Equilibrium Properties of Liquids Containing Supercritical Substances

A two-parameter, corresponding-states form for direct correlation function integrals in liquids is applied to many types of systems with one substance being supercritical. This gives a quantitative correlation for volumetric behavior, pure and mixed solvent Henry's constants, and Henry's Law deviations over wide ranges of conditions using only pure-component information and a single binary parameter. Details of the method and results are given for H_2, N_2, CO, CH_4, and other gases in pure and mixed simple, polar, and aqueous solvents and coal oils. Because of its reliable predictive capability, the present approach can serve as a generator of data for parameter estimation by other models such as equations of state.

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Introduction

Current design practice for high-pressure chemical processing and multisolvent gas absorption requires increasingly better correlations of physical properties of systems containing species at temperatures above their critical point. Treatments for systems containing H_2, N_2, CO, CH_4, or other gases, such as proposed by Soave (1972), Peng and Robinson (1976), and Brule et al. (1982), generally rely on a complete equation of state, such as the Redlich-Kwong equation. Others, such as Prausnitz and Chueh (1968), describe deviations of the liquid phase from Henry's Law. Both treatments have been of limited value when applied to liquids containing highly polar species such as ammonia, water, and alcohols. In particular, activity coefficient and pressure contributions to the supercritical component fugacities tend to compensate, so their product may be poorly described. Also, even in binary solvents, Henry's constant is often poorly predicted from pure-component solubilities and solvent properties.

The present work applies a general formulation of the problem using the fluctuation solution theory of statistical mechanics. Expressions can be written for derivatives of the activity coefficient and of the pressure with respect to the concentrations of the species. Using expressions for the direct correlation function integrals (DCFI) in terms of concentrations, these derivatives can then be integrated from any liquid reference state to any desired final state. Deviations from Henry's Law in pure and mixed solvents are one kind of application. Another is prediction of Henry's constants of a solute in pure or mixed solvents using a known Henry's constant of the same solute in another solvent. Extension to multiple solutes is also straightforward and these ideas can be applied to a diverse set of systems including hydrocarbon, polar, aqueous, and coal oil solutions of the above gases.

The result of this work is a practical and accurate method for describing the component fugacities and volumetric behavior of nonelectrolyte liquids containing supercritical components, regardless of the complexity of the intermolecular forces in the system. The DCFI have been correlated with density and temperature using two-parameter corresponding states. Parameters are given for over 55 substances, including gases, small and large hydrocarbons, polar and hydrogen-bonding solvents, and mixed coal oils. Comparisons are made for 33 high-pressure systems with excellent results. Procedures are described for obtaining parameters for other components from liquid density data. For pure or pseudopure (e.g., coal oil) solvents, analytical expressions are used to calculate changes in volume and in component fugacities as the composition and pressure are changed from the liquid reference state of Henry's Law to the system conditions. While a binary constant is used, the results are generally insensitive (±0.1) to its value. For many systems, such as H_2 in coal oils, NH_3, and methanol, pure-solvent saturation pressure and density along with a single fitted gas-solvent binary parameter are sufficient information to accurately correlate behavior over the entire range of available conditions.

For gas solubility in mixed solvents the present method appears to be the most generalized and reliable available, as

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shown by comparisons with 50 nonaqueous and 24 aqueous binary mixtures and one aqueous ternary system. In addition to the parameters, pure-solvent Henry's constants and densities and—particularly for aqueous systems—binary solvent densities are needed as input.

The present paper shows how this generalized technique can be used in its present form for even the most complex systems; the only additional requirement is an easily available vapor-phase model, for example, that of Nakamura et al. (1976). In addition, the method can generate reliable data for fitting parameters of sophisticated full equations of state for use in the critical region or in higher order multicomponent systems containing supercritical components.

