Dispersion Energy Contribution to Solute-Solvent Interaction

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Solubility of a non-polar solute in non-polar solvents is shown to depend on solvent refractive index.

In an early paper, Born [1] had pointed out that a qualitative understanding of the process of solution of ionic compounds in water can be obtained from consideration of the change in the electrostatic self-energy of each ion when it goes into solution. This self-energy in air is $(Ze)^2/2\,r_\mathrm{i}$, where r_i is the ionic radius. In a dielectric medium of dielectric constant ε, this is given by $(Ze)^2/2\,r_\mathrm{i}$. The Gibbs free energy difference of the ion in air and in solution (per mole) is given by,

$$\Delta G = 1/2\left(1 - \frac{1}{\varepsilon}\right)\frac{(Ze)^2}{r_\mathrm{i}}\,N\,. \tag{1}$$

Although Born's picture is too simple to represent the detailed processes associated with an ion going into solution, it is a reasonable one, even today, for explaining the qualitative features, particularly the role of the statistic dielectric property of the solvent. Our object here is to demonstrate the manner in which the dielectric properties of the solvent determine the free energy in another situation, when a non-polar molecule goes into solution in a non-polar solvent.

The dispersion or van der Waals interaction between non-polar solute and non-polar solvent molecules is the main part of the free energy in the present situation. A rough estimate of this can be made by a pair-wise sum of this interaction between the solute and solvent molecules, and this can be connected with the static dielectric constant of the solvent using the relationship between the latter and the static polarisability and number density of the solute molecules. This sort of approach, however, ignores three-body and other many-body dispersion forces in the system. A more rigorous approach is possible through the use of the dispersion self-energy concept [2] employed in the analysis of solvent effects on molecular spectra [3]. The details are described in our earlier paper [3] and will not be repeated here.

The expression for the change in the dispersion self-energy of the solute molecule when it goes into solution is given by,

$$\Delta E \approx -\frac{\hbar}{i}\oint \mathrm{d}\omega \int \mathrm{d}^3 r'\,\mathrm{Tr} \cdot \Big[\underset{\text{Solvent}}{\mathbf{G}(\boldsymbol{R}, \boldsymbol{r}'; \omega)} - \underset{\text{Vac}}{\mathbf{G}(\boldsymbol{R}, \boldsymbol{r}'; \omega)}\Big]\,\alpha(\boldsymbol{r}' - \boldsymbol{R}; \omega)\,. \tag{2}$$

Here $4\pi\,\mathbf{G}(\boldsymbol{R}, \boldsymbol{r}'; \omega)$ is the dyadic Green's function giving the electric field at $\boldsymbol{R}$ with a unit dipole source at $\boldsymbol{r}'$ oscillating with the frequency ω; $\alpha(\boldsymbol{r}; \omega)$ is the polarisability density of the solute molecule. Assuming the solvent to be a dielectric continuum and employing equation (18) of our earlier paper [3], we can write the expression for the free energy change as,

$$\Delta G = N\,\Delta \mathrm{E} \approx \frac{-N\hbar}{i}\oint \mathrm{d}\omega\,\alpha(\omega)\,\frac{1}{4\pi a_\mathrm{M}^3}\,\frac{1}{\varepsilon(\omega)} - 1 \tag{3}$$

$$\approx \frac{-N\hbar}{i}\oint \mathrm{d}\omega\,\alpha(\omega)\,\frac{6}{a_\mathrm{s}^3}\,\frac{\varepsilon(\omega) - 1}{2\,\varepsilon(\omega) + 1}\,, \tag{4}$$

where (3) and (4) apply to the cases with no excluded volume and with excluded volume, respectively. Here, a_M is the radius of the solute molecule, a_s the radius of the sphere representing the excluded volume and $\varepsilon(\omega)$ the dielectric function of the solvent. We shall restrict ourselves to the realistic case where the solute molecule lies within an excluded volume.

