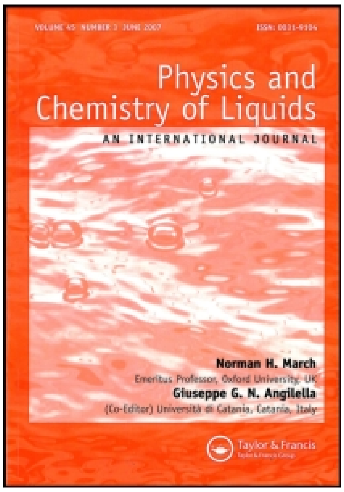

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Spectrochemical Investigations of Preferential Solvation: 4. Determination of Local Composition from Observed Probe Absorption/Emission Wavelength Shifts in Binary Solvent Mixtures

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SPECTROCHEMICAL INVESTIGATIONS OF PREFERENTIAL SOLVATION: 4. DETERMINATION OF LOCAL COMPOSITION FROM OBSERVED PROBE ABSORPTION/EMISSION WAVELENGTH SHIFTS IN BINARY SOLVENT MIXTURES

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Spectroscopic probe methods have been used in recent years to determine the local solvent composition around the dissolved solute probe. The basic method assumes that the reciprocal of the absorption wavelength, λ_{abs}, is

$$1/\lambda_{\text{abs}} = Y_A(1/\lambda_{\text{abs}})_A + Y_B(1/\lambda_{\text{abs}})_B$$

a weighted local mole fraction composition (Y_A and Y_B) average of values measured in the two pure solvents $(1/\lambda_{\text{abs}})_A$ and $(1/\lambda_{\text{abs}})_B$. Though used in numerous probe studies, the additive relationship has been derived only in the special case involving noncomplexing binary solvent systems. Derivations are presented for obtaining the simple additive relationship from the Ideal Associated Solution model, the Kretschmer-Wiebe self-association model, the Mecke-Kempter self-association model and Mobile Order theory.

KEY WORDS AND PHRASES: Spectroscopic probe methods, hydrogen bonding, self-association.

INTRODUCTION

Mixed solvents are encountered in numerous chemical, pharmaceutical and engineering applications involving separations, extractions, solubilizations, organic chemical synthesis, reaction rate and mechanistic studies, and in hydrometallurgical processes. Often, mixed solvents are the default medium from nature as is the case with crude oil samples. Over the past 50 years considerable attention has been devoted to measuring physical and thermodynamic properties of multicomponent liquid mixtures, to establishment of data bases for easy retrieval of mixture properties, and to development of theoretical solution models to enable prediction of unknown multicomponent properties from readily available pure component and published binary data.

Interpretation of solution nonideality generally has followed two dissimilar lines: the "physical" approach originated by van Laar[1] and the "chemical" approach

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proposed by Dolezalek.[2] The physical approach may be described in terms of a random distribution of molecules throughout the entire solution while the chemical approach is characterized by a specific geometric orientation of one molecule with respect to an adjacent molecule. Even in systems known to contain specific interactions, the need to properly account for nonspecific interactions has been recognized. Arnett *et al.*[3] with their "pure base" calorimetric method for determining enthalpies of hydrogen bond formation attempted to separate specific and nonspecific interactions. The sensitivity of the numerical results to the selection of "model" compound and inert solvent raised important doubts regarding the overall effectiveness of this particular method.[4] Saluja *et al.*[5] used a somewhat similar rationale in their comparison of enthalpies of transfer of alkanes and alkenes from the vapor state to methanol, dimethylformamide, benzene and cyclohexane, with the more exothermic values for the alkenes in methanol and dimethylformamide attributed to dipole-induced dipole interactions between the solvent and the polarizable π-cloud. Bertrand[6] demonstrated that neglect of nonspecific interactions in the chloroform + triethylamine system can lead to an appreciable error in the enthalpy of complex formation determined with the Ideal Associated Solution (IAS) model. Fenby *et al.*[7] presented a similar analysis of the diethyl ether + chloroform system. Smith and Hepler[8] extended the IAS model to ternary triethylamine + chloroform + cyclohexane mixtures and introduced two empirical "correctional" terms to account for triethylamine-cyclohexane and chloroform-cyclohexane nonspecific interactions. The correctional terms, which are calculable from measured binary data, have shown only limited success when used to predicted excess enthalpies and excess volumes of ternary acetone + cyclohexane + chloroform[9,10] and acetone + bromoform + alkane mixtures.[11,12] Thermodynamic consequences of the IAS model have been presented in three monographs,[13-15] several articles[16-23] and a review,[24] along with discussions of applications to select nonelectrolyte systems.

Thermodynamic studies of very weak association complexes are particularly difficult as nonspecific interactions can contribute significantly to the overall solution nonideality. Furthermore, it is conceivable that the observed nonideal behavior might simply result from preferential solvation of the solute by one of the solvent components without the formation of a distinct new chemical species. Often there is no definitive experimental evidence to prove the existence of molecular complexes in solution, and in such cases, the measured thermodynamic properties can be described equally well by one of the many associated solution models[13-15,20,21,25-30] or semiempirical local composition/preferential solvation models[13-15,30-35] derived during the past several years.

Spectroscopic probe techniques provide a convenient experimental means to study preferential solvation, which can be used to support (and perhaps to discredit) interpretations derived from calorimetric and other thermodynamic data. Preferential solvation arises whenever the proportion of molecules of any given solvent component within the probe's solvational microsphere is not equal to the bulk mole fraction composition. Although not always stated explicitly, must published spectroscopic probe techniques[34,36-42] assume an idealized situation where solvent-solvent interactions are neglected and the measured spectral response, R, in a binary solvent mixture is given by

$$R = Y_A R_A^0 + (1 - Y_A) R_B^0 \tag{1}$$

a weighted local mole/volume fraction average of the probe's spectral responses in the two pure solvents, R_A^0 and R_B^0. Initial studies treated Eqn. (1) more or less as an intuitive relationship of assumed mathematical form. Few attempts have been made in very recent years to rigorously derive this simple linear relationship. Skwierczynski and Connors[43] claimed to have derived Eqn. (1) (with $R = 1/\lambda_{\text{abs}}$) from a competitive two-step solvational exchange model

$$RA_2 + B \rightleftharpoons RAB + A \quad K_1 = X_{RAB}X_A/(X_{RAA}X_B)$$

$$RAB + B \rightleftharpoons RB_2 + A \quad K_2 = X_{RBB}X_A/(X_{RAB}X_B)$$

in which each step is described by a thermodynamic equilibrium constant. Careful examination[44] of the authors' approach revealed that the derivation violated the Beer-Lambert law in regards to absorption additivity in solutions containing multiple light-absorbing solvational chromophores (RA_2, RB_2 and RAB).