Basic Expressions

We use a liquid reference state, plus a vapor equation of state and activity coefficient model rather than a single equation of state for both phases. Prausnitz and Chueh (1968), Van Ness and Abbott (1962), and Prausnitz et al. (1986) have described this most extensively. The liquid fugacity is given as:

$$\hat{f}_i(T,P^f,\underline{x}^f) = x_i^f[(\hat{f}_i/x_i)^r(T,P^r,\underline{x}^r)] \cdot \gamma_i(T,P^r,\underline{x}^f)\exp\left\{\int_{P^r}^{P^f} \left.\frac{\bar{V}_i(T,P,\underline{x}^f)}{RT}\right|_{T,\underline{x}} dP\right\} \tag{1}$$

In Eq. 1, the final state fugacity $\hat{f}_i$ is obtained from the reference state fugacity $(\hat{f}_i/x_i)^r$ by a two-step thermodynamic process: A change in composition at constant reference pressure to obtain the activity coefficient, γ_i, followed by a change in pressure to the final value using the exponential Poynting correction. The reference state for the subcritical component is the pure-component, saturated liquid, so $(\hat{f}_i/x_i)^r$ is $\phi_i^{Vsat} P_i^{sat}$. The value of $(\hat{f}_i/x_i)^r$ for the supercritical solute is Henry's constant, H_i, the fugacity of the hypothetical pure liquid corresponding to the ideal dilute solution at the reference pressure.

$$H_i \equiv \lim_{\substack{x_i \to 0 \\ P \to P^r}} (\hat{f}_i/x_i) \tag{2}$$

The quantity in braces in Eq. 1 represents the total deviation from ideality. For low-pressure, subcritical systems, the Poynting correction is small while the (usually) large activity coefficient can be modeled by excess free energy expressions (Prausnitz et al., 1986). For systems with supercritical components, the pressure correction is large and the activity correction is small for the solvent components, while the two effects cancel to a significant extent for the supercritical solutes (Mathias, 1978; Mathias and O'Connell, 1981). Figure 1 shows this for the system hydrogen-methanol.

Thus, when supercritical components are present, the liquid fugacity can advantageously be written with the deviations combined into a single quantity, γ_i^f,

$$\hat{f}_i(T,P^f,\underline{x}^f) = x_i^f[\hat{f}_i/x_i)^r(T,P^r,\underline{x}^r)]\,\gamma_i^f(T,P^f,\underline{x}^f) \tag{3}$$

We have found that an accurate value for γ_i^f can be obtained from fluctuation solution theory, which uses integrals of the statistical mechanical direct correlation function (DCFI). These are insensitive to the nature of the intermolecular forces in the fluid (Brelvi and O'Connell, 1972, 1975a, b, c; Gubbins and O'Connell, 1974), so two-parameter corresponding states can be applied to predict the integrals of these correlation functions as a function of reduced temperature and reduced density. Because the theory yields the concentration derivatives of both the activity coefficient and the pressure, values of γ_i^f can be obtained for systems where the solvent is present. Further, by proper manipulation (O'Connell, 1981), it can be found for cases where the reference state solvent does not actually appear in the solution of interest. This potentially powerful concept takes advantage of the generality of Eq. 3 by using it in the limit of infinite dilution of component i when the solvent composition is changed from a pure reference solvent ($x_r \to 1$) to any other solvent composition. Thus, if $(\hat{f}_i/x_i)^r = H_{iR}$, then $\gamma_i^f = H_{im}(T,P^f,\underline{x}^{SF})/H_{iR}$ where H_{im} is Eq. 2 in a mixed solvent at the same temperature and the solute-free composition is $\underline{x}^{SF}$. Because of this flexibility, as well as its general insensitivity to binary parameter values, the technique may considerably reduce the data requirements for accurate modeling of systems with supercritical components, particularly in mixed solvents.

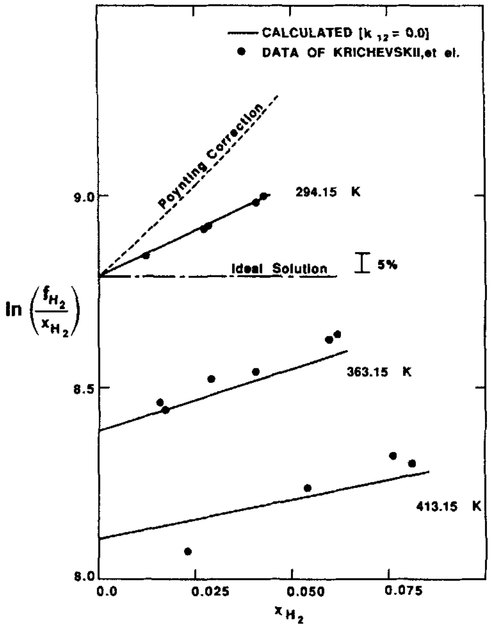

Figure 1. Fugacity of hydrogen(1) in methanol(2) at various temperatures.

