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Modeling Solutions Containing Specific Interactions

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Introduction

Strong specific intermolecular interactions generally lead to large deviations from solution ideality, which can be exploited for a variety of separation and reaction processes. Very often extractive distillations, liquid–liquid extractions, and supercritical extractions, especially with cosolvents, are designed so that these types of interactions give high specificity. We design chromatograph columns and membranes precisely for specific interactions, and engineers exploit these interactions in a variety of other processes ranging from chelation to homogeneous catalysis. This account describes methods for characterizing mathematically the thermodynamics of solutions exhibiting strong interactions, including the more realistic chemical–physical type theories as well as the application of extrathermodynamic methods for the determination of model parameters.

Many examples exist of "chemical" interactions, which have the property of being both specific and saturable. The definition excludes electrostatic interactions, ranging from van der Waals (also known as London or dispersion) forces to dipolar forces, or even the very strong nonspecific interactions of metals. The most familiar example of such chemical forces is hydrogen bonding. Prausnitz[1] cites the difference between two isomers of the compound C_2H_6O (dimethyl ether and ethanol), which differ in boiling point by about 100 °C and in heat of vaporization by a factor of more than 2, as evidence for strong hydrogen bonding. Acetic acid vapor, at room temperature and a pressure of less than 20 Torr, is more than 80% dimerized. In addition to hydrogen bonding, other important examples include charge-transfer complexing or Lewis acid–Lewis base interactions, the strong specific interactions of metals to form intermetallic compounds, the chelation of various species such as ions by crown ethers, and even the formation of micelles.

The vast majority of the representations of solution behavior that we use, be they equations of state or excess Gibbs energy expressions, are purely physical models. These are simple mathematically, they apply to a great variety of systems, and the parameters are easily determined; but in solutions with strong chemical interactions these models are often unable to represent phase behavior even qualitatively.

Chemical models, which date from the early work of Dolezalek[2] and his group, invoke the law of mass action but have generally found less favor. They are more specific, and some knowledge of the chemistry of the solution is necessary to apply them. Furthermore, they are more complex mathematically, especially as solution models go from binary to multicomponent, and the parameters are more difficult to determine. Pure chemical models do not address the physical interactions between molecules, which are often equally as important as chemical interactions. Many authors have ameliorated the limitations by using a combined chemical–physical model.[3–11]

Certainly in many nonionic solutions they are important contributions from both chemical and physical interactions, and these need to be characterized. However, even with the simplifying assumption of the separability of chemical and physical effects, the resulting equations are complex and generally have more adjustable parameters than most data sets justify.

We discuss the assumptions involved in using the more realistic chemical–physical models as well as the methods that are available to facilitate solution of the equations and to reduce the number of adjustable parameters. We do this in the context of excess Gibbs energy models, though the results are comparable if applied to equations of state. For supercritical fluids, authors have treated the solution as either an expanded liquid or a compressed gas and achieved similar results.

Physical Models

Physical models of solution behavior are the oldest and most common type of treatment. The earliest

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example is the familiar van der Waals equation (1873),

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \tag{1}$$

The b parameter is an excluded volume, and the a parameter really accounts for dispersion forces, derived from quantum mechanics half a century later and yet still proportional to $1/v^2$, dimensionally equivalent to $1/r^6$. Most of the other equations of state in use are physical models and linear descendants of the van der Waals equation, including the Redlich–Kwong, the SRK, the Peng–Robinson, and many others.

The early excess Gibbs energy models, including the Van Laar and Margules equations as well as the regular solution theory of Hildebrand and Scatchard, focused on fitting the enthalpy of mixing, accounting for primarily dispersion forces. In the early 1960s, Wilson,[12] Orye and Prausnitz,[13] and others introduced models based on entropy of mixing, using the concept of local volume fractions stemming from the work of Flory[14] and Huggins.[15] The local volume fractions permit nonrandom distribution, but they in no way account for specific interactions. They do have the property, however, of permitting a better mathematical representation of solutions with specific interactions with a smaller number of parameters. For example, the Wilson equation is quite capable, with two parameters, of representing highly associated solutions such as alcohol–hydrocarbon mixtures that simply cannot be well represented by enthalpic equations. A variety of very good equations are now available, including, in addition to the Wilson, the NRTL equation, the UNIQUAC equation, and a number of others.

