Factors which Determine Solubility

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The factors which determine solubility in regular solutions have been analyzed by Hildebrand[1]. After being trained by Hildebrand, I have directed my efforts toward applying the regular solution concept to various non-regular solutions. I have been able to extend it to many non-regular systems[2]. However, there are also many systems where the aspects of dissolution are quite different from those in regular solutions. Particularly, the solutions of a surface active agent, a polymer (including polyelectrolyte) and a poly-soap are markedly different from regular solutions. Yet these solutions are very important for practical purposes and are interesting to tackle. The present paper was undertaken to analyse the dominant factors which determine the solubility of these substances.

Factors which Determine Solubility in Regular Mixtures.—The entropy of mixing, the heat of mixing and the free energy of the solute in equilibrium with the solute molecule in solution are the most important factors controling solubility in regular solutions. The basic solubility equation of the regular solution theory is[1]:

$$\ln a_2 = \ln x_2 + \frac{V_2 \phi_1^2 (\delta_1 - \delta_2)^2}{RT} \qquad (1)$$

where a_2 is the relative activity of the solute in equilibrium with the solute molecule in solution, x_2, the solubility expressed as mole fraction, V_2, the molal volume of solute, ϕ_1, the volume fraction of the solvent, and δ_1 and δ_2, the solubility parameters of the solvent and the solute.

Accordingly, devices to increase the solubility of certain substances at a constant temperature are 1) to decrease the heat of the solution by selecting a suitable solvent, 2) to increase the activity of the solute, for example, to increase the solute pressure in the case of gas solubility, and 3) to use a solvent of a small molecular size so that when the solubility expressed as the mole fraction, x_2, remains the same, the amount which dissolves in the same volume of solvent is large. If the use of solutes of a small molecular volume and of similar chemical properties is permitted, the solubility increases very much, because the heat of solution can be reduced by a factor of V_2'/V_2. (V_2' is the molal volume of a solute of chemical properties similar to those of solute 2.)

If the super-cooled liquid state is easily attainable and relatively stable, the solubility can be increased metastably by cooling (at the temperature at which the crystal is a preferred state for the solute). In this case a solubility increase results from the enhanced free energy. In polymer, poly-soap, and surface active agent solutions this process is a rather important one as a means of increasing the solubility.

If the temperature can be changed, one way to increase the solubility of ordinary substances is to raise the temperature, because 1) the heat of mixing usually decreases with the temperature and the heat term (second term

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[1] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", Reinhold Publishing Corp., New York (1950), p. 131. "Regular Solutions", Prentice-Hall Inc., New Jersey (1962).

[2] a) K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, 66, 577 (1962); b) K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, "Colloidal Surfactants", Academic Press Inc., New York (1962).

in Eq. 1), which is divided by the temperature, decreases more rapidly, and because 2) the relative activity of the solid increases so very rapidly that the solubility of the solid also increases very rapidly. The relative activity does not change in a liquid solute, and the solubility does not increase so much as in the case of a solid at a temperature well below critical mixing. In the case of gases, the solubility, which is usually measured under constant pressure, decreases somewhat, usually because the relative activity decreases as compared with the liquid state.

If there is a strong dipole-dipole interaction or a dipole-induced dipole interaction, the molecules orientate so as to decrease the heat of mixing. Any intermolecular force, such as hydrogen bonding or differences in the positive and negative character of the components, causes a deviation from regular behavior and increases solubility. We should now add a charge transfer force³⁾ as a new type of intermolecular force. These, the ordinary procedures to increase the solubility, are widely applicable in many non-regular systems.

Pseudo-phase Dispersion of Surface Active Agent.—The substances studied in the solution theory are usually nearly symmetrical in their physical nature. However, molecules which have completely different properties at either end show quite non-regular behavior. Yet this type of molecule, the surface active molecule, is becoming more and more important in almost all fields of industry. In the case of surface active substances, the mechanism of dissolution is quite different. If we immerse a dry surface active agent in water, the water molecule penetrates into the hydrophilic layer so that the distance between bimolecular leaflets becomes large. If the temperature is high enough for the interior of bimolecular leaflet, i. e. the hydrocarbon chain, to be in the liquid state, the hydrocarbon chains orient end to end and the hydrophilic groups are directed to the aqueous environment. This particle, consisting of scores of surface active agent molecules (ions), is called a micelle. Since the micelle is slightly more stable than the solid hydrated surface active agent, as has been discussed elsewhere²⁾, a large amount of surface active agent disperses into the solution. The micelle is a small particle compared with the wave length of light and gives a clear transparent solution. Micelles are in equilibrium with singly-dispersed surface active molecules (ions), and this saturation concentration stays almost constant above the concentration at which micelle formation begins. Hence, the solubility of a surface active agent proceeds at first, up to the critical concentration for the formation of the micelle, just like an ordinary solution, but above the CMC the solubility increases very much, without any appreciable difference in the partial molal heat, entropy or free energy. The solubility of sodium dodecyl sulfate just below the Kraff point (above this temperature, the liquid state becomes preferable) is about 0.2%, but above the Kraff point it is about 10∼20%. The longer the chain of surface active salts, the larger the ratio of the solubility. It becomes several hundred times more soluble as a result of micellar dispersion. The temperature rise is the most important process in increasing the solubility. Another device may be to change the structure of the molecule or to add a third component, such as alcohol, thus depressing the Krafft point. We may assume complete random mixing, as in the regular solution for singly dispersed molecules, but micelle formation is treated on the basis of a complete orientation and a complete non-mixing of water and surface active ions in the micelle.