Acree and coworkers[44,45] offered a completely different derivation based upon expressing the chromophore's ground-state and excited-state energies in terms of expressions derived from the Nearly Ideal Binary Solvent (NIBS) model.[46–48] The solvational sphere was treated as a pseudo binary solvent mixture of composition Y_A and $1 - Y_A$, and the chromophore's energies were written as

$$E_R^{GS} = Y_A^{GS} E_{R,A}^{GS} + (1 - Y_A^{GS}) E_{R,B}^{GS} - \Delta E_{AB}^{\text{mix}} (\text{at } Y_A^{GS}) \tag{2}$$

$$E_R^{ES} = Y_A^{ES} E_{R,A}^{ES} + (1 - Y_A^{ES}) E_{R,B}^{ES} - \Delta E_{AB}^{\text{mix}} (\text{at } Y_A^{ES}) \tag{3}$$

weighted mole fraction averages of energies in the two pure solvents minus the energy needed to create the "solvent cavity" wherein the chromophore resides. The change in the energy corresponding to the ground state→excited state transition:

$$\text{Chromo} (\text{at} Y_A^{GS}) + h\nu_{\text{abs}} \rightarrow \text{Chromo}^* (\text{at} Y_A^{GS})$$

$$\Delta E_{\text{trans}} = Y_A^{GS} (E_{R,A}^{ES} - E_{R,A}^{GS}) + (1 - Y_A^{GS}) (E_{R,B}^{ES} - E_{R,B}^{GS}) \tag{4}$$

$$\text{Chromo} (\text{at} Y_A^{GS}) + h\nu_{\text{abs}} \rightarrow \text{Chromo}^* (\text{at} Y_A^{ES})$$

$$\Delta E_{\text{trans}} = Y_A^{ES} E_{R,A}^{ES} - Y_A^{GS} E_{R,A}^{GS} + (1 - Y_A^{ES}) E_{R,B}^{ES} - (1 - Y_A^{GS}) E_{R,B}^{GS}$$

$$- \Delta E_{AB}^{\text{mix}} (\text{at } Y_A^{ES}) + \Delta E_{AB}^{\text{mix}} (\text{at } Y_A^{GS}) \tag{5}$$

depends upon whether a change in the solvational sphere composition occurs during the excitation process. The latter transition was excluded on the argument that an electronic transition is rapid compared to nuclear motion (Frank-Condon principle). Solvent molecules contain several atoms/nuclei which are "fixed" in space with chemical bonds. Molecular diffusion, viewed as movement of several nuclei, should be much slower than an electronic transition. Since absorption wavelength is inversely proportional to $|E_R^{ES} - E_R^{GS}|$, Eqn. (4) predicts that

$$1/\lambda_{\text{abs}} = Y_A^{GS}(1/\lambda_{\text{abs}})_A + (1 - Y_A^{GS})(1/\lambda_{\text{abs}})_B \qquad (6)$$

reciprocals of the absorption wavelength, $1/\lambda_{\text{abs}}$, are additive on a preferential solvation basis.

Readers are reminded that this latter derivation used the NIBS model, and is thus restricted to solvent mixtures which contain only nonspecific physical interactions. Specific interactions are excluded from the basic NIBS model. In the present study we extend our earlier discussions[44,45] to include the more complex solvent systems which involve either heterogeneous solvent-solvent complexation (A_iB_j) or a self-associating solvent component. Solution models considered include the Kretschmer-Wiebe self-association model, the Mecke-Kempter self-association model, the Ideal Association Solution (IAS) model with nonspecific interactions added, and Mobile order theory.

DERIVATION BASED UPON THE KRETSCHMER-WIEBE SELF-ASSOCIATION MODEL

For years one of the more challenging problems facing researchers in the field of solution thermodynamics has been the prediction of phase equilibria in hydrogen bonding systems containing a self-associating alcohol cosolvent. Much of the earlier research concerning mixtures containing alcohols, as summarized by Pimentel and McClellan,[49] treated hydrogen bonding as a stepwise polymerization process resulting in a continuum of species. Thus, at low alcohol concentrations dimers would be the predominant polymeric species, with larger polymer chains becoming more significant with increasing alcohol concentration. Van Ness *et al.*[50] compared infrared data with heat of mixing data for ethanol + *n*-heptane and ethanol + methylbenzene, and concluded that the results were best explained by a model containing monomers, cyclic dimers and linear polymers having 20 or more units per chain. Tucker and Christian[51] noted that the simplest model (1–3–∞) that can adequately describe the vapor pressure data for ethanol + *n*-hexadecane systems contained two equilibrium constants, one for trimer formation and the other for the sequential addition of the monomer. Other studies have indicated that a simple polymer of definite size may dominate. Fletcher and Heller[52,53] explained the infrared data of 1-octanol in *n*-decane (from dilute solutions to the pure alcohol) in terms of a monomer-tetramer self-association model. Dixon[54] also found that the monomer-tetramer model gave the best correlations for his proton magnetic resonance data on the hydroxyl shift for methanol dissolved in cyclohexane. Anderson *et al.*[55,56] explained the vapor pressures of several linear and branched alcohols in 2,2,4-trimethylpentane with a monomer-pentamer model.

The excess Gibbs free energy ΔG_{RAB}^{ex} for a ternary solution containing an inert chromophore (component *R*), a saturated hydrocarbon (component *B*) and alcohol cosolvents is described by the sum of two separate contributions, one contribution representing the chemical interactions and the other representing physical interactions:

$$\Delta G^{ex}_{RAB} = (\Delta G^{ex}_{RAB})_{\text{chem}} + (\Delta G^{ex}_{RAB})_{\text{phys}} \tag{7}$$

This separation is an artificial one because there is no sharp dividing line between interactions that may be regarded as strictly physical in origin and those that may be regarded as purely chemical in nature. Nevertheless, the distinction between the two contributions is useful if one of the contributions is much smaller than the other.

The chemical contribution is based upon the Kretschmer-Wiebe association model$^{57-60}$ that basically assumes the alcohol forms continuous hydrogen-bonded polymers, $A_1, A_2, A_3, \ldots, A_i, \ldots$ by successive chemical reactions:

$$A_i + A_1 \rightleftharpoons A_{i+1}$$

described by a single isodemic equilibrium constant of the form

$$K_A = \left[\frac{\hat{\phi}_{A_{i+1}}}{(\hat{\phi}_{A_1}\hat{\phi}_{A_i})}\right]\left[\frac{i}{(i+1)}\right] \tag{8}$$

with the volume fraction of the i-mer calculated using the molar volume of the monomer multiplied by i. The overscript ($\hat{}$) used in this and subsequent sections denotes values for the "true" associated solution. An isodemic equilibrium constant is defined as having identical numerical values for each consecutive, stepwise association.