——— calculated; –·–·– Henry's Law; ––– Poynting correction only

The present paper describes extensive, but not exhaustive, applications of the method. The following sections include basic expressions, DCFI model equations, pure-liquid properties and parameter evaluation, high-pressure binary system correlation and prediction, mixed-solvent applications including Henry's constants, and improvements and extensions.

The DCFI between species i and j, C_{ij}, can be related to derivatives of the activity coefficient of Eq. 3 (Mathias, 1978; Mathias and O'Connell, 1981).

$$\left.\frac{\partial \ln(\hat{f}_i/x_i)}{\partial \rho_j}\right|_{T,\rho_{k\neq j}} = \left.\frac{\partial \ln \gamma_i^f}{\partial \rho_j}\right|_{T,\rho_{k\neq j}} = \frac{1 - C_{ij}(T,\underline{\rho})}{\sum_{k=1}^{N} \rho_k} \tag{4}$$

The Gibbs-Duhem equation, together with Eq. 4, yields

$$\left.\frac{\partial P/RT}{\partial \rho_i}\right|_{T,\rho_{j\neq i}} = \sum_{k=1}^{M} x_k[1 - C_{ik}(T, \underline{\rho})] \qquad (5)$$

As described by O'Connell (1981), if the system changes from the state $(T,P^r,x^r) = (T,\underline{\rho}^r)$ to the state $(T,P^f,\underline{x}^f) = (T,\underline{\rho}^f)$, Eq. 4 and 5 can be integrated to provide values for the changes in activity coefficient and pressure. For example, if $P^r,\underline{x}^r$, $P^f,\underline{x}^f,\rho^r$ are known, integration of Eq. 5 for all components i yields ρ^f. Integration of Eq. 4 for all components j yields values of $\ln \gamma_i^f$.

DCFI Model

The basis of the model in corresponding states is described elsewhere (Mathias and O'Connell, 1981). The result is an expression based on hard spheres and is of the van der Waals form

$$C_{ij}(T, \underline{\rho}) = C_{ij}^{hs}(\underline{\xi}) - 2\rho[\tilde{B}_{ij}V_{ij}^{*} - B_{ij}^{hs}] \qquad (6)$$

This form has been used previously in a different context (Bienkowski et al., 1973). The expressions we use for C_{ij}^{hs}, $\tilde{B}_{ij}$ and B_{ij}^{hs} are given in the Appendix. There are two pure-component parameters, T_i^{*} and V_i^{*}, and a binary constant k_{ij}, which appears only in $\tilde{B}_{ij}$. This allows the integrations of Eqs. 4 and 5 to be carried out analytically.

Thus, ρ^f can be found directly by solving

$$\frac{P^f - P^r}{RT} = \frac{P^{hs}(T, \underline{\rho}^f) - P^{hs}(T, \underline{\rho}^r)}{RT} + \sum_{i=1}^{M}\sum_{j=1}^{M} [\rho_i^f\rho_j^f - \rho_i^r\rho_j^f][\tilde{B}_{ij}V_{ij}^{*} - B_{ij}^{hs}] \qquad (7)$$

Then the activity coefficient can be calculated from

$$\ln \gamma_i^f = \frac{\mu_i^{hs}(T, \underline{\rho}^f) - \mu_i^{hs}(T, \underline{\rho}^r)}{RT} + 2\sum_{j=1}^{M} (\rho_j^f - \rho_j^r)[\tilde{B}_{ij}V_{ij}^{*} - B_{ij}^{hs}] \qquad (8)$$

and used in Eq. 3. Equation 8 with its implied single integral should be compared to Eq. 1, in which there are two steps, an integral over pressure and an activity coefficient. As noted previously (Mathias and O'Connell, 1981), these two cancel significantly for a supercritical component. Because the C_{ij} values are considerably different, the results from Eqs. 7 and 8 are not highly sensitive to errors in their modeling.