In virtually every case, the excess Gibbs energy equations were derived from a model which assigned a physical meaning to the adjustable parameters.[7,16] Moreover, most excess Gibbs energy equations have parameters, usually two per binary, that are easily determined and readily extended to multicomponent mixtures. However, it has now become clear[17,18] that in general the physical meaning of the parameters was illusory, because the parameters are highly correlated, not unique, and/or incapable of representing multiple properties. In short, the common excess Gibbs energy expressions are useful, but are not true.

Unlike most excess Gibbs equations, the original meaning of the parameters in regular solution theory has been maintained when it is used where intended with nonionic, nonpolar solutions (excluding fluorinated compounds). Though not exact, regular solution theory is never far wrong; perhaps this is why the regular solution type treatment has had such appeal for extension to more complex situations.[3,9,19,20]

Statistical mechanical methods have also been used to model associated and solvated mixtures by physical models. These solutions are treated as a mixture of molecules interacting through specific and saturable forces, but still treated as physical forces. For example, Chapman et al.[21,22] have studied a solvation mixture of A and B in which only AB dimers form. The like pairs interact as hard spheres, and the unlike pairs interact as hard spheres with a sum of Coulombic interactions. They have achieved results that are in qualitative agreement with real mixtures and Monte Carlo simulation. While this holds great promise for the future, at the present, applications to systems of engineering interest are as yet limited.

In summary, physical models in general have highly empirical parameters that are relatively easy to determine. The methods are mathematically simple and in general easily extended to multicomponent systems, but they are often poor in representing systems with strong specific chemical interactions.

Chemical Models

Chemical models assume that complexes of known stoichiometry are formed and invoke the law of mass action to treat the solution as a multicomponent solution rather than a binary solution:

$$a_iA + b_jB \rightarrow A_{a_i}B_{b_j}$$

where the equilibrium constant for each compound is defined by

$$K_i = K_zK_\alpha = \left(\frac{z_i}{z_1^{a_i}z_2^{b_j}}\right)\left(\frac{\alpha_i}{\alpha_1^{a_i}\alpha_2^{b_j}}\right) = \exp\left(-\frac{\Delta g_i^f}{RT}\right) \tag{2}$$

with 1 and 2 being the components of the mixture (A and B), and Δg_i^f is the Gibbs energy of formation of the compound. The true mole fraction, z, is given by

$$z_i = n_i/(n_1 + n_2 + \sum_{j=3}^{N} n_j) \tag{3}$$

where the n's are mole numbers, and N is the number of components in the true solution (i.e., there are $N - 2$ compounds formed). The true activity coefficient α is related to the apparent or measured activity coefficient γ by[23]

$$x_i\gamma_i = z_i\alpha_i \tag{4}$$

The measured activity coefficient, be it from vapor pressure, boiling point, or emf data, is assumed to be that of monomer only in the analysis of raw data. This means, for example, that in a vapor pressure measurement any adducts in solution are involatile and contribute negligibly to the total pressure. Such an assumption is necessary and appears to have little effect on the model results.

Any excess Gibbs energy expression may be used to correlate or calculate the α values in the multicomponent true mixture: regular solution theory, Van Laar

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Table I. Adjustable Parameters for GCPT Using Strictly Regular Solution Theory

no. of compds.	equilib constants, K	interchange energies, ω	total parameters
1	1	3	4
2	2	6	8
3	3	10	13

equation, Wilson equation, NRTL, etc. This formulation constitutes the general chemical–physical theory (GCPT).[24]

The GCPT assumes that the identity of the compounds formed in solution is known and further assumes that the chemical and physical interactions are separable and additive. The number of adjustable parameters depends on the form of the physical interaction term. If one chooses the simplest possible physical interaction term (the strictly regular solution theory of Guggenheim with a single adjustable parameter per binary pair), the number of parameters required for a binary solution can be quite large, as shown in Table I.

