Simple Prediction of Limiting Activity Coefficients of Nonelectrolytes in Water at 25°C

Agnes M. Padovani and David Suleiman
Dept. of Chemical Engineering, University of Puerto Rico, Mayagüez, PR 00681

Many researchers have been trying to predict limiting activity coefficients of nonelectrolytes in water and found that they are complicated and include a large number of parameters which are not always available. This investigation presents a simple semiempirical model that combines the enthalpic contribution from regular solution theory, and the entropic contribution from Flory-Huggins. A single empirical parameter is introduced to correct for nonaccounted effects. The nature of this parameter indicates that it corrects the entropic description. The parameter is a linear function of the solute's molar volume. The model is extremely simple, since it only requires the molecular structure to obtain the solubility parameters and molar volumes from a group-contribution method (such as Fedors). The model has been tested with alcohols, aldehydes, amides, amines, aromatics, esters, halogenated hydrocarbons, ketones, nitro-compounds, and other miscellaneous nonelectrolytes in aqueous solutions at 25°C.

Aqueous solutions are found in almost every industrial process. Due to the wide applicability of these solutions, it is important to understand their phase equilibria behavior, so that effective separation processes can be designed. Activity coefficients (γ) describe the nonideal behavior, and can be used to design separation systems directly. Infinite-dilution activity coefficients (γ^∞) provide a descriptor for dilute solutions. They are not only vital to solve specialty separations for dilute solutions, but the two limiting activity coefficients of a binary system are the only requirements to understand the complete phase equilibria diagram, provided that a two-parameter model is applied. They also provide an indication of the size and type of intermolecular forces between unlike molecules.

Although the scientific community has looked at the prediction of γ's and γ^∞'s in numerous ways (such as ASOG, UNIFAC, MOSCED, SPACE), these models do not work well when water is the solvent. This is mainly due to the unique size and shape of the water molecule (entropic contributions), which differs from almost all other molecules. Also, the hydrogen bonding capacity of water (both as donor and acceptor) makes it a unique solvent.

Reid, Prausnitz, and Poling (1987) provide empirical relationships to describe γ^∞'s in water. However, if one examines today's database in water (Sherman et al., 1996) one can only obtain values within two to three orders of magnitude away from the correct value. Empirical correlations alone cannot describe the complex enthalpic and entropic effects in water.

Other models such as the linear solvation energy relationship (LSER) of Abraham (1993) and Sherman et al. (1996), specifically designed for aqueous solutions, might be more accurate (such as 0.294 Ln units). However, they incorporate numerous parameters (such as L^{16}, π_2^*, α_2, β_2, ν_2, P_2^{sat}), which are often not available or easily calculated.

This investigation proposes a simple semi-empirical model to predict limiting activity coefficients of nonelectrolytes in water. The model is analogous to that proposed by Ziger and Eckert (1983) for supercritical fluids (SCFs). The only requirement for the model is knowledge of the chemical structure since a group contribution approach by Fedors (1974) is used to obtain the parameters.

Model

Our model combines the residual contribution from regular solution theory (RST) (Hildebrand et al., 1980), and the combinatorial part from Flory-Huggins (FH) (Flory, 1941; Huggins, 1941). However, since this theoretical model does not properly describe the phase equilibria, an empirical parameter b is introduced to correct for nonaccounted effects

$$\ln(\gamma_2^\infty) = \left[\frac{\nu_2}{RT}(\delta_2 - \delta_1)^2 + \ln\left(\frac{\nu_2}{\nu_1}\right) + 1 - \left(\frac{\nu_2}{\upsilon_1}\right)\right] + b \quad (1)$$

δ is the solubility parameter and ν the molar volume; subscripts 2 and 1 refer to the solute and the solvent (water), respectively. R is the universal gas constant, and T the absolute temperature in this study, 298 K. δ and ν are evaluated at T.