The overall stiochiometric volume fraction of the alcohol (ϕ_A) is the sum of the volume fractions of each individual alcohol species:

$$\phi_A = \sum_{i=1}^{\infty} \hat{\phi}_{A_i} = \left(\frac{1}{K_A}\right)\sum_{i=1}^{\infty} i(K_A\hat{\phi}_{A_1})^i = \hat{\phi}_{A_1}(1 - K_A\hat{\phi}_{A_1})^{-2} \tag{9}$$

It should be noted that $|K_A\hat{\phi}_{A_1}| < 1$ for the infinite series to converge. The volume fraction of the alcohol monomer in the ternary solution is

$$\hat{\phi}_{A_1} = \frac{[(2K_A\phi_A + 1) - (1 + 4K_A\phi_A)^{1/2}]}{(2K_A^2\phi_A)} \tag{10}$$

obtained by solving Eqn. (9).

The chemical part of the Gibbs free energy is based upon the Flory-Huggins athermal model and may be written as

$$(\Delta G_{RAB})_{\text{chem}} = RT[\hat{n}_R \ln\hat{\phi}_R + \sum_{i=1}^{\infty} \hat{n}_{A_i}\ln\hat{\phi}_{A_i} + \hat{n}_B \ln\hat{\phi}_B] \tag{11}$$

The respective chemical potentials relative to the pure or hypothetical liquid components, $\mu_i^{\bullet}$, are obtained through differentiation with respect to the number of moles of each chemical species:

$$\frac{(\hat{\mu}_R - \mu_R^\bullet)}{RT} = \ln \hat{\phi}_R + 1 - \left(\frac{V_R}{\hat{V}_{\text{soln}}}\right) \tag{12}$$

$$\frac{(\hat{\mu}_{A_i} - \mu_{A_i}^\bullet)}{RT} = \ln \hat{\phi}_{A_i} + 1 - \left(\frac{V_A}{\hat{V}_{\text{soln}}}\right) \tag{13}$$

$$\frac{(\hat{\mu}_B - \mu_B^\bullet)}{RT} = \ln \hat{\phi}_B + 1 - \left(\frac{V_B}{\hat{V}_{\text{soln}}}\right) \tag{14}$$

where $\hat{V}_{\text{soln}}$ is the true molar volume of the ternary solution

$$\begin{aligned} \frac{1}{\hat{V}_{\text{soln}}} &= \frac{\hat{\phi}_R}{V_R} + \sum_{i=1}^{\infty} \frac{\hat{\phi}_{A_i}}{V_{A_i}} + \frac{\hat{\phi}_B}{V_B} \\ &= \frac{\hat{\phi}_R}{V_R} + \left(\frac{1}{K_A V_A}\right) \sum_{i=1}^{\infty} (K_A \hat{\phi}_{A_1})^i + \frac{\hat{\phi}_B}{V_B} \\ &= \frac{\phi_R}{V_R} + \frac{\hat{\phi}_{A_1}}{[V_A(1 - K_A \hat{\phi}_{A_1})]} + \frac{\phi_B}{V_B} \end{aligned} \tag{15}$$

and for the pure alcohol

$$\frac{1}{\hat{V}^*_{\text{soln}}} = \frac{\hat{\phi}^*_{A_1}}{[V_A(1 - K_A \hat{\phi}^*_{A_1})]} \tag{16}$$

As shown in many thermodynamic textbooks (e.g., Prigogine and Defay,[61] Acree,[13] Prausnitz *et al.*[15]), the chemical potential of stoichiometric component A is equal to the chemical potential of the monomeric (uncomplexed) species in solution

$$\hat{\mu}_{A_1} = \mu_A \tag{17}$$

To obtain the customary mixing properties, pure substance A must be taken as the new reference state

$$\frac{(\mu_A - \mu_A^*)}{RT} = \ln\left(\frac{\hat{\phi}_{A_1}}{\hat{\phi}^*_{A_1}}\right) - \left(\frac{V_A}{\hat{V}_{\text{soln}}}\right) + \left(\frac{V_A}{\hat{V}^*_{\text{soln}}}\right) \tag{18}$$

Combining Eqns. (11)–(18), one obtains the following expression for $(\Delta G_{RAB})_{\text{chem}}$

$$(\Delta G_{RAB})_{\text{chem}} = RT\left\{n_R \ln \phi_R + n_A \ln\left(\frac{\hat{\phi}_{A_1}}{\hat{\phi}^*_{A_1}}\right) + n_A K_A (\hat{\phi}_{A_1} - \hat{\phi}^*_{A_1}) + n_B \ln \phi_B\right\} \tag{19}$$

The simplest equation that might be expected to adequately describe the physical contributions to the excess Gibbs free energy $(\Delta G^{ex}_{RAB})_{\text{phys}}$ is

$$(\Delta G^{ex}_{RAB})_{\text{phys}} = \left(\hat{n}_R V_R + \sum_{i=1}^{\infty} \hat{n}_{A_i} V_{A_i} + \hat{n}_B V_B\right)^{-1} \times \left[\sum_{i=1}^{\infty} \hat{n}_R V_R \hat{n}_{A_i} V_{A_i} A_{RA_i} + \hat{n}_R V_R \hat{n}_B V_B A_{RB} + \sum_{i=1}^{\infty} \hat{n}_B V_B \hat{n}_{A_i} V_{A_i} A_{BA_i}\right] \tag{20}$$

in which the A_{ij} terms represent binary interaction parameters. Obviously, Eqn. (20) contains far too many parameters for useful applications, but reasonable assumptions enable the number of parameters to be greatly reduced. Treatment of the A_{RA_i} and A_{BA_i} interaction parameters in a manner similar to that employed by Bertrand[6] for the chloroform-triethylamine complex leads to

$$A_{KA_i} = (\delta'_K - \delta'_{A_i})^2 \quad \text{where } K = R, B \tag{21}$$

$$\delta'_{A_i+1} = \left(\frac{V_{A_i}\delta'_{A_i} + V_{A_1}\delta'_{A_1}}{(V_{A_i} + V_{A_1})}\right) = \left(\frac{i\,\delta'_{A_i} + \delta'_{A_1}}{(i+1)}\right) = \delta'_{A_1} \tag{22}$$

$$A_{KA_i} = A_{KA_1} \quad \text{where } K = R, B \tag{23}$$

where δ'_i is the modified solubility parameter of component i. The modified solubility parameters account for only nonspecific interactions, and in the case of the alcoholic cosolvents the hydrogen-bonding contributions have been removed. Combination of Eqns. (20)–(23) enables $(\Delta G^{ex}_{RAB})_{\text{phys}}$ to be expressed as