These parameters are at one temperature only; additional parameters are required for temperature dependence. Few experimental data justify four adjustable parameters at one temperature, much less the higher numbers required to characterize two- and three-compound systems. Also the solution theory used here is strictly regular solution theory, which is too simplistic to give a realistic representation of even moderately complex physical interactions. A more complex treatment, such as Van Laar or Wilson type equations, would require at least two parameters per binary pair, doubling the number of physical parameters. An additional complication exists in the mathematics of applying GCPT; the K_z and the K_α are interdependent, and the convergence properties of the coupled equations for iterative solutions are inherently poor. As a result, the GCPT is almost never used in its pure form; various devices are used either to reduce the number of parameters or to determine some of them independently, or in some cases both.

Ideal Chemical Theory

In its simplest form, the GCPT can be reduced to ideal chemical theory, ICT, by setting the α's at unity: equivalent to assuming Raoult's Law for the true mixture. Dolezalek[2] first propounded chemical theory, but it is perhaps more easily explained by the treatment of Lambert,[25] who used chemical theory to represent second virial coefficients by the formation of a dimer $2A \rightarrow A_2$, where the subsequent mixture of monomer and dimer was treated as an ideal gas. The sole adjustable parameter is the equilibrium constant for dimer formation in this form. The second virial coefficient will always be negative, giving a compressibility factor of less than unity, but for most physical situations of interest the deviations from ideality are in fact negative (attractive). Another early example of the ICT was solvation in binary solutions by McGlashon and Rastogi,[5] where the strong negative deviations from Raoult's Law were well characterized.

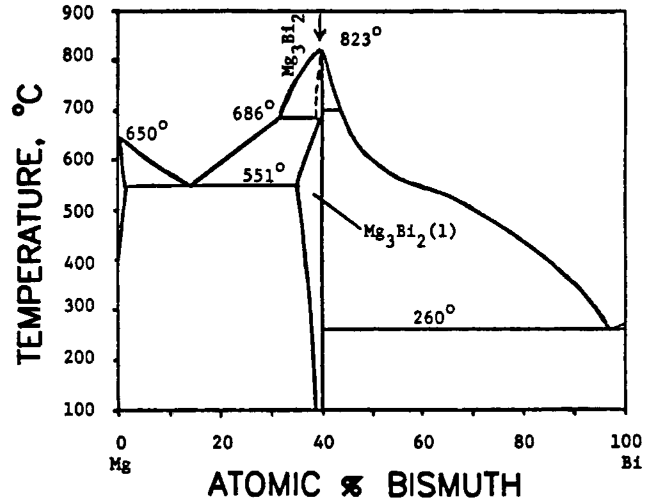

Figure 1. Phase diagram solid–liquid boundary for the magnesium–bismuth system.[67]

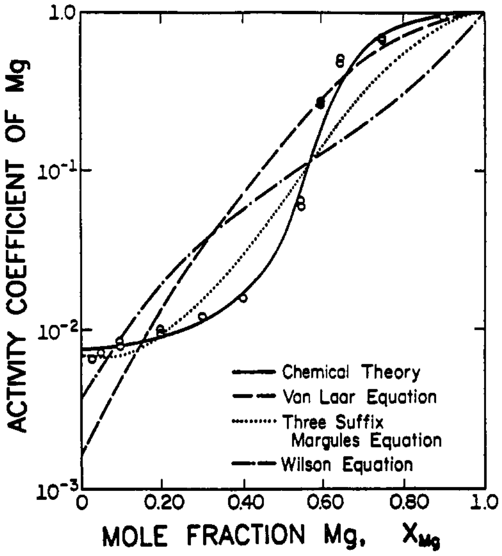

Figure 2. Comparison of various two-parameter excess Gibbs energy models for the magnesium–bismuth system at 850 °C.[27]