The concept of the semi-empirical model is not new; it was first suggested by Ziger and Eckert (1983), but for SCFs. It was also used by Gurdial and coworkers (1989) in SCFs also. In their study, it was found that the intercept was a function

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Correspondence concerning this article should be addressed to D. Suleiman.

of the solute only. We tried to make the analogy from the concepts applied in SCFs and found that the intercept indeed seemed to be a function of the solute only. This investigation correlated the empirical parameter, so that predictions of b (and subsequently γ_2^∞) could be obtained.

Results

A critically reviewed database by Sherman et al. (1996) was used as the source of γ_2^∞ data at 25°C. Solubility parameters and molar volumes were obtained from the Fedors' group contribution method (Fedors, 1974) including water's $[\delta_1 = 23.4\ (\mathrm{cal/cm^3})^{1/2}$ and $\nu_1 = 18.0\ (\mathrm{cm^3/mol})]$. Using the experimental γ_2^∞ and Eq. 1, the parameter b was regressed for about 128 solutes in water (those reported by Sherman et al. (1996) with direct methods). The systems studied included alcohols, aldehydes, amides, amines, aromatics, esters, halogenated hydrocarbons, ketones, nitro-compounds, and other miscellaneous nonelectrolytes in aqueous solutions.

The parameter b was regressed and correlated with different physical properties (such as, P_2^{vap}, δ_2, ν_2, and so on). The best correlation was with the solute's molar volume. Figure 1 presents parameter b vs. the solute's molar volume for the aldehydes and the esters (two representative groups). Most of the other groups studied also had excellent correlations. The only irregularity was observed with the halogenated hydrocarbons and with miscellaneous solutes (Figure 2). The irregularity for miscellaneous solutes could be explained from their heterogeneous nature (such as acids, NMP, DMSO, and a fluorinated alcohol). A possible explanation for the halogenated hydrocarbons' group is that there might be different contributions depending on if it is a primary, secondary, or tertiary halogenated hydrocarbon, or if it has a combination of halogens. These differences might lead to different degrees of interactions that the model cannot characterize. This implies that further discrimination should be done at least for these systems. Several discrimination schemes were attempted. For example, fluorinated, chlorinated, brominated, and aromatic compounds were isolated. However, the improvement did not justify the effort. Also, since simplicity was one of the main goals of this investigation, and since the correlations were within the error of the model (discussed later), the system was not further discriminated. This observation does not imply that the proposed correlation is poor for multifunctional solutes. The correlation is weaker for such solutes, but predictions can be made within reasonable accuracy (better than that from other models).

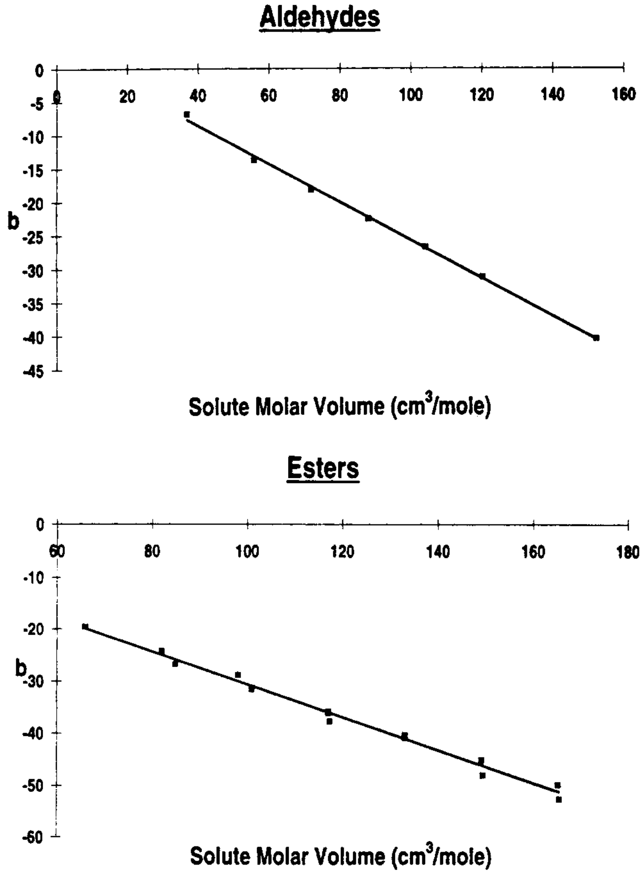

Figure 1. Correlations for parameter *b* for aldehydes and esters in water at 25°C.

