

Solubilities and Free Volumes

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Summary A new treatment for the estimation and correlation of solubilities is described.

CERTAIN properties and combinations of properties of unassociated liquids are often about equal if the liquids have the same free volume,¹ or, in other words, when the ratios of their volume to the actual volume of their molecules are equal. Thus, it seems possible first, that unassociated liquids might be miscible if they have the same free volumes and secondly, that the work required to transfer the liquid from the saturated solution into an ideal solution of the same concentration might be approximately equal to the work required to compress or expand the liquid isothermally until it has the same free volume as the solvent, *i.e.* until equation (1) applies. ϕ and ϕ' are the

$$\frac{V}{\phi} = \frac{V'}{\phi'} \quad (1)$$

molecular parachors (used as measures of the actual volumes of the molecules and calculated as previously described²) and V and V' are molecular volumes of the solute and solvent respectively.

An equation, relating the isothermal compressibility of liquids to the pressure, has been combined^{3,4} with an

$$\frac{9P}{P^*} = \frac{\phi^6 V_0^3}{V^9} - \frac{\phi^6}{V_0^6} \quad (2)$$

equation, relating the isothermal compressibility to the free volume, to give equation (2). P^* is a constant and

equals $8.58 \times 10^6 \text{ N m}^{-2}$. At pressure P , V is the molecular volume and V_0 that at zero pressure (or for practical purposes, at one atmosphere). The work $\int P dV$ for isothermal compression or expansion of a solute from V_0 to the value of V , given in equation (1) with $V' = V'_0$, can be calculated from equation (2). This work should, according to the arguments put forward previously,⁵⁻⁷ equal $RT \log_e y$ where y is the volume fraction of the solute in the saturated solution and T is the absolute temperature. Further, the treatment may be extended to the solubility of solids if the term $\Delta H_f (1 - T/T_m)$ is added in the usual way:⁵ ΔH_f is the latent heat of fusion of the solid at T_m the melting point. Thus we have equation (3).

$$RT \log_e y + \left[\Delta H_f \left(1 - \frac{T}{T_m} \right) \right] = P^* \phi \left[\frac{1}{8} \left(\frac{\phi}{V_0} \right)^5 - \frac{1}{72} \left(\frac{\phi'}{V'_0} \right)^8 \left(\frac{V_0}{\phi} \right)^3 - \frac{1}{9} \left(\frac{\phi}{V_0} \right)^6 \left(\frac{V'_0}{\phi'} \right) \right] \quad (3)$$

In Figure 1, equation (3) is tested for solubilities of iodine. Densities of liquid iodine⁸ were extrapolated, using equation (1) in ref. 3, to give $V_0 = 5.96 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ at 298 K (Benesi and Hildebrand⁹ use 5.9×10^{-5}). Other densities were taken from Timmermanns,¹⁰ or in a few cases from Hildebrand and Scott.¹¹ According to Frederick and Hildebrand,¹² $[\Delta H/(2.3026R)][1/T - 1/T_m] = 0.59$ at 298 K and this figure was used. Hildebrand and Scott¹¹ give one list of solubilities of iodine at 298 K for solvents which

they consider form complexes with iodine and another list for solvents which they believe do not form complexes. For all the compounds on the second list, except pentaerythritol tetra-perfluorobutyrate, titanium tetrachloride, the

The ratio ϕ/V_0 drops as the temperature rises; at the boiling point this ratio for many liquids is *ca.* 2.0 whilst at the critical point the ratio is only *ca.* 0.8. Thus for a permanent gas, the ratio will be even lower and the first and

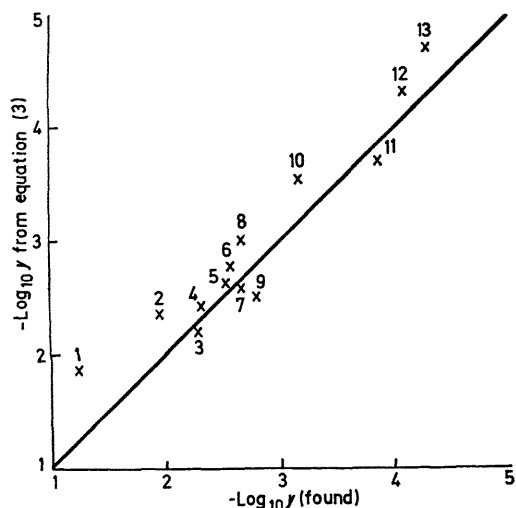


FIGURE 1. Solubilities of iodine

Solvents; 1 carbon disulphide, 2 chloroform, 3 cyclohexane, 4 carbon tetrachloride, 5 n-Heptane, 6 silicon tetrachloride, 7 2,2-dimethylbutane, 8 2,4,4-trimethylpentane, 9 octamethylcyclotetrasiloxane, 10 1,2,2-trichloro-1,1,2-trifluoroethane, 11 perfluorotributylamine, 12 perfluoromethylcyclohexane, 13 perfluoroheptane.

fluorinated cyclic ether $C_8F_{16}O$ for which densities were not given in the sources used, and dichlorohexafluorocyclobutane which is strained so that the method used to calculate the parachor would not be reliable, $\log_{10}y$ has been calculated on the assumption that there is no volume change when liquid iodine and the solvents are mixed. In Figure 1, the experimental values of $\log_{10}y$ are plotted against those calculated from equation (3) and the points lie close to a straight line of unit slope.

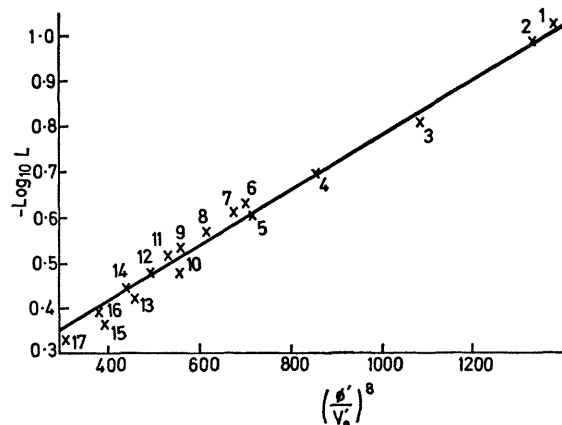


FIGURE 2. Solubilities of argon

Solvents; 1 iodobenzene, 2 nitrobenzene, 3 bromobenzene, 4 chlorobenzene, 5 toluene, 6 benzene, 7 n-tetradecane, 8 n-dodecane, 9 fluorobenzene, 10 cyclohexane, 11 n-decane, 12 n-nonane, 13 3-methylheptane, 14 n-octane, 15 2,4,4-trimethylpentane, 16 n-heptane, 17 n-hexane.

third terms on the right-hand side of equation (3) may, as a first approximation, be neglected compared with the second term. In Figure 2, the logarithms of the Ostwald coefficients L (the ratio of volume of gas absorbed to the volume of absorbing liquid) for argon^{13,14} at 298 K and one atmosphere have been plotted against $(\phi'/V_0)^8$ for the solvents. The points fall near a straight line and this indicates that equation (3) can be used not only for solutes like iodine which have to be expanded but also for those like argon which have to be compressed to give the free volume of the solvents.

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