Prediction of 1-octanol–water partition coefficient and infinite dilution activity coefficient in water from the PR + COSMOSAC model

Chieh-Ming Hsieh, Shiang-Tai Lin*

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

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ABSTRACT

The Peng–Robinson equation of state (PR EOS) is used for the prediction of 1-octanol–water partition coefficients (K_{OW}) and infinite dilution activity coefficients (γ^∞). Unlike the conventional approach where the EOS parameters must be determined from the critical properties and acentric factor of each chemical species in addition to using some mixing rule to account for composition dependence, these parameters are determined here using a solvation model developed based on first principle COSMO calculations. Consequently, this approach, denoted as PR + COSMOSAC, requires input of only molecular connectivity and is capable of describing both temperature and pressure effects in fluid phase equilibria. It is found that the predicted mutual solubility of water and 1-octanol, the partition coefficient K_{OW} of a third chemical and γ^∞ in water are in good agreement with reported experimental data. In response to the 5th fluid challenge, linear correlation equations with the correlation coefficient (R^2) better than 0.96 are developed for highly accurate predictions of properties specifically for alcohols and amines.

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1. Introduction

The partition K_{OW} of a chemical species between the two liquids from partially miscible 1-octanol and water in equilibrium is considered as a measure of the hydrophobicity of the chemical. Its value was found to correlate highly with the bioaccumulation phenomena of long-lived chemicals in the food chain [1,2]. Together with the infinite dilution activity coefficients (γ^∞) in water and other thermophysical properties such as the vapor pressure, one may estimate the fate of chemical pollutants when released to the environment [3]. It was estimated that there are about 2000 new chemicals being synthesized every day [4]. It would be impractical to measure all the physical properties of all the new chemicals because of the cost and potential hazards. Therefore, a robust and reliable predictive method for the thermophysical properties such as K_{OW} and γ^∞ is highly desirable.

There have been many predictive methods developed for K_{OW} and/or γ^∞, most of which are based on group contribution [5–8], QSPR [9–11], neural network [12,13], or molecular simulations [14]. Most of these methods are highly accurate; however, they are usu-

ally limited to estimation of one type of property at one temperature with a (maybe very large) set of parameters that are parameterized using the same property of selected compounds.

A different approach, i.e., utilization of an equation of state, is taken here. An EOS provides the interrelationship between temperature, pressure, volume, and compositions and can be used in all types of fluid phase equilibrium [15–20] and thermophysical properties [21–26], including (and not limited to) K_{OW} and γ^∞. In general, input of experimental critical properties and acentric factor of each chemical species are necessary for the determination of the energetic and molecular volume parameters in a cubic EOS (CEOS). For mixtures, additional assumptions, referred to as the mixing rule, are needed to describe the composition dependence of the EOS parameters.

In this work the need of experimental input for the two parameters in the Peng–Robinson EOS is replaced by first principle solvation calculations. In particular, the solvation cavity volume is used to approximate the molecular volume parameter b, and the charging component of the solvation free energy is used to determine the energetic parameter a. All the parameters in the solvation model [27,28] have been determined previously using the vapor pressure of selected liquids. It has been shown that accurate vapor liquid equilibrium of mixtures can be obtained from the same model without using any adjustable binary interaction parameters [29,30]. This method, denoted as PR + COSMOSAC, is used directly to determine K_{OW} and γ^∞ in water.

* Corresponding author at: Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan. Tel.: +886 2 3366 1369; fax: +886 2 2362 3040.

E-mail address: stlin@ntu.edu.tw (S.-T. Lin).

2. Theory

2.1. Connection between CEOS and solvation free energy

The solvation free energy ($\Delta \underline{G}^{*sol}_{i/S}$), as defined by Ben-Naim [31], is the energy needed for transferring one molecule from a fixed position in an ideal gas phase to a fixed position in the fluid phase at constant temperature and pressure. The subscript i/S denotes solute i dissolves in solution S. The solvation free energy is usually considered to have two components, the cavity formation free energy ($\Delta \underline{G}^{*cav}_{i/S}$) and the charging free energy ($\Delta \underline{G}^{*chg}_{i/S}$), corresponding to the work needed to create a cavity (repulsive) in order to accommodate the solute and the work to turn on the interactions (attractive) between the solute and the solvent, respectively. It can be shown that the total solvation free energy can be determined from the compressibility factor $z = P\underline{V}/RT$ [32,33] as

$$\frac{\Delta \underline{G}^{*sol}}{RT} = z - 1 + \int_{\underline{V}=\infty}^{\underline{V}} \frac{(1-z)}{\underline{V}} d\underline{V} \tag{1}$$

where $\underline{V}$ is molar volume, R is ideal gas constant, and T is temperature, and the total solvation energy is the sum of solvation free energy from all the C species in the solution

$$\Delta \underline{G}^{*sol} = \sum_{i=1}^{C} x_i \Delta \underline{G}^{*sol}_{i/S} \tag{2}$$

Eq. (1) provides the basis for determining the total solvation free energy from any CEOS, for instance, in the case of the PR EOS [34]

$$z = \frac{P\underline{V}}{RT} = \frac{\underline{V}}{\underline{V} - b} - \frac{a}{RT} \frac{\underline{V}}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)} \tag{3}$$

The solvation free energy becomes

$$\frac{\Delta \underline{G}^{*sol}}{RT} = \left(\ln \frac{\underline{V}}{\underline{V} - b} + \frac{b}{\underline{V} - b} \right)$$
$$+ \frac{a}{bRT} \left[\frac{1}{2\sqrt{2}} \ln \frac{\underline{V} + b(1 - \sqrt{2})}{\underline{V} + b(1 + \sqrt{2})} - \frac{b\underline{V}}{\underline{V}^2 + 2b\underline{V} - b^2} \right] \tag{4}$$

