



A new theoretical model for predicting the solubility of solid solutes in different solvents



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ABSTRACT

We present a new theoretical solubility model, which uses the statistical mechanical expression of activity coefficient and an estimation equation of molar intermolecular potential energy for species in fluid mixtures. The model equation of molar intermolecular potential energy consists of non-polar (van der Waals), electrostatic and hydrogen bonding interaction terms. The average accuracy of the model in correlating the molar intermolecular potential energy of pure species (30 solvents, 10 temperature points for each solvent) is 6.6%. We have examined this model for the solubility of 15 solutes in 36 different solvents (85 systems, 302 data points) over a temperature range of 268.15–402.4 K and a wide solubility range of 10^{-7} – 10^{-1} (mole fraction scale); the overall average relative error in predicted solubility (302 data points) is 17.384%; which shows that this method is reliable for the prediction of solute solubility in various solvents.

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1. Introduction

The solubility data is essential for the design and optimization of industrial crystallization process [1,2]. When the solubility data is unavailable, a thermodynamic method is usually used to predict the solubility of solid solute in various solvents, and select appropriate solvents for the purification of crude product of pharmaceuticals. Until now, there are two main groups of solubility models [3]: correlative and predictive methods. The correlative methods include extended Hansen solubility approach [4] and extended Hildebrand solubility approach [5]. The second group methods predict the solubility of drugs by Solid–Liquid Equilibrium equation based on activity coefficient models, which comprise UNIFAC [6,7], COSMO-SAC [8–11] and NRTL-SAC [12,13] methods. The UNIFAC model [6,7] considers that molecules in solution are interacting via functional groups and a large number of group interaction parameters have been regressed by Vapor–Liquid Equilibrium and Liquid–Liquid Equilibrium experimental data. The COSMO-SAC model [8–11] interprets that the intermolecular potential energy between two molecules is the summation of local pair-wise interactions of surface segments, which is a rigorous statistical thermodynamic method with only a few adjustable

parameters. The UNIFAC [6,7], COSMO-SAC [8–11] and NRTL-SAC [12,13] methods are practical tools for drug solvent selection and crystallization process design. Our previous work [14] presented the statistical mechanical theory of fluid mixtures, which expresses the thermodynamic quantities (separation factor α_{ij} and activity coefficient γ_i) in terms of ensemble average potential energy $\langle u_i \rangle$ for one molecule.

In this work, we first develop a model equation expressing the molar intermolecular potential energy for components in solution as a function of density, temperature and composition; then obtain a new theoretical solubility model based on this energy equation, and verify the applicability of this new solubility model for practical uses.

2. Theory

2.1. Solubility predictions

The solubility of a solid solute (component 2) in a solvent (component 1) is determined by the equation of Solid–Liquid Equilibrium (SLE) [7].

$$\ln(\gamma_2 x_2) = -\frac{\Delta H_m}{RT} \left(1 - \frac{T}{T_m}\right) \quad (1)$$

where x_2 is the solute solubility (mole fraction); ΔH_m and T_m are the

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molar melting enthalpy and melting point of solid solute correspondingly; R is the gas constant; T is the system temperature; γ_2 is the activity coefficient of solute in the solution, which can be calculated by the statistical mechanical expression [14].

$$\begin{aligned}\gamma_i &= \frac{V_{m,i}^{(o)}}{V_m^{(s)}} \exp \left[\frac{(\langle u_i^{(s)} \rangle - \langle u_i^{(o)} \rangle)}{kT} \right] \\ &= \frac{V_{m,i}^{(o)}}{V_m^{(s)}} \exp \left[\frac{(U_{m,i}^{(s)} - U_{m,i}^{(o)})}{RT} \right]\end{aligned}\quad (2)$$

where $V_m^{(s)}$ is the molar volume of liquid mixture (solution), $V_{m,i}^{(o)}$ is the molar volume of pure liquid i at system temperature, $\langle u_i^{(s)} \rangle$ is the ensemble average potential energy experienced by a molecule i in liquid mixture, $\langle u_i^{(o)} \rangle$ is the mean potential energy deserved by one molecule of pure liquid i at system temperature, k is Boltzmann's constant. $U_{m,i}^{(s)}$ is the molar potential energy of component i in liquid mixture, $U_{m,i}^{(o)} = N_A \langle u_i^{(o)} \rangle$, N_A is Avogadro's constant; $U_{m,i}^{(o)}$ is the molar potential energy of pure liquid i at system temperature. The superscripts "s" and "o" stand for solution (mixture) and pure fluid, respectively.