$$(\Delta G^{ex}_{RAB})_{\text{phys}} = (n_R V_R + n_A V_A + n_B V_B)^{-1}\,[n_R V_R n_A V_A A_{RA_1} + n_R V_R n_B V_B A_{RB} + n_B V_B n_A V_A A_{BA_1}] \tag{24}$$

in terms of three binary interactional parameters. Substitution of Eqns. (19) and (24) into Eqn. (7) yields the following expression for the total Gibbs free energy of the ternary system (per stoichiometric mole of solution):

$$(\Delta G_{RAB}) = RT\left\{x_R \ln\phi_R + x_A \ln\left(\frac{\hat{\phi}_{A_1}}{\hat{\phi}^*_{A_1}}\right) + x_A K_A(\phi_{A_1} - \phi^*_{A_1}) + x_B \ln\phi_B\right\} + (n_R V_R + n_A V_A + n_B V_B)^{-1}\,[x_R V_R n_A V_A A_{RA_1} + x_R V_R n_B V_B A_{RB} + x_B V_B n_A V_A A_{BA_1}] \tag{25}$$

An expression for the excess molar enthalpy of mixing is obtained by differentiating the Gibbs free energy of mixing with respect to temperature

$$\Delta H^{ex}_{RAB} = -h_A K_A x_A(\hat{\phi}_{A_1} - \hat{\phi}^*_{A_1}) + (n_R V_R + n_A V_A + n_B V_B)^{-1}\,[x_R V_R n_A V_A E_{RA_1} + x_R V_R n_B V_B E_{RB} + x_B V_B n_A V_A E_{BA_1}] \tag{26}$$

in accordance with standard thermodynamic principles. In the above expression h_A denotes the standard molar enthalpy of hydrogen bond formation and $E_{ij} = \partial(A_{ij}/T)/\partial(1/T)$. Enthalpies and energies are used interchangeably in the present discussion since the Kretschmer-Wiebe association model assumes a negligible volume change upon mixing. Inherent in this particular treatment is the additional assumption that volume fraction compositions are independent of temperature. This latter approximation is consistent with both the lattice model used in the original development of the Kretschmer-Wiebe model, and with the NIBS weighting factor requirement, i.e., $\Gamma_i \neq \Gamma_i(T, P)$.

Spectral transitions are related to differences in the chromophore's electronic energy levels, which in turn are affected by molecular interactions between the dissolved chromophore and surrounding solvent molecules. To a first approximation, the absorption and/or emission wavelength shifts observed in the various solvent mixtures result from differences in the solvational-energies associated with either the ground electronic state, first electronic excited state, or both. Solvational effects in binary alcohol + hydrocarbon mixtures can be easily modeled in terms of the Kretschmer-Wiebe self-association model. The chromophore's energy in the ground and excited states, E_R^{GS} and E_R^{ES}, are approximated by the chromophore's enthalpy of solution

$$E_R^{GS} \approx H_R^{GS} = -h_A K_A n_A \left(\frac{\partial \hat{\phi}_{A_1}^{GS}}{\partial n_R}\right) + V_R\,[\phi_A^{GS}(1-\phi_R)\,E_{RA_1}^{GS} + \phi_B^{GS}(1-\phi_R)\,E_{RB}^{GS} - \phi_A^{GS}\,\phi_B^{GS}\,E_{BA_1}] \tag{27}$$

$$E_R^{ES} \approx H_R^{ES} = -h_A K_A n_A \left(\frac{\partial \hat{\phi}_{A_1}^{ES}}{\partial n_R}\right) + V_R\,[\phi_A^{ES}(1-\phi_R)\,E_{RA_1}^{ES} + \phi_B^{ES}(1-\phi_R)\,E_{RB}^{ES} - \phi_A^{ES}\,\phi_B^{ES}\,E_{BA_1}] \tag{28}$$

in a binary solvent mixture having a composition identical to that of the solvational sphere. Superscripts GS and ES refer to the chromophore in its ground and first electronic excited states, respectively. Readers should note that $E_{RA_1}^{GS}$ and $E_{RA_1}^{ES}$ are not necessarily equal as the chromophore does have different dipole moments in both the ground and excited state. The same is true for the binary interaction parameters involving the chromophore and solvent component B, i.e., $E_{RB}^{GS} \neq E_{RB}^{ES}$.

The first term in Eqns. (27) and (28) has not been differentiated explicitly since it contains only quantities associated with the alcohol cosolvent. Careful examination of both equations reveals that if the solvent composition remains constant during the absorption process (Frank-Condon Principle, $\hat{\phi}_{A_1}^{GS} = \hat{\phi}_{A_1}^{ES}$), then the first terms are identical. Under normal experimental conditions, the concentration of the chromophore (or fluorophore in the case of fluorescence) is extremely small and the limiting condition of infinite dilution, $\phi_R \approx 0$, applies. Recalling that the energy difference $|E_R^{ES} - E_R^{GS}|$ is inversely proportional to the reciprocal of the absorption wavelength, combination of Eqns. (27) and (28) yields

$$\Delta E_{\text{trans}} = \phi_A^{GS}(E_{R,A}^{ES} - E_{R,A}^{GS}) + \phi_B^{GS}(E_{R,B}^{ES} - E_{R,B}^{GS}) \tag{29}$$

$$1/\lambda_{\text{abs}} = \phi_A^{GS}(1/\lambda_{\text{abs}})_A + \phi_B^{GS}(1/\lambda_{\text{abs}})_B \tag{30}$$

the simple additive relationship derived previously by Acree and coworkers[44,45] for systems containing only nonspecific interactions. Here, the generalized weighted mole fraction Y_A^{GS} [see Eqn. (6)] is volume fraction because all NIBS weighting factors were approximated by molar volumes. Emission processes can be modeled in similar fashion, except that the transition begins with the solute probe in the excited state, and the fluorescent photon is emitted when the molecule returns to its ground electronic state. In the case of fluorescence spectroscopy, calculated Y_A and Y_B concentrations [See Eqn. (6)] may correspond to the preferential solvation around the excited fluorophore. There is sufficient time during the excited state lifetime for redistribution of solvent molecules.

DERIVATION BASED UPON THE MECKE-KEMPTER SELF-ASSOCIATION MODEL

Although the Kretschmer-Wiebe model is one of the most popular solution models for interpreting the thermodynamic properties of alcohol + hydrocarbon mixtures, it is by no means the only self-association model. Equally popular is the Mecke-Kempter model,[62,63] which describes formation of hydrogen-bonded polymers

$$A_i + A_1 \rightleftharpoons A_{i+1}$$

with an isodesmic equilibrium constant

$$K_A = \frac{\hat{\phi}_{A_{i+1}}}{(\hat{\phi}_{A_1}\hat{\phi}_{A_i})} \tag{31}$$

expressed in terms of volume fractions rather than molar concentrations (moles/liter). To conserve space, we will limit our discussion to the $(\Delta H_{RAB}^{ex})_{\text{chem}}$ term and simply assume the same mathematical form for the nonspecific physical interactions as before.