Dissolution by the Addition of a Third Component.—We well know that the addition of a third component, such as acetic acid, to the benzene+water system increases the mutual solubility of water and benzene, finally leading to a single homogeneous phase. This is more or less a result of the orientation of the acetic acid. The methyl group will be directed more strongly toward the benzene molecule, and the carboxylic group may be bonded to the water molecules, on a statistical average.

The extreme case would be micelle formation by the third component and the solubilization of the second component by the micelle. In this case, the acetic acid is replaced by a paraffin chain salt. Alcohols, hydrocarbons, etc. dissolve in the aqueous phase and in the micelle. The process is something like dissolution into a heterogeneous mixture of water+hydrocarbon, the hydrocarbon chain aggregate of the surface active agent comprising the hydrocarbon medium⁴⁾. In addition, it is known that the addition of surface active agent as a third component increases the solubility of some substances, such as dimethyl phthalate⁵⁾ and some kinds of dyes, which are rather difficult to dissolve in either water or hydrocarbon. We may classify this process as partition dissolution in aqueous solution containing a pseudo-phase.

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3) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

4) M. E. L. McBain and E. Hutchinson, "Solubilization and Related Phenomena", Academic Press Inc., New York (1955).

5) J. W. McBain, "Colloid Science", Heath, Boston (1950).

Solubility of the Macromolecule.—Flory and Huggins[6] proposed to use the excess entropy of mixing due to an excess configuration based on the lattice model of a liquid. However, as was revealed by a recent study[7], the Flory-Huggins excess entropy is certainly an overestimate for a molecule which is not completely flexible.

If a polymer (macromolecule) in an equilibrium with solution is in the crystalline form, it is rather difficult to dissolve. Even a very small heat of mixing per unit volume results in a large heat of mixing per mole of polymer. However, if the polymer is in the liquid state, the solvent molecule, which is usually much smaller than the polymer, can easily dissolve because of the small heat of mixing. Even the more concentrated phase of the two phases which are in equilibrium contains much more solvent than polymer[8]. Hence, it is very important that a macromolecule be in the liquid state in order for it to dissolve in a solvent.

This can be seen from the basic solubility equation of a liquid-liquid mixture[1]:

$$\ln x'_2+\frac{V_2\phi'^2_1(\delta_1-\delta_2)^2}{RT}=\ln a_2$$

polymer rich phase

$$=\ln x_2+\frac{V_2\phi_1^2(\delta_1-\delta_2)^2}{RT} \qquad (2)$$

solvent rich phase

or

$$\ln \phi'_2+\phi'_1\left(1-\frac{V_2}{V_1}\right)+\frac{V_2\phi'^2_1(\delta_1-\delta_2)^2}{RT}=\ln a_2$$

$$=\ln \phi_2+\phi_1\left(1-\frac{V_2}{V_1}\right)+\frac{V_2\phi_1^2(\delta_1-\delta_2)^2}{RT} \qquad (2')$$

Flory-Huggins entropy of mixing is used in Eq. 2′.

In the ordinary liquid-liquid solubility of sparingly soluble compounds, $\phi_1'^2$, the volume fraction of the solvent in the solute phase, is very small, so that $\ln x'_2 \cong \ln a_2 \cong 1$.

Hence,

$$-\ln x_2 \cong \frac{V_2\phi_1^2(\delta_1-\delta_2)^2}{RT} \cong \frac{V_2(\delta_1-\delta_2)^2}{RT}$$

If the heat of mixing is large, this is compensated for by a very small value of x_2. However, in the case of polymer solutions, the volume fraction of solvent in the polymer phase is large. This is because the heat of solution of the solvent molecule in the polymer is much smaller than in the inverse process. This means that the heat term on the left-hand side of Eqs. 2 or 2′ largely cancels the heat term on the right-hand side of the equation or, in other words, that the heat of the transfer of the polymer molecule from the concentrated phase to the dilute phase is small because the volume fraction of the solvent in both phases is large. Hence, we can conclude that the dissolution of a polymer (macromolecule) essentially means the dissolution of solvent in the polymer. Polymers which do not swell in a solvent do not dissolve well.