Alger and Eckert[24] have developed a general mathematical treatment for ICT and have applied it to systems where chemical forces dominate. An example is the formation of very strong stoichiometric intermetallic compounds in liquid alloys, such as the compound Mg_3Bi_2, as shown in the phase diagram in Figure 1. The high apparent melting point of the intermetallic compound, hundreds of degrees above a normal eutectic temperature, indicates an extremely stable compound. Measurements by an emf technique[26] show that the very strong solvation gives activity coefficients that deviate from unity by as much 3 orders of magnitude. These results have been fit successfully by an ICT model,[27] whereas common physical models with the same number of adjustable parameters are incapable of representing the same data (Figure 2). Even the excess partial molal enthalpy data, with a profound extremum at the composition of the 3-2 compound, are well represented by the ICT (Figure 3). Many liquid

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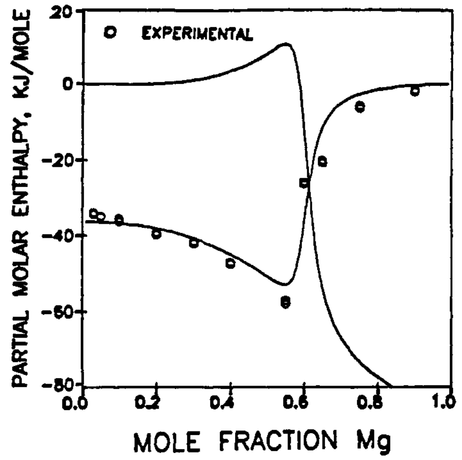

Figure 3. Ideal chemical model fit of magnesium partial molal enthalpy data for the magnesium–bismuth system at 1073 K.[68]

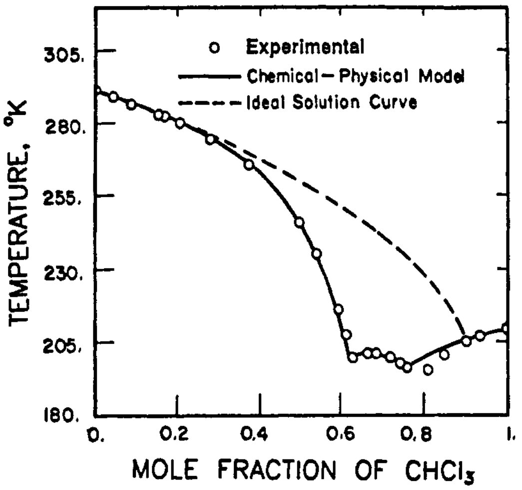

Figure 4. Solid–liquid phase diagram for the chloroform–dioxane system (data of Goates et al.[29]).

metal systems form even stronger intermetallics such as Mg-Sb[26] where $\gamma_{Mg}^{\infty} \approx 10^{-5}$ and U-Sn[28] where $\gamma_{U}^{\infty} \approx 10^{6}$.

Chemical–Physical Models

Chemical–physical models have the advantage of being far more realistic than either ICT or physical models alone, especially in situations when the chemical and physical forces are comparable in magnitude. The realism incurs the penalty of increased complexity; the equations are often impossible to solve in closed form, and the number of adjustable parameters may become unreasonable. Nonetheless, it is clear that there are an enormous number of physical situations which cannot be well represented without some type of chemical–physical model. For example, Figure 4 shows the solid–liquid phase diagram for the system chloroform–dioxane[29] represented by a chemical–physical model with regular solution theory for the physical part.[30] Many other examples exist: Prausnitz and co-workers[31] have used such a method for representing Henry's law constants for methane in water. Donohue and his group have applied an association model to the representation of VLE data in the acetic acid–heptane system.[32] A family of statistical mechanical models recently developed by Stell and co-workers[33,34] uses the law of mass action and can be classified as chemical–physical models; these have not yet been extended to systems of industrial importance.