The chemical part of the total excess enthalpy represents a change in the number of individual alcohol species (i-mers) between the ternary solution and the pure alcohol

$$(\Delta H_{RAB}^{ex})_{\text{chem}} = h_{\text{chem}} - n_A h_{\text{chem}}^{*} \tag{32}$$

where the total enthalpy of the alcohol complexes is

$$h_{\text{chem}} = h_A \sum_{i=1}^{\infty} (i-1)\hat{n}_{A_i} = h_A \sum_{i=1}^{\infty} \left[\frac{(i-1)}{i}\right] \hat{n}_{A_1} (K_A \hat{\phi}_{A_1})^{i-1}$$

$$= \frac{h_A \hat{n}_{A_1}}{(K_A \hat{\phi}_{A_1})} \sum_{i=1}^{\infty} \left[\frac{(i-1)}{i}\right] (K_A \phi_A)^i (1 + K_A \phi_A)^{-i} \tag{33}$$

Combination of Eqns. (32) and (33) gives

$$(\Delta H^{ex}_{RAB})_{\text{chem}} = -h_A n_A \left\{ \frac{\ln(1 + K_A \phi_A)}{(K_A \phi_A)} - \frac{\ln(1 + K_A)}{K_A} \right\} \tag{34}$$

for the chemical contribution to the excess enthalpy. The chromophore's enthalpy of solution is

$$H_R = -h_A n_A \frac{\partial \left\{ \dfrac{\ln(1 + K_A \phi_A)}{K_A \phi_A} \right\}}{\partial n_R} + V_R[\phi_A (1 - \phi_R) E_{RA_1}$$
$$+ \phi_B (1 - \phi_R) E_{RB} - \phi_A \phi_B E_{BA_1}] \tag{35}$$

obtained by differentiating Eqn. (34) with respect to n_R, and then adding the contributions from nonspecific interactions.

The chemical term has not been explicitly differentiated since it makes an identical contribution to the chromophore's ground and excited state solvational enthalpies/energies. The Frank-Condon Principle requires that the solvational sphere composition remain constant during the spectral transition. Of the four terms in Eqn. (35), only $V_R \phi_A (1 - \phi_R) E_{RA_1}$ and $V_R \phi_B (1 - \phi_R) E_{RB}$ contribute to the transition energy

$$\Delta E_{\text{trans}} = \phi_A^{GS} (E^{ES}_{R,A} - E^{GS}_{R,A}) + \phi_B^{GS} (E^{ES}_{R,B} - E^{GS}_{R,B}) \tag{36}$$

Again the simple additive relationship is derived, showing that the reciprocal of the probe's absorption wavelength observed in a binary alkane + alcohol solvent mixture is a volume fraction average of values determined in the two pure solvents.

It should be noted that the inert hydrocarbon solvent can be replaced with a second self-associating solvent, and the derivation remains essentially unchanged. A second chemical contributional term is added to Eqns. (34) and (35);[64,65] however, the additional term makes absolutely no contribution to ΔE_{trans}. The self-associating solvent need not be a monofunctional alcohol. A similar association model,[66] with a mole fraction based isodesmic equilibrium constant [i.e., $K_A = \hat{x}_{A_{i+1}} / (\hat{x}_{A_1} \hat{x}_{A_i})$] has been used successfully to mathematically reproduce vapor-liquid equilibria of binary mixtures containing simple aliphatic amines in saturated hydrocarbons over the entire mole fraction range. Three other studies[67-69] assumed the Kretschmer-Wiebe model to describe the self-association behavior of binary aniline + hydrocarbon and aliphatic amine + hydrocarbon mixtures. Heterogeneous complex formation between two self-associating alcohol cosolvents can be incorporated into both the Kretschmer-Wiebe and Mecke-Kempter models using empirically deduced mixing rules for how the self-association equilibrium constant varies with binary solvent composition.[70,71] At fixed solvent composition, the numerical value of $K^{\text{ave}}_{\text{alcohol}}$ is constant and Eqn. (36) is again derived.

DERIVATION BASED UPON MOBILE ORDER THEORY

Ruelle, Huyskens and coworkers[72–77] recently suggested an alternative thermodynamic treatment for complexing systems which is based upon the theory of mobile order in fluid solution. It is assumed that all molecular groups perpetually move, and that neighbors of a given external atom in a molecule constantly change identity. All molecules of a given kind dispose of the same volume, equal to the total volume, V, of the liquid divided by the number, N_A, of molecules of the same kind, i.e., Dom $A = V/N_A$. The center of this domain perpetually moves. Highest mobile disorder is achieved whenever groups visit all parts of their domain without preference. Preferential contacts lead to deviations with respect to this "random" visiting. This is especially true in the case of hydrogen bonding as specific interactions result in a specific orientation of the "donor" molecule with respect to an adjacent "acceptor" molecule.

The Gibbs free energy of mixing for a ternary solution containing an inert chromophore (component R), a monofunctional alcohol (component A) and a saturated hydrocarbon (component B) is separated into three contributions:

$$\Delta G_{RAB}^{\text{mix}} = (\Delta G_{RAB})_{\text{conf}} + (\Delta G_{RAB})_{\text{chem}} + (\Delta G_{RAB})_{\text{phys}} \tag{37}$$

The first term describes the configurational entropy based upon the Huyskens and Haulait-Pirson[78] definition of solution ideality

$$(\Delta G_{RAB})_{\text{conf}} = (0.5)RT[n_R \ln \phi_R + n_A \ln \phi_A + n_B \ln \phi_B + n_R \ln x_R + n_A \ln x_A + n_B \ln x_B] \tag{38}$$

whereas the latter two terms in Eqn. (37) result from formation of hydrogen-bonded complexes and weak, nonspecific physical interactions in the ternary solution, respectively.

The chemical contribution depends upon the functional groups present and the characteristics of the self-associating component. Monofunctional alcohols have one hydrogen "donor" site and the lone electron pairs on the oxygen atom provide two "acceptor" sites. The maximum possible number of hydrogen bonds is determined by the number of sites that are in the minority. According to Mobile Order theory,[73] the hydrogen-bonding contribution is given by

$$(\Delta G_{RAB})_{\text{chem}} = n_A RT \ln\left[\frac{1 + (K_A/V_A)}{1 + (K_A \phi_A/V_A)}\right] \tag{39}$$

where K_A refers to the stability (equilibrium) constant of the hydrogen bond.