The first term on RHS of Eq. (4) represents the repulsive interactions between molecules and is equivalent to the cavity formation free energy of hard spheres, i.e.

$$\frac{\Delta \underline{G}^{*cav}}{RT} = \ln \frac{\underline{V}}{\underline{V} - b} + \frac{b}{\underline{V} - b} \tag{5}$$

Therefore, the remaining part (second on the RHS of Eq. (4)) gives the charging free energy, that is,

$$\frac{\Delta \underline{G}^{*chg}}{RT} = \frac{a}{bRT} \left[\frac{1}{2\sqrt{2}} \ln \frac{\underline{V} + b(1 - \sqrt{2})}{\underline{V} + b(1 + \sqrt{2})} - \frac{b\underline{V}}{\underline{V}^2 + 2b\underline{V} - b^2} \right] \tag{6}$$

Thus, the temperature and composition dependent energy parameter $a(T, \underline{x})$ in PR EOS can be determined from the charging free energy by rewriting Eq. (6) as

$$a(T, \underline{x}) = \frac{b(\underline{x})}{C_{PR}} \Delta \underline{G}^{*chg}(T, \underline{x}) \tag{7}$$

where the coefficient $C_{PR} = [(1/2\sqrt{2}) \ln((\underline{V} + b(1 - \sqrt{2}))/(\underline{V} + b(1 + \sqrt{2}))) - (b\underline{V}/(\underline{V}^2 + 2b\underline{V} - b^2))]$ should be evaluated at a liquid density $(1/\underline{V})$ in accordance with that in the solvation calculations for $\Delta \underline{G}^{*chg}$. One possible choice is the infinite pressure limit where $\underline{V} = b$ and $C_{PR} = -1.123$ [30]. We have found that for vapor–liquid equilibrium of binary mixtures a value of $\underline{V} = 2.118b$ and $C_{PR} = -0.623$ leads to the best results [29].

The volume parameter b is determine from

$$b(\underline{x}) = \sum_i x_i b_i \tag{8}$$

where the volume parameter b_i for pure substance i is set to be the solvation cavity volume.

The fugacity coefficient $\bar{\phi}_i$ (or the fugacity $\bar{f}_i$) needed in phase equilibrium calculations can be obtained from [32]

$$\ln \bar{\phi}_i = \ln \frac{\bar{f}_i(T, P, \underline{x})}{x_i P}$$
$$= \frac{\Delta \underline{G}^{*chg}_{i/S}}{RT} - \ln \left(1 - \frac{Pb}{zRT} \right) + \frac{Pb_i}{zRT - Pb} - \ln z \tag{9}$$

2.2. Evaluation of solvation charging free energy

The charging free energy is evaluated in a way similar to the solvation model proposed by Lin et al. [28]. In this model, the solute is initially screened by a solvent of perfect conductor. The screening charges are then removed so that the solvent restores to its natural state. In such a case, the charging free energy contains four contributions

$$\Delta \underline{G}^{*chg}_{i/S} = \Delta \underline{G}^{*is}_i + \Delta \underline{G}^{*cc}_i + \Delta \underline{G}^{*res}_{i/S} + \Delta \underline{G}^{*dsp}_i \tag{10}$$

where the superscript is, cc, res, and dsp are the abbreviation of ideal solvation, charging correction, restoring, and dispersion, respectively.

The ideal solvation term considers the energy difference of solute in the ideal gas and in the ideal conductor state, i.e.

$$\Delta \underline{G}^{*is}_i = E^{COSMO}_i - E^{IG}_i \tag{11}$$

E^{IG}_i and E^{COSMO}_i are the total energy of molecule i in vacuum and in ideal conductor [35] and can be obtained from quantum mechanical COSMO calculation.

The charging correction which accounts for the energy shift due to a charge averaging process necessary for latter $\Delta \underline{G}^{*res}$ calculations

$$\Delta \underline{G}^{*cc}_i = f^{1/2}_{pol} [E_{diel}(\underline{q}) - E_{diel}(\underline{q}^*)] \tag{12}$$

where $f_{pol} = 0.6916$ [28] is the polarization factor. The dielectric energy is defined as $E_{diel}(\underline{q}^*) = \frac{1}{2} \sum_v \phi_v q^*_v$ where ϕ_v is the electrostatic potential due to the solute at position v and q^*_v is the screening charge at some position v on the cavity surface. $\underline{q}^*$ and $\underline{q}$ are the surface charges before and after charge averaging process. An empirical charging average method [36] is adopted

$$\sigma_m = \frac{\sum_n \sigma^*_n ((r^2_n r^2_{eff})/(r^2_n + r^2_{eff})) \exp(-f_{decay}((d^2_{mn})/(r^2_n + r^2_{eff})))}{\sum_n ((r^2_n r^2_{eff})/(r^2_n + r^2_{eff})) \exp(-f_{decay}(d^2_{mn}/(r^2_n + r^2_{eff})))} \tag{13}$$

where $\sigma_n = q_n/a_n$ is the charge density of segment (a_n is the surface area of the segment m), $r_n = \sqrt{a_n/\pi}$ is the radius of segment n, $r_{eff} = \sqrt{a_{eff}/\pi}$ ($a_{eff} = 7.50 \, \text{Å}^2$) is the radius of a standard surface segment, d_{mn} is the distance between segments m and n, and the empirical parameter f_{decay} set to 3.57. The charge averaging basically produces the effective charge density on a surface whose size a_{eff} is thought to be the average contact area between molecules in the liquid phase.

The restoring solvation free energy is the free energy needed to remove the screening charges on the molecular cavity. It is calculated from the sum of contributions from all the surface segments,