Effect of Dissociation.—If a compound contains an ionic bond and it the solvent has a large dielectric constant, the compound dissociates in solution. Dissociation proceeds as a result of the increase of entropy, and the electrical energy for dissociation acts so as to supress dissociation. If either anion or cation is readily soluble in the solution and the opposite ion is not, the soluble ion dissolves first and the solid phase in equilibrium with the solution becomes charged and becoms more soluble because of the electrical repulsion. If the anion and cation have the same tendency to dissolve, the separate solute phase may not be charged. However, the solubility is very large because the heat of solution per ion is much smaller, approximately one half, as compared with that of an ionic pair. The solubility expressed in the unit of mole fraction increases to roughly the square root as compared with a hypothetical non-dissociated species. In fact, the saturation concentrations of a single dispersion of ionic agents are roughly the square root of those of non-ionic agents which have the same oleophilic group and a similar hydrophilic group except with regard to dissociation[2b].

Solubility of Poly-soap.—In the case of the dissolution of a poly-soap polymer, to the long chain of which soap-like side chains are attached[9], many factors come into play. The poly-soap is a polymer; hence, the molecule has to have a shape and properties which make it difficult to crystallize in order for the solvent to dissolve into poly-soap. Poly-soaps have oleophilic groups as well as hydrophilic groups in the molecule. At least a fairly large part of the molecule must be strongly solvated with solvent in order to decrease the heat of mixing. However, the most important factor in the dissolution of poly-soap seems to be 1) a large amount of dissolution of the solvent into the poly-soap and 2) something similar to an inversion of the phase in the poly-soap rich phase. This means that in the first

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6) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); P. J. Flory, ibid., **9**, 660 (1941).

7) K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, **61**, 789 (1957); **62**, 481 (1958); J. H. Hildebrand, *Z. physik. Chem.* [*N. F.*], **16**, 3 (1958).

8) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, New York (1953), p. 546.

9) U. P. Strauss and B. L. Williams, *J. Phys. Chem.*, **65**, 1390 (1961).

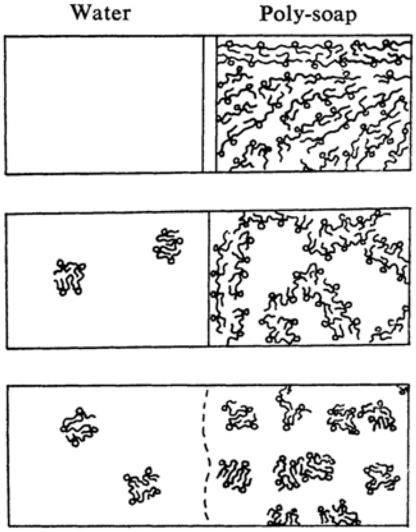

Fig. 1. Schematic diagram to illustrate probable mode of mutual dissolution of water—poly-soap.

instance the poly-soap is the solvent medium and that water (a common solvent for poly-soap) is the dispersed solute in the poly-soap phase, but in the next step the poly-soap molecules orient themselves so as to decrease the heat of mixing, hydrophilic groups being oriented outside and less hydrophilic groups inside, and finally water becomes the solvent medium and the poly-soap molecules the solute particles. Once this pseudo-phase inversion occurs in the poly-soap phase, the dispersion can be easily diluted by the very dilute poly-soap solution, formerly a separate liquid phase in an equilibrium with the poly-soap phase. The micro-Brownian motion, convection current, etc. may be sufficient for mixing. The solution is transparent because both phases are transparent. The solution may show a relatively intense light-scattering owing to the fluctuations of the concentration and the large size of the poly-soap molecule.

The addition of a certain amount of surface active agent as a third component seems to promote the solubility of the surface active polymers(10), including protein(11) in some systems.

Summary

The factors which determine solubility in various systems have been analyzed and discussed. The orientation of the molecule, the pseudo-phase dispersion, the liquid state of the solute, solvation and the pseudo-phase inversion are important factors in increasing solubility in various non-regular solutions.

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10) T. Isemura and Y. Kimura, *J. Polymer Sci.*, **16**, 90 (1955).

11) K. Aoki, *J. Am. Chem. Soc.*, **80**, 2904 (1958).