Physical effects are expressed in terms of the NIBS model developed by Bertrand and coworkers[46–48]

$$(\Delta G_{RAB}^{ex})_{\text{phys}} = (n_R\Gamma_R + n_A\Gamma_A + n_B\Gamma_B)^{-1}[n_R\Gamma_R n_A\Gamma_A A_{RA} + n_R\Gamma_R n_B\Gamma_B A_{RB} + n_A\Gamma_A n_B\Gamma_B A_{AB}] \tag{40}$$

where Γ_i is the weighting factor for component i and A_{ij} is a binary interaction parameter that is independent of composition. Equation (40) is a little more generalized form of the nonspecific physical contribution description used in the derivations involving the Kretschmer-Wiebe and Mecke-Kempter self-association models. The NIBS model has been shown to provide accurate predictions for biphenyl, naphthalene, iodine, *p*-dibromobenzene, benzil, *p*-benzoquinone, thianthrene, anthracene, pyrene and carbazole solubilities in systems containing only nonspecific interactions when all three weighting factors are approximated with molar volumes.[13,79] The precise applicability of Eqn. (40) to Gibbs free energy and its temperature and pressure derivatives requires that weighting factors be independent of both variables.[47] Therefore, molar volumes and other experimentally determined weighting factors must be regarded as approximations of these "true" weighting factors, and for application to conditions of varying temperature and/or pressure, they should be referred to a specific condition, such as 298.15 K and 1 atm, or to an extrapolated state, such as "close-packed" volume. For purposes of this discussion, all weighting factors will be approximated with molar volumes.

Combining Eqns. (37)–(40) the Gibbs free energy of mixing is written as

$$(\Delta G^{\text{mix}}_{RAB}) = (0.5)RT[n_R \ln\phi_R + n_A \ln\phi_A + n_B \ln\phi_B + n_R \ln x_R + n_A \ln x_A$$

$$+ n_B \ln x_B] + n_A RT \ln\left[\frac{1+(K_A/V_A)}{1+(K_A\phi_A/V_A)}\right] + (n_R V_R + n_A V_A + n_B V_B)$$

$$[\phi_R\phi_A\, A_{RA} + \phi_R\phi_B\, A_{RB} + \phi_A\phi_B\, A_{AB}] \tag{41}$$

Standard thermodynamic principles relate the excess enthalpy and Gibbs free energy

$$\frac{\Delta H^{ex}_{RAB}}{R} = \frac{\partial(\Delta G^{\text{mix}}_{RAB})/RT}{\partial(1/T)} \tag{42}$$

Assuming that molar volumes of the pure components are independent of temperature (and $\Gamma_i \neq \Gamma_i(T)$ in the case of the generalized NIBS equation (40)), differentiation of Eqn. (41) with respect to $1/T$ and then n_R gives the following expressions for the excess enthalpy of mixing

$$\Delta H^{ex}_{RAB} = -h_A n_A\left[\frac{K_A/V_A}{1+(K_A/V_A)} - \frac{(\phi_A K_A/V_A)}{1+(\phi_A K_A/V_A)}\right]$$

$$+ (n_R V_R + n_A V_A + n_B V_B)\,[\phi_R\phi_A\, E_{RA} + \phi_R\phi_B\, E_{RB} + \phi_A\phi_B\, E_{AB}] \tag{43}$$

and for the chromophore's enthalpy of solution

$$H_R = h_A n_A \frac{\partial \left[\dfrac{\phi_A K_A/V_A}{1+(\phi_A K_A/V_A)} \right]}{\partial n_R}$$

$$+ V_R[\phi_A(1-\phi_R)E_{RA_1} + \phi_B(1-\phi_R)E_{RB} - \phi_A\phi_B E_{BA_1}] \qquad (44)$$

respectively, where $E_{ij} = \partial(A_{ij}/T)/\partial(1/T)$ and h_A is the standard enthalpy of formation of a hydrogen bond.

Of the four terms in Eqn. (44), only $V_R\phi_A(1-\phi_R)E_{RA_1}$ and $V_R\phi_B(1-\phi_R)E_{RB}$ contribute to the transition energy

$$\Delta E_{\text{trans}} = \phi_A^{GS}(E_{R,A}^{ES} - E_{R,A}^{GS}) + \phi_B^{GS}(E_{R,B}^{ES} - E_{R,B}^{GS})$$

Again the simple additive relationship is derived, showing that the reciprocal of the probe's absorption wavelength observed in a binary alkane + alcohol solvent mixture is a volume fraction average of values determined in the two pure solvents. For discussion purposes, a monofunctional alcohol was specified as the self-associating cosolvent. The above derivation, with perhaps minor modification of the first term to properly "count" the number of hydrogen bonds, is valid for all other solvents such as carboxylic acids, diols, and amines which undergo self-association. Modifications, if required, do not affect ΔE_{trans}.

DERIVATION BASED UPON THE IDEAL ASSOCIATED SOLUTION (IAS) MODEL WITH NONSPECIFIC INTERACTIONS INCLUDED

Analysis of the thermodynamic properties of nonelectrolyte solutions are generally made by comparing measured properties with properties the solution should exhibit if it behaved ideally. In mixtures in which chemical reactions or molecular complexations are expected (or known) to occur between the components, a first approximation to the thermodynamic treatment of nonideality can be made by considering all deviations from ideal behavior to arise from chemical interactions. That is, weak nonspecific physical interactions (usually accounted for by activity coefficients) to be negligible in comparison to chemical interactions. The liquid mixture is thus considered to be an ideal solution of all species present at equilibrium.

In the Ideal Associated Solution (IAS) model[13–15,24] a ternary solution containing a chromophore (component R) and two solvent components, in which A and B interact according to the equilibrium

$$A + B \rightleftharpoons AB \quad K_{AB} = \frac{\hat{x}_{AB}}{(\hat{x}_A \hat{x}_B)} = \frac{r_{AB}(1 - r_{AB})}{[(x_A - r_{AB})(x_B - r_{AB})]} \tag{45}$$

$$r_{AB} = \frac{\hat{n}_{AB}}{(n_R + n_A + n_B)}$$

and

$$x_A = \frac{n_A}{(n_R + n_A + n_B)}$$

is treated as an ideal quaternary mixture. Symbols $\hat{n}_{AB}$ refers to the number of moles of complex formed, and n_A and n_B are the formal (stoichiometric) amounts of components A and B present before complexation occurs. The enthalpy of mixing of an ideal associated solution is directly proportional to the number of moles of AB complex formed

$$(\Delta H^{ex}_{RAB})_{\text{chem}} = r_{AB} h_{AB} = \frac{\hat{n}_{AB} h_{AB}}{(n_R + n_A + n_B)} \tag{46}$$

where h_{AB} is the standard enthalpy of formation of the AB complex. Note that $(\Delta H^{ex}_{RAB})_{\text{chem}}$ is calculated relative to the formal number of moles in the liquid mixture $n_R + n_A + n_B$. This is consistent with the general convention for reporting thermodynamic properties of multicomponent solution, regardless of whether they are associated or unassociated solutions. Reporting experimental data relative to the true number of moles in solution $(\hat{n}_R + \hat{n}_A + \hat{n}_B + \hat{n}_{AB})$ is confusing because the numerical values would always depend on how many of each chemical entity is presumed to be present. The formal number of moles is an unambiguous quantity and not subject to interpretation.