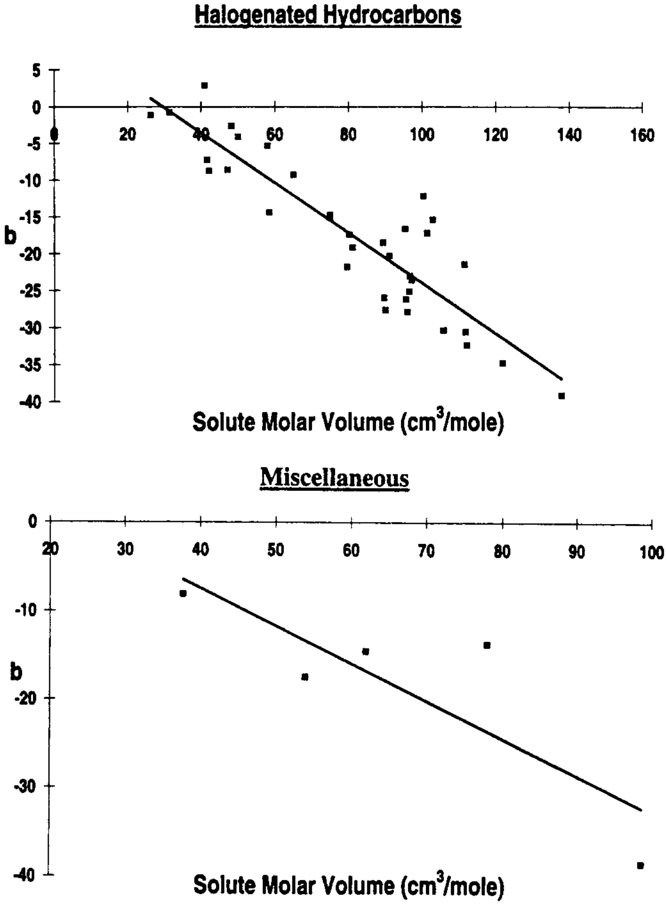

Figure 2. Correlations for parameter *b* for halogenated hydrocarbons and miscellaneous in water at 25°C.

The final equations to predict b are presented in Table 1. The estimated error in the prediction of γ_2^∞ is also shown. The equations can be used to predict b for a particular group, as needed for the subsequent calculation of γ_2^∞ (Eq. 1). When we back-calculate the γ_2^∞'s from the regressed model, the error in the predictions goes from 16% to one order of magnitude away in the worst cases (halogenated hydrocarbons and

Table 1. Correlations to Predict b

$b = mv_2$ (cm^3/mol) + b'

Group	m	b'	$r^{2\dagger}$	% Diff. in Pred. of γ_2^∞
Alcohols*	−0.2178	3.192	0.953	84
Aldehydes*	−0.2509	1.469	0.996	45
Amides*	−0.2248	−2.256	1.000	0
Amines*	−0.5057	16.276	1.000	0
Aromatics	−0.2797	6.823	0.949	90
Esters*	−0.2744	−1.159	0.985	54
Halogenated Hydrocarbons	−0.3104	8.972	0.773	127
Ketones*	−0.2585	−2.150	0.958	66
Miscellaneous*	−0.4235	9.506	0.709	151
Nitriles*	−0.2453	3.126	0.993	50
Nitro-compounds	−0.2218	4.207	0.999	16
All solutes	−0.3640	10.190	0.819	121

*No aromatics substances included.

