln \phi_2 + \phi_1(1 - V_2/V_1)\}; \tag{1}$$

(*b*) Assuming $V^f{}_1 = V^f{}_2$, *i.e.*, the solutions are ideal, then

$$\Delta S_2 = -\boldsymbol{R} \ln x_2. \tag{2}$$

Also, the heat of mixing is given by

$$\Delta H_2 = V_2\phi_1{}^2(\delta_1 - \delta_2)^2. \tag{3}$$

Similar expressions can be written for ΔS_1 and ΔH_1, while from the usual free-energy expression, $\Delta G = \Delta H - T\Delta S$, we have

$$\Delta G_2/\boldsymbol{R}T = \ln a_2 = (\ln \phi_2)(1 - V_2/V_1) + V_2\phi_1{}^2(\delta_1 - \delta_2)_2/\boldsymbol{R}T. \tag{4}$$

With the present systems, if water is taken as component 2, then since the solubilities are small, $\phi_2 = \delta_2$, $\phi_1 = 1$, and $a_2 = 1$ so from (4) we have

$$\ln s_2 + 1 - V_2/V_1 + V_2(\delta_1 - \delta_2)^2/\boldsymbol{R}T = 0, \tag{5}$$

where s_2 is the solubility in ml. per ml. of organic solvent. Equation (5) is used to calculate $\delta_2 - \delta_1$, whence δ_2 is obtained after δ_1 has been calculated as follows.

If E is the total energy of a system, since $E = H - PV = H - \boldsymbol{R}T$, then if E_1 is the energy of vaporisation of the solvent to gas at zero pressure, while[8]

$$\delta_1{}^2 = E_1/V_1 \tag{6}$$

then

$$\delta_1{}^2 = (\Delta H_1 - \boldsymbol{R}T)/V_1, \tag{7}$$

where ΔH_1 is the molar heat of vaporisation of the organic solvent at a temperature T. The values of δ_1 and δ_2 at 25° are given in Table 2, and are based on a recent reference[9] for ΔH_1 and densities d_1 for calculating $V_1 = M_1/d_1$ where M_1 is the molecular weight of the solvent; V_2 is taken as 18·07 ml.

---

[6] Rosenbaum and Walton, *J. Amer. Chem. Soc.*, 1930, **52**, 3571.

[7] Hildebrand, *J. Chem. Phys.*, 1949, **17**, 1346.

[8] Hildebrand and Scott, "The Solubility of Non-electrolytes," Reinhold Publ. Corp., New York, 3rd edn., 1950.

[9] "Physical Properties of Chemical Compounds," Advances in Chemistry Series No. 15, Amer. Chem. Soc., 1955.

TABLE 2.

Solubility parameters and entropies of mixing at 25°.

(*a*, *b*, *c* = equations 1, 2, and 8, respectively.)

Solvent	ΔH_1 (kcal./mole)	V_1 (ml.)	δ_1	δ_2	$\Delta S_2{}^a$	$\Delta S_2{}^b$	$\Delta S_2{}^c$
Benzene	8·09	89·40	9·16	$23{\cdot}9_5$	13·3	11·6	17
Toluene	9·08	106·85	8·91	$24{\cdot}0_5$	13·9	12·0	23
Ethylbenzene	10·10	123·05	8·79	24·0	14·1	12·0	23
n-Butylbenzene	12·14	156·7	8·59	$23{\cdot}8_5$	14·1	11·6	22
Chlorobenzene	10·17	102·3	9·68	25·0	14·2	12·5	17
Bromobenzene	10·87	105·5	9·97	$24{\cdot}9_5$	13·9	12·0	14
Iodobenzene	11·85	111·9	10·03	$24{\cdot}9_5$	13·5	11·5	15
o-Dichlorobenzene ...	12·00	113·1	10·04	25·4	14·3	12·3	16

Hildebrand and Scott,[8] using the data of Black, Joris, and Taylor,[2] found that $\delta_2 = 24{\cdot}0 \pm 0{\cdot}1$ for the solubilities of a series of normal paraffins, benzene, and toluene in water at 20°. The present results show this value applies also to a number of normal aromatic hydrocarbons. For the C_6H_5X series, Wing and Johnston [4] found $\delta_2 = 24{\cdot}8$ where X is any one of the four halogens; the present answer of just under 25 on average is a little higher. The last result shows that increasing the chlorine content in the benzene ring causes δ_2 to increase.

The values of ΔS_2 shown in Table 2 have been calculated from eqn. (1) by taking $\phi_1 = 1$ and $\phi_2 = s_2$, from eqn. (2) by taking $x_2 = s_2V_1/V_2$, and by a third method based on discussions by Hildebrand [10] on the temperature-dependence of solubilities. From the standard thermodynamic functions $\partial(\Delta G)/\partial T = -\Delta S$ and $\Delta G = \boldsymbol{R}T \ln a$, since $\partial \ln a/\partial \ln x$ is only slightly <1 when x is small, we have, at constant temperature,

$$\Delta S_2 = \boldsymbol{R}\partial(\ln x_2)/\partial(\ln T), \tag{8}$$

so that ΔS_2 is obtained from a plot of $\boldsymbol{R} \log x_2$ against $\log T$. In view of the approximations involved together with experimental limitations, all three sets of data are in reasonable agreement, except for toluene, ethylbenzene, and n-butylbenzene, and this suggests that these three systems are not so near to ideality as are the others.

Experimental.—" AnalaR " benzene and toluene were purified by standard methods,[11] The other organic solvents (laboratory grade) were dried over calcium chloride before fractional distillation. For a solubility measurement, a few ml. of tritiated water of about 2 mc/ml. were shaken for at least 4 hr. with 10—25 ml. of organic solvent in a glass-stoppered flask in a thermostat-bath. Most of the saturated organic phase was decanted into a warmed tube, and 5 ml. were transferred by warm pipette to a 10-ml. flask to which 5 ml. of water were added before the whole was shaken for about 4 hr. Portions (1 ml.) of the aqueous phase were taken for tritium assay, the count rates being obtained with high-stability equipment (Nuclear Enterprises, type 8301) and a typical liquid scintillator solution.[12] As a reference, the original HTO was diluted 1000 times and portions (1 ml.) were counted at the time of the tests. Corrections were made for background, and sufficient counts were taken for a statistical accuracy of $\pm 0{\cdot}3\%$.

The D.S.I.R. is thanked for a maintenance grant to J. R. J.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

[*Received, February 28th*, 1962.]

---

[10] Hildebrand, *J. Chem. Phys.*, 1952, **20**, 190.

[11] Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 1956.

[12] Manning and Monk, *J.*, 1962, 2573.