Comments on the Competitive Preferential Solvation Theory

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Simple additive relationships for the physico-chemical properties of a solute dissolved in binary solvent mixtures are developed from the competitive preferential solvation model. Additive expressions for solute mole fraction solubility and logarithm of solute solubility are mathematically identical to equations derived previously from the microscopic partition and basic nearly ideal binary solvent models. Calculated values based on the various additive relationships are compared to carbazole solubilities in ten binary solvent mixtures containing dibutyl ether with n-hexane, n-heptane, n-octane, cyclohexane, cyclo-octane, methylcyclohexane, iso-octane, n-hexadecane, squalane and t-butylcyclohexane.

In two recent papers,^{1,2} B. Nagy and co-workers used the competitive preferential solvation (COPS) theory to explain ion transport in liquid membranes and solute spectroscopic properties in binary solvent mixtures containing weak molecular association complexes. Our aim is not to criticize the controversial COPS model, but rather to point out several important similarities and differences between expressions based on the COPS model and those derived from conventional non-electrolyte solution models. According to the COPS theory the solvent components B and C compete for solvating the solute (component A) to the extent of their electronic-geometric affinity $P_{A(B)}$ and $P_{A(C)}$, respectively. Solvents B and C continuously relax between complexing and solvating states in the solvation shell. The composition of the latter depends not only on these affinity constants but also on the number of potentially available solvent molecules present in the binary solvent mixture, i.e. on their actual molar concentrations C_B^0 and C_C^0 (expressed as molarities). When solvent-solvent interactions may be neglected, the solvent effect on a given physico-chemical property (W) is considered to be additive.^{1–3}

$$W = g_B^0(W_A)_B + g_C^0(W_A)_C$$

$$g_B^0 = 1 - g_C^0 = P_{A(B)} C_B^0 / (P_{A(B)} C_B^0 + P_{A(C)} C_C^0) \quad (1)$$

$$= P_{A(B)} X_B^0 / (P_{A(B)} X_B^0 + P_{A(C)} X_C^0)$$

where g_i^0 is the generalized partitioning factor, X_i is the mole fraction, and $(W_A)_B$ and $(W_A)_C$ refer to the actual properties measured in pure B and C solvents, respectively. Experimentally the majority of complexation studies are performed near infinite dilution of the solute, and in practice the solvent molar and mole fraction compositions are calculated as if the solute were not present. When the appropriate COPS equation is developed for a given physicochemical technique its linearization allows one to characterize quantitatively the solute-solvent interactions.

There are a number of physicochemical properties that one might wish to consider. Assuming for a moment that the reciprocal of the solute infinite dilution activity coefficient, $1/(\gamma_A^\infty)$, is the additive property, then eqn (1) becomes

$$\frac{1}{\gamma_A^\infty} = \frac{g_B^0}{(\gamma_A^\infty)_B} + \frac{g_C^0}{(\gamma_A^\infty)_C} \quad (2)$$

This particular mathematical form is by no means unique. It corresponds to the generalized form of the microscopic parti-

tion model^{4–6}

$$\frac{1}{\gamma_A^\infty} = \frac{X_B^0}{(\gamma_A^\infty)_B} + \frac{X_C^0}{(\gamma_A^\infty)_C} \quad (3)$$

which has appeared in the chemical literature in terms of chromatographic partition coefficients, K_R ,^{4–10}

$$K_R = \phi_B^0(K_R)_B + \phi_C^0(K_R)_C$$

$$\phi_B^0 = 1 - \phi_C^0 = X_B^0 \bar{V}_B / (X_B^0 \bar{V}_B + X_C^0 \bar{V}_C) \quad (4)$$

and saturation solubilities of solid solutes, $X_A^{\text{sat}} = a_A^{\text{solid}}/\gamma_A^{\text{sat}}$,¹¹

$$X_A^{\text{sat}} = X_B^0(X_A^{\text{sat}})_B + X_C^0(X_A^{\text{sat}})_C \quad (5)$$

where $\gamma_A^{\text{sat}} \approx \gamma_A^\infty$, ϕ_i is volume fraction, $\bar{V}_i$ is the molar volume of component i and a_A^{solid} refers to the activity of the solid solute. The activity is defined as the ratio of the fugacity of the solid to the fugacity of the pure hypothetical subcooled liquid. During the past several years, Purnell, Laub and co-workers^{2–8} have reported that this simple linear relationship between solvent volume fraction and partition coefficient is obeyed in over 300 systems studied to date, irrespective of the complexing nature of the solvents. Based on the mathematical equivalence of eqn (2) and (3) when the affinity constant ratio is unity, i.e. $P_{A(B)}/P_{A(C)} = 1$, we claim that the COPS model will describe the same 300 systems. Realizing now that both models describe more than 300 different systems, it will be fruitless to argue the validity of one theoretical model over the other solely on the basis of 'goodness of fit' of experimental data.