Evaluation of Parameters

The parameters in chemical–physical models are most often regressed from activity coefficient, VLE, or solid–liquid equilibria (SLE) data as indicated above. Unfortunately, one can adjust the parameters from almost any type of model to fit VLE data; it simply is not a sensitive enough test to discriminate parameters accurately in complex systems. Moreover, excellent data are required to justify more than a single parameter. This points to the importance of evaluating parameters so that they retain some physical significance as well as utility.

There are basically three different ways in which one can reduce the number of parameters in a chemical–physical theory. These are by the use of various mathematical techniques, by the use of subsidiary thermodynamic data along with models, and by the use of various nonthermodynamic techniques, primarily various types of spectroscopy.

Mathematical Models. The simplest approach is to use what is called the simplified chemical physical theory, SCPT, as presented by many authors.[35–39] The number of physical parameters is reduced by assuming that the physical interactions take place according to the bulk, not the true, composition. The number of components for physical interactions is 2, and those systems forming a single compound may have as few as two adjustable parameters at one temperature. For example, the Scatchard equation[40] can be used in the SCPT for representing the physical interactions,

$$g^E(\text{physical}) = \omega_{12}(T)\Phi_1\Phi_2$$

where Φ is the bulk or apparent volume fraction, and ω_{12} is the (temperature-dependent) interchange energy. This application not only reduces the number of parameters but, more importantly, uncouples the equations (since the K_α is independent of the true composition). An example[39] of SCPT is shown for the partial molal enthalpy in the Zn-Sb system (Figure 5), which also depicts the separated chemical and physical contributions.

A second mathematical method for parameter reduction is the adoption of some predictive solution theory such as regular solution theory. For a solvated solution the parameters needed are the volume and the

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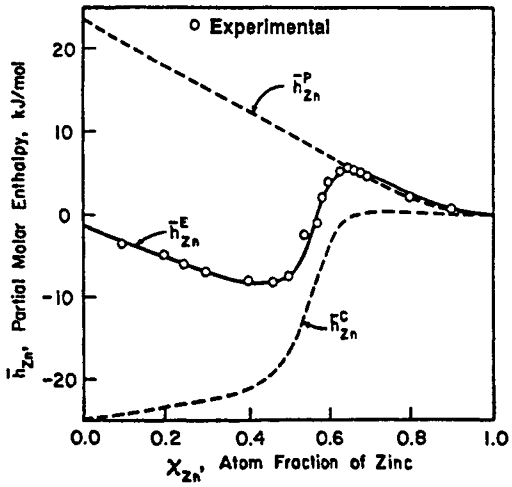

Figure 5. Physical and chemical contributions to the partial molar enthalpy in the zinc–antimony system at 823 K (data of Rubin et al.[69]).

solubility parameter of the complex. Results tend to be very insensitive to the volume, and the assumption of a zero volume change on formation of the complex works quite well. The solubility parameter of the complex can be estimated by a variety of means or used as an adjustable parameter. An example of this application is shown in Figure 4.

Renon and Prausnitz[7] also used regular solution theory in their work on associated alcohol solutions, which form alcohol oligomers by hydrogen bonding. The chemical part of the problem was treated by Flory–Huggins statistics, and the physical interactions were characterized by regular solution theory. The authors reduced the number of adjustable parameters yet further by assuming a constant heat of formation of hydrogen bonds for alcohols.

Another mathematical method for the reduction of parameters is a linearization technique,[41] analogous to the linear free energy relationships used so often by organic chemists. This approach combines an SCPT treatment for the physical forces, using one adjustable parameter, with a linearization of the free energy of formation of compounds, resulting in one adjustable parameter for the chemical forces.