The chromophore's enthalpy of solution is

$$H_R = h_{AB}\left(\frac{\partial \hat{n}_{AB}}{\partial n_R}\right) + V_R[\phi_A(1 - \phi_R)E_{RA_1} + \phi_B(1 - \phi_R)E_{RB} - \phi_A\phi_B E_{BA_1}] \tag{47}$$

obtained by differentiating $(n_R + n_A + n_B)(\Delta H^{ex}_{RAB})_{\text{chem}}$ with respect to n_R, and then adding the contributions from nonspecific interactions. Rigorous application of the NIBS model to the true quarternary system requires that there initially be six terms in the mathematical description of nonspecific interactions to account for all of the different binary interactions. The three interaction parameters involving the AB molecular complex (E_{RAB}, E_{AAB} and E_{BAB}) can be removed from the final derived expression. Mathematical details of the elimination are discussed elsewhere.[25]

Of the four terms in Eqn. (47), only $V_R\phi_A(1 - \phi_R)E_{RA_1}$ and $V_R\phi_B(1 - \phi_R)E_{RB}$ contribute to the transition energy

$$\Delta E_{\text{trans}} = \phi_A^{GS}(E^{ES}_{R,A} - E^{GS}_{R,A}) + \phi_B^{GS}(E^{ES}_{R,B} - E^{GS}_{R,B})$$

Even in solvent mixtures containing heterogeneous A_iB_j-type solvent complexation, it is possible to derive the simple additive relationship showing that the reciprocal of the probe's absorption wavelength observed in a binary solvent mixture is a volume fraction average (weighted mole fraction average in the most general Γ_i case) of values determined in the two pure solvents. Equation (6) was originally derived for noncomplexing systems. Derivations presented in this study, however, document that the expression can be applied to preferential solvation in more complex solvent mixtures.

We do not imply that the approaches presented here are necessarily the most rigorous, the best or the only ways for deriving Eqn. (6). We opted to derived Eqn. (6) from four thermodynamic mixing models which treat molecular interactions in terms of complexation and "bulk" A_{ij} interactional parameters. There are a large number of other similar thermodynamic models that could have been employed in deriving Eqn. (6). The fact that there have been so many solution models published in the literature indicates that no simple model derived to date satisfactorily describes all systems encountered. Alternatively, we suspect that it is possible to derive the simple additive reciprocal wavelength relationship from perhaps a more microscopic treatment involving dipole moments, molecular polarizabilities, dielectric constants, and principles from statistical and molecular mechanics.

References

1. J. J. van Laar, *Z. Physik. Chem.*, **72**, 723 (1910).
2. F. Dolezalek, *Z. Physik. Chem.*, **64**, 727 (1908).
3. E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murthy, T. M. Gorrie and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2365 (1970).
4. W. C. Duer and G. L. Bertrand, *J. Am. Chem. Soc.*, **92**, 2587 (1970).
5. P. P. S. Saluja, T. M. Young, R. F. Rodewald, F. H. Fuchs, D. Kohli and R. Fuchs, *J. Am. Chem. Soc.*, **99**, 2949 (1977).
6. G. L. Bertrand, *J. Phys. Chem.*, **79**, 48 (1975).
7. D. V. Fenby, A. Chand, A. Inglese, J.-P. E. Grolier and H. V. Kehiaian, *Austr. J. Chem.*, **30**, 1401 (1977).
8. J. F. Smith and L. G. Hepler, *Can. J. Chem.*, **67**, 1153 (1989).
9. W. E. Acree, Jr., A. I. Zvaigzne and S. A. Tucker, *Phys. Chem. Liq.*, **21**, 169 (1990).
10. W. E. Acree, Jr., A. I. Zvaigzne and S. A. Tucker, *Thermochim. Acta*, **161**, 189 (1990).
11. P. P. Singh, R. Malik, S. Maken, W. E. Acree, Jr. and S. A. Tucker, *Thermochim. Acta*, **162**, 291 (1990).
12. P. P. Singh, R. Malik, S. Maken, W. E. Acree, Jr., *J Chem. Soc., Faraday Trans.*, **86**, 2853 (1990).
13. W. E. Acree, Jr., *Thermodynamic Properties of Nonelectrolyte Solutions*, Academic Press, Inc., Orlando, FL (1984).
14. M. L. McGlashan, *Chemical Thermodynamics*, Academic Press, Inc., New York, NY (1979).
15. J. M. Prausnitz, R. N. Lichtenthaler and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibra*, 2nd Edition, Prentice-Hall, Englewood Cliffs, NJ (1986).
16. L. Barta, Z. S. Kooner, L. G. Hepler, G. Roux-Desgranges and J.-P. E. Grolier, *J Solution Chem.*, **18**, 663 (1989).
17. J.-P. E. Grolier, G. Roux-Desgranges, Z. S. Kooner, J. F. Smith and L. G. Hepler, *J Solution Chem.*, **16**, 745 (1987).
18. L. G. Hepler, Z. S. Kooner, G. Roux-Desgranges and J.-P. E. Grolier, *J Solution Chem.*, **14**, 579 (1985).
19. L. Barta, Z. S. Kooner, L. G. Hepler, G. Roux-Desgranges and J.-P. E. Grolier, *Can. J. Chem.*, **67**, 1225 (1989).
20. W. E. Acree, Jr. and S. A. Tucker, *Phys. Chem. Liq.*, **19**, 23 (1989).
21. W. E. Acree, Jr., S. A. Tucker and L. E. Cretella, *Thermochim. Acta*, **145**, 245 (1989).
22. H. P. Singh, P. P. Singh and S. Dagar, *Can. J. Chem.*, **66**, 290 (1988).
23. A. Apelblat, A. Tamir and M. Wagner, *Fluid Phase Equilibr.*, **4**, 229 (1980).