In principle, the ω-integral (which is over a contour enclosing the positive axis) can be evaluated if we know the analytic structure of $\varepsilon(\omega)$. If the solute molecule has one principal absorption frequency

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ω_0, we can write

$$\alpha(\omega) = \alpha(0)\,\omega_0^2/(\omega_0^2 - \omega^2)\,, \tag{5}$$

where $\alpha(0)$ is the static polarisability. Thus, assuming that $\varepsilon(\omega)$ is well-behaved, (4) becomes,

$$\Delta G \approx -N\,\frac{6\pi}{a_s^3}\,(\hbar\,\omega_0)\,\alpha(0)\,\frac{\varepsilon(\omega_0)-1}{2\,\varepsilon(\omega_0)+1} \tag{6}$$

Figure 1 gives plots of the solubilities of two typical non-polar solutes, naphthalene and anthracene, in non-polar solvents, corresponding to different values of the parameter,

$$\frac{\varepsilon(\omega_0)-1}{2\,\varepsilon(\omega_0)+1} = \frac{n^2-1}{2\,n^2+1}\,, \tag{7}$$

where n is the refractive index. The trends are unmistakably according to the formula (6). The corresponding data on iodine and sulphur in non-polar solvents show similar trends, though with some scatter. We believe that the observation that solubilities of non-polar solutes in non-polar solvents can be explained on the basis of the solvent refractive index is significant.

One would not expect this sort of simple relation between solubility and dielectric constants of polar solvents because of two reasons. Firstly, the dispersion energy will be only a part of the total self-energy of the molecule in solution, the rest coming from polarisation induced by the permanent moments of the solvent molecules. Secondly, there will be strong association effects. Such lack of correlation is indeed observed.

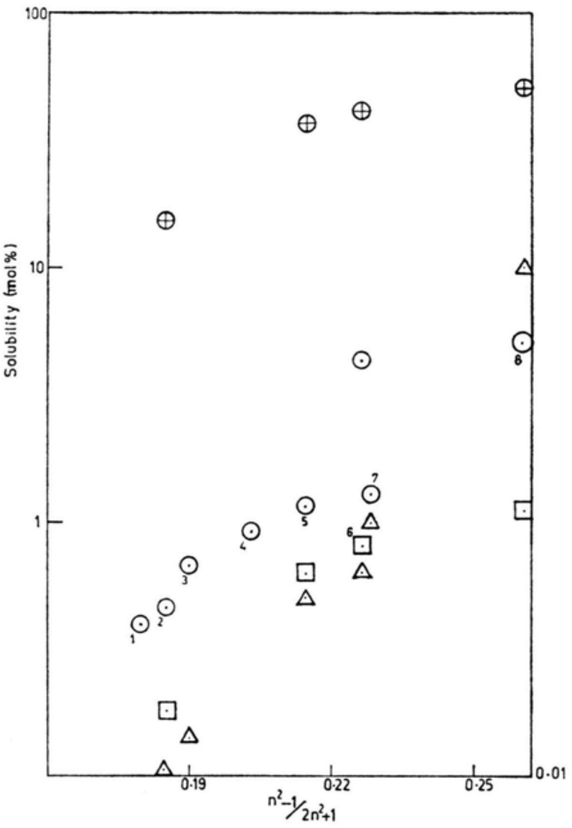

Fig. 1. Plot of solubility (in mol%) against $(n^2-1)/(2n^2+1)$ of the solvent: Circles with a cross, naphthalene; Squares, anthracene; Triangles, Sulfur; Open circles, iodine. 1. Pentane; 2. Hexane; 3. Heptane; 4. Cyclohexane; 5. Carbontetrachloride; 6. Benzene; 7. Tetrachloroethylene; 8. Carbon disulfide.

[1] M. Born, Z. Physik **1**, 45 (1920).
[2] J. Mahanty, Nuovo Cim. **22 B**, 110 (1974).
[3] J. Mahanty and C. N. R. Rao, Z. Naturforsch. **31a**, 1094 (1976).