Note also that if one assumes that infinite dilution partial molar Gibbs free energy, $(\Delta \bar{G}_A^{\text{ex}})^\infty$, is additive, then eqn (1) is

$$(\Delta \bar{G}_A^{\text{ex}})^\infty = g_B^0(\Delta \bar{G}_A^{\text{ex}})_B^\infty + g_C^0(\Delta \bar{G}_A^{\text{ex}})_C^\infty \quad (6)$$

$$(\Delta \bar{G}_A^{\text{ex}})_i^\infty = RT \ln (\gamma_A^\infty)_i = RT \ln [a_A^{\text{solid}}/(X_A^{\text{sat}})_i];$$

$$i = B, C$$

$$\ln X_A^{\text{sat}} = g_B^0 \ln (X_A^{\text{sat}})_B + g_C^0 \ln (X_A^{\text{sat}})_C \quad (7)$$

identical to expressions derived from the nearly ideal binary solvent (NIBS) model^{12–15}

$$\ln X_A^{\text{sat}} = f_B^0 \ln (X_A^{\text{sat}})_B + f_C^0 \ln (X_A^{\text{sat}})_C$$

$$+ \Gamma_A (X_B^0 \Gamma_B + X_C^0 \Gamma_C)^{-1} (RT)^{-1} \Delta \bar{G}_{BC}^{\text{ex}} \quad (8)$$

$$f_B^0 = 1 - f_C^0 = X_B^0 \Gamma_B / (X_B^0 \Gamma_B + X_C^0 \Gamma_C)$$

except that Γ_i refers to pure-component weighting factors, rather than affinity constants. The NIBS weighting factors provide a rough measure of the skew of the binary $\Delta \bar{G}_{ij}^{\text{ex}}$ mixing property from a symmetric curve with an extremum at the equimolar composition. Past studies have documented

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Table 1. Comparison of experimental carbazole solubilities to calculated values based on the competitive preferential solvation and extended NIBS models

solvent (B)–solvent (C)	eqn (2)				eqn (7)		eqn (9)	
	ratio ^a	dev. ^b	ratio	dev.	ratio	dev.	K_{AC}^ϕ	dev.
n-hexane–dibutyl ether ^c	1.00	31.8	1.88	3.2	0.35	6.6	24.0	2.0
n-heptane–dibutyl ether	1.00	31.4	1.88	3.5	0.39	5.7	22.0	1.8
n-octane–dibutyl ether	1.00	25.4	1.77	2.5	0.37	6.1	25.0	1.7
cyclohexane–dibutyl ether	1.00	11.8	1.26	1.9	0.26	6.6	24.0	2.2
methylcyclohexane–dibutyl ether	1.00	12.9	1.30	2.6	0.29	5.3	26.0	1.8
cyclo-octane–dibutyl ether	1.00	3.7	0.91	2.3	0.25	3.1	25.0	2.1
iso-octane–dibutyl ether	1.00	37.4	2.17	4.5	0.39	5.6	30.0	1.7
n-hexadecane–dibutyl ether	1.00	22.7	1.75	1.3	0.52	3.9	24.0	1.4
squalane–dibutyl ether	1.00	23.3	2.11	2.2	0.79	3.8	23.0	1.7
t-butylcyclohexane–dibutyl ether	1.00	12.4	1.33	1.6	0.32	4.4	30.0	1.5

^a Affinity constant ratios, $P_{A(B)}/P_{A(C)}$, used in the calculations. ^b Deviations = $100/N \sum |\ln(X_A^{\text{cal}}/X_A^{\text{exp}})|$. ^c Experimental data taken from papers by McCargar and Acree.^{23–25}

that eqn (7) provides very reasonable predictions for naphthalene, anthracene, biphenyl, iodine, benzoic acid, benzil, *p*-benzoquinone and pyrene solubilities in binary solvent systems that are free of association when weighting factors are approximated by molar volumes.^{13–20} Justification for approximating weighting factors with molar volumes can be found in the literature in the form of comparisons between the basic NIBS model and the Scatchard–Hildebrand solubility parameter theory.²¹ The majority of solvent systems studied thus far were nearly ideal, and contributions from the $\Gamma_A \Delta \bar{G}_{BC}^{\text{st}}/(X_B^0 \Gamma_B + X_C^0 \Gamma_C)(RT)$ ‘unmixing’ term amounted to only a few per cent of the predicted value. Through judicious selection of the affinity constant ratio, the COPS model should also be able to describe these solubility data.