24. D. V. Fenby and L. G. Hepler, *Chem. Soc. Reviews*, **3**, 193 (1974).
25. W. E. Acree, Jr., D. R. McHan and J. H. Rytting, *J. Pharm. Sci.*, **72**, 929 (1983).
26. J. W. McCargar and W. E. Acree, Jr., *Phys. Chem. Liq.*, **17**, 123 (1987).
27. W. E. Acree, Jr. and J. W. McCargar, *J. Mol. Liq.*, **37**, 251 (1988).
28. J. W. McCargar and W. E. Acree, Jr., *J Solution Chem.*, **17**, 1081 (1988).
29. W. E. Acree, Jr. and J. W. McCargar, *J. Pharm. Sci.*, **76**, 575 (1987).
30. C. Panayiotou and J. H. Vera, *Fluid Phase Equilibr.*, **5**, 55 (1980).
31. L. L. Lee and K. E. Starling, *Fluid Phase Equilibr.*, **21**, 77 (1985).
32. O. B. Nagy, M. WaMuanda and J. B. Nagy, *J Chem. Soc., Faraday Trans., 1*, **74**, 2210 (1978).
33. M. Szpakowska and O. B. Nagy, *J. Phys. Chem.*, **93**, 3851 (1989).
34. M. Szpakowska and O. B. Nagy, *J Chem. Soc., Faraday Trans., 1*, **85**, 2891 (1989).
35. W. E. Acree, Jr., A. I. Zvaigzne and S. A. Tucker, *J Chem. Soc., Faraday Trans.*, **86**, 307 (1990).
36. P. Chatterjee and S. Bagchi, *J. Phys. Chem.*, **95**, 3311 (1991).
37. P. Chatterjee and S. Bagchi, *J Chem. Soc., Faraday Trans.*, **86**, 1785 (1990).
38. W. P. Zurawsky and S. F. Scarlata, *J. Phys. Chem.*, **96**, 6012 (1992).
39. E. Bosch and M. Roses, *J Chem. Soc., Faraday Trans.*, **88**, 3541 (1992).
40. P. Chatterjee and S. Bagchi, *J Chem. Soc., Faraday Trans.*, **87**, 587 (1991).
41. K. Tamori, Y. Watanabe and K. Esumi, *Langmuir*, **8**, 2344 (1992).
42. D. J. Phillips and J. F. Brennecke, *Ind. Eng. Chem. Res.*, **32**, 943 (1993).
43. R. D. Skwierczynski and K. A. Connors, *J Chem. Soc., Perkin Trans., 2*, 467 (1994).
44. W. E. Acree, Jr., J. R. Powell and S. A. Tucker, *J Chem. Soc., Perkin Trans., 2*, 529 (1995).
45. W. E. Acree, Jr., D. C. Wilkins, S. A. Tucker, J. M. Griffin and J. R. Powell, *J. Phys. Chem.*, **98**, 2537 (1994).
46. T. E. Burchfield and G. L. Bertrand, *J. Solution Chem.*, **4**, 205 (1975).
47. W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, **81**, 1170 (1977).
48. W. E. Acree, Jr. and G. L. Bertrand, *J. Phys. Chem.*, **83**, 2355 (1979).
49. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Freeman, San Francisco, CA (1960).
50. H. C. Van Ness, J. van Winkle, H. H. Richtol and H. B. Hollinger, *J Phys. Chem.*, **71**, 1483 (1967).
51. E. E. Tucker and S. D. Christian, *J. Phys. Chem.*, **81**, 1295 (1977).
52. A. H. Fletcher and C. A. Heller, *J. Phys. Chem.*, **71**, 3742 (1967).
53. A. H. Fletcher and C. A. Heller, *J. Phys. Chem.*, **72**, 1839 (1968).
54. W. B. Dixon, *J. Phys. Chem.*, **74**, 1396 (1970).
55. B. D. Anderson, J. H. Rytting and T. Higuchi, *Int. J. Pharm.*, **1**, 15 (1978).
56. B. D. Anderson, J. H. Rytting and T. Higuchi, *J. Am. Chem. Soc.*, **101**, 5194 (1979).
57. C. B. Kretschmer and R. Wiebe, *J. Chem. Phys.*, **22**, 1697 (1954).
58. A. Anderko, *Fluid Phase Equilibr.*, **45**, 39 (1989).
59. H. Renon and J. M. Prausnitz, *Chem. Eng. Sci.*, **22**, 299 (1967).
60. I. Nagata and Y. Kawamura, *Chem. Eng. Sci.*, **34**, 601 (1979).
61. I. Prigogine and R. Defay, *Chemical Thermodynamics*, John Wiley & Sons, New York NY (1954).
62. H. Kempter and R. Mecke, *Z Phys. Chem.*, **46B**, 229 (1940).
63. H. Kehiaian and A. Treszczanowicz, *Bull Acad. Pol. Sci.*, **16**, 445 (1968).
64. C. Pando, J. A. R. Renuncio, R. W. Hanks and J. J. Christensen, *Ind. Eng. Chem. Process. Des. Dev.*, **23**, 67 (1984).
65. C. Pando, J. A. R. Renuncio, R. W. Hanks and J. J. Christensen, *Ind. Eng. Chem. Process. Des. Dev.*, **23**, 73 (1984).
66. I. Nagata and K. Tamura, *Thermochim. Acta*, **101**, 305 (1986).
67. I. Nagata and K. Ohtsubo, *Thermochim. Acta*, **97**, 37 (1986).
68. H. Runke, M. Wetzel and A. Heintz, *Pure Appl. Chem.*, **61**, 1429 (1989).
69. I. Nagata, *Thermochim. Acta*, **108**, 305 (1986).
70. I. Nagata and K. Kazuma, *J. Chem. Eng. Data.*, **22**, 79 (1977).
71. I. Nagata, *J. Chem. Eng. Data*, **20**, 110 (1975).
72. P. L. Huyskens and G. G. Siegel, *Bull. Soc. Chim. Belg.*, **97**, 821 (1988).
73. P. L. Huyskens, M. C. Haulait-Pirson, G. G. Siegel and F. Kapuku, *J Phys. Chem.*, **92**, 6841 (1988).
74. P. Ruelle, C. Rey-Mermet, M. Buchmann, H. Nam-Tran, U. W. Kesselring and P. L. Huyskens, *Pharm. Res.*, **8**, 840 (1991).
75. P. Ruelle, M. Buchmann, H. Nam-Tran and U. W. Kesselring, *Int. J. Pharm.*, **87**, 47 (1992).
76. P. Ruelle, M. Buchmann, H. Nam-Tran and U. W. Kesselring, *Pharm. Res.*, **9**, 788 (1992).
77. G. G. Siegel, P. L. Huyskens and G. Vanderheyden, *Ber. Bunsenges. Phys. Chem.*, **94**, 549 (1990).
78. P. L. Huyskens and M. C. Haulait-Pirson, *J Mol. Liq.*, **31**, 135 (1985).
79. W. E. Acree, Jr., *Polycyclic Aromatic Hydrocarbons in Pure and Binary Solvents*, 54 in *IUPAC Solubility Data Series*, Oxford University Press, London, England (1994).