The average potential energy for one molecule $\langle u_i \rangle$ consists of mean intra-molecular potential energy and mean intermolecular potential energy [15,16].

$$\langle u_i \rangle = \langle u_{intra,i} \rangle + \langle u_{inter,i} \rangle \quad (3)$$

We think that the mean intra-molecular potential energy term makes little difference between liquid mixture and pure liquid approximately

$$\langle u_{intra,i}^{(s)} \rangle \approx \langle u_{intra,i}^{(o)} \rangle \quad (4)$$

Substituting Eqs. (3) and (4) into Eq. (2), we obtain

$$\begin{aligned}\gamma_i &= \frac{V_{m,i}^{(o)}}{V_m^{(s)}} \exp \left[\frac{(\langle u_{inter,i}^{(s)} \rangle - \langle u_{inter,i}^{(o)} \rangle)}{kT} \right] \\ &= \frac{V_{m,i}^{(o)}}{V_m^{(s)}} \exp \left[\frac{(U_{inter,i}^{(s)} - U_{inter,i}^{(o)})}{RT} \right]\end{aligned}\quad (5)$$

where $\langle u_{inter,i}^{(s)} \rangle$ is the average intermolecular potential energy experienced by one molecule of species i in liquid mixture, $\langle u_{inter,i}^{(o)} \rangle$ is the mean intermolecular potential energy for one molecule of pure liquid i at system temperature.

The intermolecular potential energy contains contributions from non-polar (van der Waals), electrostatic (coulombic) and hydrogen bonding interactions [8].

$$u_{inter} = u_{vdw} + u_{cou} + u_{hb} \quad (6a)$$

The molar volume of mixture as a function of temperature and composition is usually unavailable for the solvent and solute system. We compute the volume ratio of the pure liquid and the mixture approximately

$$\frac{V_{m,i}^{(o)}(T)}{V_m^{(s)}(T)} \approx \frac{V_{m,i}^{(o)}(T_0)}{V_m^{(s)}(T_0)} \quad (6b)$$

$$V_m^{(s)}(T_0) \approx \sum_{j=1}^{n_c} V_{m,j}^{(o)}(T_0) x_j \quad (6c)$$

where T_0 is the reference temperature ($T_0 = 293.15\text{K}$), x_j is the mole fraction of component j , n_c is the number of components, $V_{m,i}^{(o)}(T_0)$ is the molar volume of pure liquid i at temperature T_0 .

2.2. Estimation of the hydrogen bonding energy for pure fluids

The hydrogen-bond interactions play an important role in the dissolving process of solute in polar and associating solvents, therefore the accurate description of hydrogen bonding energy is of vital importance for solute solubility predictions. The hydrogen bond [17,18] is a D–H ...:A weak link that connects a proton donor (covalently bound hydrogen atom) to a proton acceptor or lone-pair carrier (an electronegative atom or a multiple π bond). The proton acceptors [17,18] are in the upper right-hand corner of the periodic table (C, N, O, S, halogens and π -bonds). The hydrogen bond has some features of covalent bonds [19], such as directionality, specificity and saturation (a limited number of interaction partners). The strength of hydrogen bond is dependent on temperature, environment and density. We present a new expression of hydrogen bonding energy for pure fluids as follows

$$u_{hb} = -c_{hb} n_{hb} P_{acc} P_{don} \eta \frac{V^{1/3}_{cosmo}}{r_{ij}} \frac{(X_{acc} - X_{don})}{X_{don}} \quad (7)$$

where n_{hb} is the number of hydrogen bonds for a pair of molecules, η is the packing fraction, X_{acc} is the Pauling's electronegativity of proton acceptor (atom or group), X_{don} is the Pauling's electronegativity of proton donor (hydrogen atom). P_{acc} and P_{don} are hydrogen-bonding probability of acceptor and donor sit correspondingly, which is defined as

$$P(q) = \frac{1}{\sqrt{2\pi}\sigma_q} \int_0^q \exp \left[-\frac{(x - q_{hb})^2}{2\sigma_q^2} \right] dx \quad (8a)$$

where q is the absolute value of partial charge at acceptor or donor sit, q_{hb} is the charge-value cutoff for hydrogen bonding, σ_q^2 is the variance of partial charge. With this normal distribution, the full width at half maximum (fwhm) is set to $fwhm = 3\sigma_q = q_{hb}$, then Eq. (8a) becomes

$$P(q) = \frac{1}{2} \left[\text{erf} \left(\frac{q_{hb}}{\sqrt{2}\sigma_q} \right) + \text{erf} \left(\frac{q - q_{hb}}{\sqrt{2}\sigma_q} \right) \right] \quad (8b)$$

where $\text{erf}(z)$ is the error function

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) dt \quad (8c)$$

and

$$\text{erf} \left(\frac{q_{hb}}{\sqrt{2}\sigma_q} \right) = \text{erf} \left(\frac{3}{\sqrt{2}} \right) = 0.997283 \approx 1 \quad (8d)$$

Combining Eq. (8d) with Eq. (8b) gives

$$P(q) = \frac{1}{2} \left[1 + \text{erf} \left(\frac{q - q_{hb}}{0.471405q_{hb}} \right) \right] \quad (8e)$$

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