Other Thermodynamic Data. One can use a variety of thermodynamic data other than the traditional VLE data or activity coefficient data along with a model of the system to evaluate parameters. Often used are enthalpy of mixing data, which have the additional benefit of yielding temperature dependence. Hepler and Fenby[42] used molar excess enthalpy data to find a 1:1 equilibrium constant and the enthalpy of complex formation in the chloroform–triethylamine system, in good agreement with spectroscopic results. A limitation is that a single h^E curve cannot be expected to give more than two parameters accurately. Therefore, the method is limited to known stoichiometries, symmetric h^E curves, and a positive temperature coefficient. In the case of a chemical model only, the magnitude of the excess enthalpy at its maximum should exceed at least 2 kJ/mol in order to neglect physical contributions.[42] All parameters determined in this way are model-dependent.

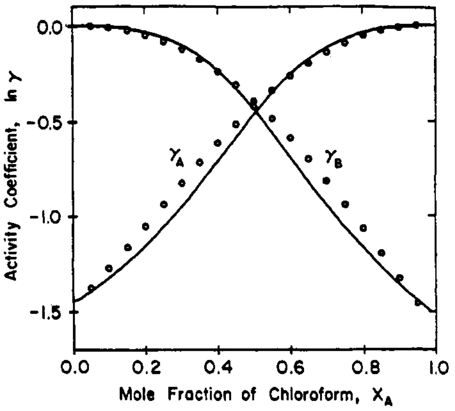

Figure 6. Chemical–physical model fit of activity coefficients in the chloroform–tetrahydrofuran system at 30 °C (data of Van Ness and Abbott[70]).

Other thermodynamic properties can be used, such as SLE. Grigg et al.[43] investigated the correlation between excess volume and the tendency toward charge-transfer-complex formation for mixtures of carbon tetrachloride with *N,N*-dimethylformamide and carbon tetrachloride with *N,N*-dimethylacetamide. SLE data have also been used for metal alloys.[27,44]

Nonthermodynamic Methods. All thermodynamic methods deal with chemical potential or fugacities, and the relationship between composition and fugacities is always model-dependent. Spectroscopic methods measure numbers of molecules and numbers of interactions and give different information which may be used to evaluate directly the composition of complexes formed. A traditional method was the use of infrared spectroscopy to look at hydrogen bonding in solution. More recently FTIR and NMR have proven to be even more powerful tools.

Information about equilibrium constants is readily extracted from spectroscopic information by such treatments as the Benesi–Hildebrand method[45] and the more general approach of Rose and Drago.[46] The *K*'s determined from this method are solvent-dependent since the activity coefficients of the species change; to get the thermodynamic equilibrium constant, a physical model such as the Scatchard equation must be adopted.

Such models can readily be extended to include both chemical and physical interactions by the addition of a physical model. An example for solvated systems is the NMR measurement of the equilibrium constant coupled with a thermodynamic method, the limiting activity coefficient from differential ebulliometry, to get the parameter needed for the physical model[35] (Figure 6). Note that there are no adjustable parameters in this model.

A combination of these methods has been extended to the case of associated solutions by Karachewski et al.[47,48] with the AVEC model, combining NMR data and linearization techniques such as those discussed above to treat the oligomers occurring in alcohol–hydrocarbon systems. Again, the sole physical param-

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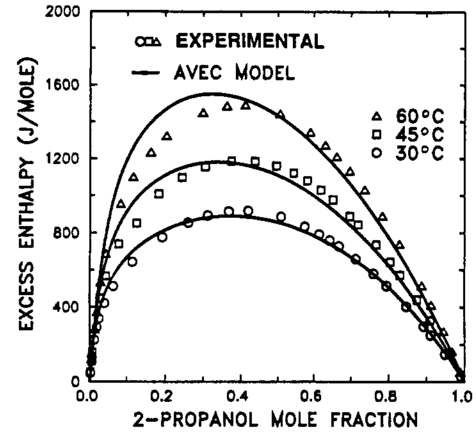

Figure 7. AVEC model prediction of excess enthalpy for 2-propanol and heptane (data of Van Ness et al.[71]).