Similarities between eqn (1)–(4), and eqn (7) and (8) suggest that the COPS model may be applicable to a much larger number of thermodynamic and physical properties than hitherto envisioned. However, the model is not expected to describe all systems which might be encountered. As an example, the basic NIBS model is limited in application to systems containing only non-specific interactions. Expressions for systems containing solute complexation with a single solvent^{22–25}

$$\begin{aligned}
 A_1 + C_1 &\rightleftharpoons AC; \quad K_{AC}^\phi = \hat{\phi}_{AC}/(\hat{\phi}_{A_1} \hat{\phi}_{C_1}) \\
 \ln \phi_A^{\text{sat}} &= \phi_B^0 \ln(\phi_A^{\text{sat}})_B + \phi_C^0 \ln(\phi_A^{\text{sat}})_A \\
 &+ \ln[1 + \bar{V}_A K_{AC}^\phi \phi_C^0/(\bar{V}_A + \bar{V}_C)] \\
 &- \phi_C^0 \ln[1 + \bar{V}_A K_{AC}^\phi/(\bar{V}_A + \bar{V}_C)] \\
 &+ \frac{\bar{V}_A \Delta \bar{G}_{BC}^{\text{th}}}{RT(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)} \quad (9)
 \end{aligned}$$

and for systems where the solute complexes with both solvent components^{26,27}

$$\begin{aligned}
 A_1 + C_1 &\rightleftharpoons AC; \quad K_{AC}^\phi = \hat{\phi}_{AC}/(\hat{\phi}_{A_1} \hat{\phi}_{C_1}) \\
 A_1 + B_1 &\rightleftharpoons AB; \quad K_{AB}^\phi = \hat{\phi}_{AB}/(\hat{\phi}_{A_1} \hat{\phi}_{B_1}) \\
 \ln \phi_A^{\text{sat}} &= \phi_B^0 \ln(\phi_A^{\text{sat}})_B + \phi_C^0 \ln(\phi_A^{\text{sat}})_C \\
 &- \phi_B^0 \ln[1 + \bar{V}_A K_{AB}^\phi/(\bar{V}_A + \bar{V}_B)] \\
 &- \phi_C^0 \ln[1 + \bar{V}_A K_{AC}^\phi/(\bar{V}_A + \bar{V}_C)] \\
 &+ \ln[1 + \bar{V}_A K_{AB}^\phi \phi_B^0/(\bar{V}_A + \bar{V}_B)] \\
 &+ \bar{V}_A K_{AC}^\phi \phi_C^0/(\bar{V}_A + \bar{V}_C)] \\
 &+ \frac{\bar{V}_A \Delta \bar{G}_{BC}^{\text{th}}}{RT(X_B^0 \bar{V}_B + X_C^0 \bar{V}_C)} \quad (10)
 \end{aligned}$$

have much different mathematical forms. It is doubtful whether eqn (6) will be able to imitate the behaviour of the extended NIBS and competitive associated NIBS models, eqn (9) and (10), respectively.

Table 1 summarizes the ability of the COPS model to describe published carbazole solubilities in ten binary dibutyl ether–alkane solvent mixtures. The various affinity constant ratios were selected so as to reduce differences between the calculated and observed values. For completeness, we have included calculations based on the extended NIBS model. Inspection of the first six columns of table 1 reveals that the COPS model fails to describe the measured solubility data. Absolute average deviations for the ‘most realistic’ of the three additive equations, eqn (7), are on the order of 4–8%. Eqn (5) grossly overpredicts the observed solubilities. It is only by assuming that carbazole is preferentially solvated by the inert hydrocarbon cosolvent B, $P_{A(B)} > P_{A(C)}$, can the deviations of eqn (2) be reduced. This assumption is completely inconsistent with the experimental data. Carbazole is over 15 times more soluble in dibutyl ether than in any of the hydrocarbon cosolvents studied. Furthermore, spectroscopic studies of carbazole with similar ethers, such as tetrahydrofuran^{28,29} and dipropyl ether,³⁰ also suggest complexation between carbazole and dibutyl ether. In comparison, the extended NIBS model [eqn (9)] described the carbazole solubilities to within an average deviation of 2% using a single carbazole–dibutyl ether association constant, which varied from $K_{AC}^\phi = 22$ for n-heptane to $K_{AC}^\phi = 30$ for iso-octane. The success of eqn (9) is even more remarkable if one realizes that the mole fraction solubilities covered up to a 25-fold range, and the inert cosolvents included both small (cyclohexane, n-hexane) and large (n-hexadecane, squalane) saturated hydrocarbon molecules. Expressed in terms of molar concentrations, the magnitude of the carbazole–dibutyl ether association constant of $K_{AC}^\phi = 1.76$ –2.39 does indicate a very weak molecular complex. Failure of the COPS model to describe these ten non-electrolyte systems documents that the model does have its limitations. Recalling that the COPS model was developed specifically as an alternative thermodynamic treatment for systems having weak molecular complexation, its failure in the present study is particularly disturbing. One naturally must wonder if published affinity constant ratios are meaningful. For example, in the recent study of the electronic spectroscopic behaviour of copper chloride with both 4-ethylpyridine and 2,4-dimethylpyridine Szpakowska and B. Nagy² noted an unusual order of interacting power of the inert cosolvents, namely benzene > n-heptane > n-hexane > cyclohexane > chlorobenzene. Of the

five cosolvents, chlorobenzene surprisingly turned out to be the weakest interacting cosolvent. In closing, readers are reminded that it is only through continued testing and objective questioning, of which failures are an important part, that we recognize the deficiencies in our ability to describe thermodynamically a particular non-electrolyte system. It is hoped that the comments made in the present study will prompt the future development of better thermodynamic solution models.

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