**All correlations should be used over the range of ν_2 studied (25–175 cm^3/mol).

†Linear regression parameter (1.000 = perfect fit).

miscellaneous). This might seem high; however, the empirical correlations can only predict these values within two to three orders of magnitude. UNIFAC can predict from 22% to one order of magnitude away in the worst cases (amines, miscellaneous, and halogenated hydrocarbons). Looking at all the solutes studied, our model (% difference = 74%) does slightly better than UNIFAC (% difference = 86%). However, our method is much simpler, and our parameter is easier to obtain/predict. The model presented by Sherman et al. (1996), might be more precise than ours for the halogenated hydrocarbons and the miscellaneous, but in general our model is better than theirs (% difference ~ 100%) for the solutes studied. Sherman and coworkers (1996) used a second database of inverse solubility data whose accuracy is unknown. This database was not included in our study.

The accuracy of the used data is about 10% for γ_2^∞ values less than 1,000, and 20% for γ_2^∞ higher than 1,000 (Sherman et al., 1996). Since the accuracy of the model is limited by the accuracy of the data itself, we conducted an error analysis of our model. Given a 10–20% error in the γ_2^∞ values, a 10% error in the molar volumes, and 10–20% error in the solubility parameter, the prediction should have a margin of error of at least 50–70%.

An attempt to correlate all solutes is presented in Figure 3. The complete correlation for all the solutes studied is also presented in Table 1. When the general equation is used, the correlation is good to predict γ_2^∞ within one order of magnitude only. Although this general correlation is not capable of describing all the solutes within a reasonable accuracy, the relationship is pleasantly surprising. The incredible feature is how this simple model can describe such an extensive array of nonelectrolytes so well. This is exactly the major accomplishment of the model, since no other simpler model can predict the complex phase equilibria behavior of nonelectrolytes in water effectively.

Although RST properly addresses the enthalpic contribution in water, the entropic contributions are not well described by FH. RST was never intended for polar molecules. Apparently, the enthalpic contribution when water is used as the solvent, which comes mostly from the hydrogen-bonding effect, seems to be consistently represented by RST. The parameter b seems to correct the entropic characterization of water (because of its molar volume dependence), which is not properly done with FH.

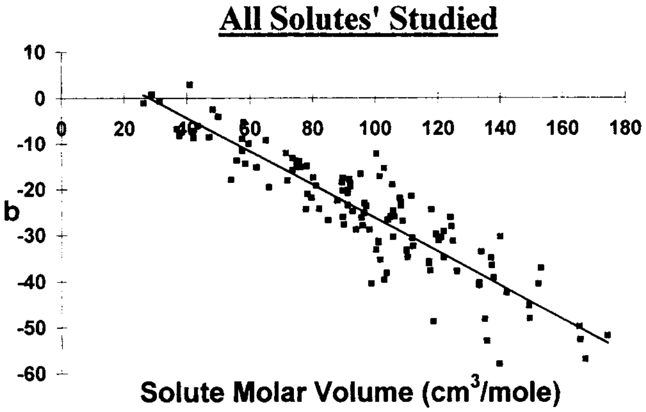

Figure 3. Correlation for parameter *b* for all solutes studied in water at 25°C.

Conclusions

A simple semi-empirical model to predict limiting activity coefficients of nonelectrolytes in water at 25°C was presented. The main advantage of the model is simplicity, since only knowledge of the molecular structure is required to obtain the parameters from a group-contribution method (that is, Fedors). The model has been tested with alcohols, aldehydes, amides, amines, aromatics, esters, halogenated hydrocarbons, ketones, nitro-compounds, and other miscellaneous nonelectrolytes in aqueous solutions. Predictions can be as accurate as the experimental data if individual correlations are used, but a simpler overall correlation can still provide results that are within one order of magnitude from the correct value.

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