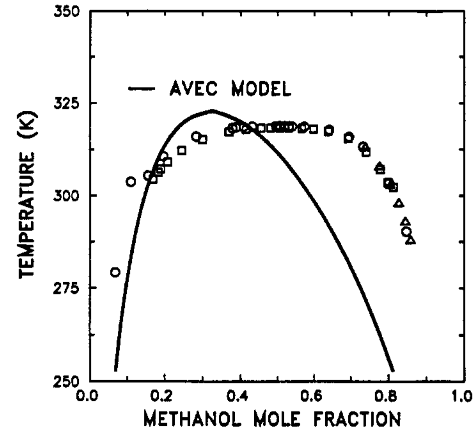

Figure 8. AVEC model prediction of coexistence curve for methanol and cyclohexane (data of Jones et al.[72] Eckfeldt et al.,[73] and Kiser et al.[74]).

eter was found independently by a limiting activity coefficient measurement. An example of the results is shown in Figure 7, the excess enthalpy predictions for the 2-propanol–heptane system. These types of results can even be extended to the very severe challenge for any solution theory: that of predicting LLE behavior. Karachewski's AVEC model gives a not unreasonable representation of such behavior for highly associated systems, as is shown in Figure 8.

Efforts are now underway to use spectroscopy to investigate interactions in supercritical fluid (SCF) solutions, to yield information for chemical or chemical–physical models. Early work concentrated on characterizing the SCF using the π^* solvatochromic indicators[49-53] and indicated a distinct change in the solvent behavior in the region of high solvent compressibility. UV and fluorescence spectroscopy have revealed enhanced local densities about a solute molecule in a SCF, presumably due to the high solvent compressibility and strong interactions between solute and solvent.[54-56] This enhanced density effect can also be seen in molecular dynamics simulations[57] and described by integral equation theories.[58] Direct comparisons between fluorescence spectroscopy and simulations agree well.[59]

The effect of cosolvents which may enhance solubilities in SCFs through specific chemical interactions is of particular interest. Donohue and co-workers have used IR spectroscopy to explain cosolvent effects in terms of chemical association and applied their chemical–physical model (APACT) to supercritical fluid solutions containing a cosolvent.[60] This effort falls short of using independent experimental data to find parameters for the model but provides a good basis for further work. Lemert and Johnston[61] inferred the existence of strong chemical interactions in the hydroquinone–tributylphosphate–supercritical CO_2 system from solubility measurements and successfully modeled the results using the Peng–Robinson equation for physical interactions. Spectroscopic probes such as phenol blue and 2-nitroanisole have been used in CO_2–acetone and CO_2–2-propanol mixtures, respectively, to show local composition enhancements of cosolvent around the dye molecule.[62,63] Time-resolved fluorescence spectroscopy of probes in SCF–alcohol mixtures[64] allows more precise interpretation of the results in terms of ground-state vs excited-state interactions and may lead to clearer relationships between spectroscopy and thermodynamics. Recent work has been carried out using spectroscopy to probe the cosolvent/solute interaction directly.[65,66]

To date, the connection between the spectroscopic results and chemical theory equilibrium constants is incomplete, but this is clearly the next step. In any event, it is clear that the extrathermodynamic information from spectroscopy will make significant contributions to the eventual thermodynamic models.

Summary/Conclusions

Many examples exist of solutions where chemical forces are important. If the chemical forces are quite

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dominant, a simple ideal chemical theory will generally give better results than any physical model. However, in the majority of systems of interest, both chemical and physical forces are important, and in order to use any combined theory, it is necessary to reduce the number of adjustable parameters by mathematical, thermodynamic, or nonthermodynamic methods. The mathematical methods in general simplify the problem by making it tractable; without some mathematical method one could almost never get enough parameters to use a general chemical–physical theory. The thermodynamic methods are frequently useful but have the disadvantage of being model-dependent, while the spectroscopic methods have the advantage of measuring compositions of chemical complexes directly instead of chemical potential or fugacity. In conclusion, a properly used chemical–physical model is a powerful tool in the rational design of specialty separations.

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