Application to Pure-Liquid Properties and Parameter Evaluation

In the case of pure liquids, Eq. 7 becomes

$$\frac{P^f - P^r}{RT} = \rho^f[1 + (\xi_3^f)^4 - 2(\xi_3^f)^3]/[1 - \xi_3^f]^4 - \rho^r[1 + (\xi_3^r)^4 - 2(\xi_3^r)^3]/[1 - \xi_3^r]^4 + (\tilde{B}_{ii}V_{ii}^{*} - B_{ii}^{hs})[(\rho^f)^2 - (\rho^r)^2] \qquad (9)$$

Using volumetric data for compressed liquids over a range of temperatures, a least-squares fit can be made to obtain V_{ii}^{*} and T_{ii}^{*}. While the functional form chosen for C_{ii} describes simple fluids over all conditions of states, the correlation will work well for other substances only for $\rho > 1.5\ \rho_c$ when $T < 2T_c$. As the temperature is raised, the density limit falls. We have systematically excluded all data where T/T_c is within 0.05 of unity and where $V/V_c < 1.3$ except if $T/T_c > 3$. Table I of the supplementary material (SM) shows values obtained from compression data for 59 different substances, including inorganics, hydrocarbons, polar organics, and coal oils. In general, the values of T_{ii}^{*} and V_{ii}^{*} are near the critical values for nonpolar species (this fact has been used for coal oils), but are significantly less for polar components. The results are not particularly sensitive to the value of T_{ii}^{*}, so reasonably close estimates are satisfactory. However, the sensitivity to V_{ii}^{*} may preclude estimating this value; only experimental compression data accurate to within a few percent in the compressibility

$$\kappa_T = -\left.\frac{1}{V}\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho RT(1 - C_{ii})} \qquad (10)$$

are sufficient.

Equation 9 represents an isothermal equation of state in the same spirit as that used by Brelvi and O'Connell (1975b, c) for liquids and liquid mixtures in the reduced density range from 1.5 to 3.65 or higher. For mixed liquids, the pseudocharacteristics, such as

$$V_m^{*} = \sum_{i=1}\sum_{j=1} x_i x_j[(V_{ii}^{*1/3} + V_{jj}^{*1/3})/2]^3 \qquad (11a)$$

$$T_m^{*} = \sum_{i=1}\sum_{j=1} x_i x_j[(V_{ii}^{*1/3} + V_{jj}^{*1/3})/2]^3 \cdot (T_{ii}^{*}T_{jj}^{*})^{1/2}(1 - k_{ij})/V_m^{*} \qquad (11b)$$

should be somewhat more accurate in Eq. 9 than the earlier Brelvi method. However, we have not tested this extensively because only a small improvement in accuracy would be obtained from increased complexity. In addition, a much more accurate method has recently been developed (Huang, 1986).

Application to High-Pressure Binary Systems—Correlation

For systems with a supercritical component 1 and a subcritical component 2, we choose the reference state as the pure saturated solvent (2) at the temperature of interest. Equation 3 is then

$$\hat{f}_1(T, P^f, x_1^f) = x_1^f H_{12}(T, P_2^{sat})\gamma_1^f(T, P^f, x_1^f) \qquad (12a)$$

$$\hat{f}_2(T, P^f, x_1^f) = (1 - x_1^f)\phi_2^{Vsat}(T)P_2^{sat}(T)\gamma_2^f(T, P^f, x_1^f) \qquad (12b)$$

The values of the γ_i^f can be obtained from Eqs. 7 and 8 ($P^r = P_2^{sat}$), the parameters, and the solvent density ($\rho^r = \rho_2^{sat}$). If a vapor equation of state is available to calculate vapor fugacities $\hat{f}_1(T, P^f, y_1)$ and $\hat{f}_2(T, P^f, y_1)$ at the conditions, vapor-liquid equilibria can be calculated by setting the vapor fugacities equal to the righthand sides of Eqs. 12a and 12b. Here we input T, P^f, and solve for x_1^f and y_1 in order to compare results with the most sensitive liquid property, x_1^f. The vapor equations we use are those of Prausnitz and Chueh (1968), Nakamura et al. (1976), or Hayden and O'Connell (1975), depending on the system.

If only high-pressure data are available, the Henry's constant is normally not known except by extrapolation to low pressure. In such cases our correlation procedure has been to use Eqs. 8 and 9 to determine γ^f and to find the parameters a_0, a_1, a_2 in such equations as

$$\ln H_{12} = a_0 + a_1 T + a_2 T^2 \tag{13}$$

by minimizing the sum of errors squared $\Sigma(x_1^{exp} - x_1^{calc})^2$ for all measured points. The results of fitting a variety of systems with H_2, CO, N_2, CH_4, and CO_2 in 15 nonpolar, three polar, and three associating solvents (H_2O, NH_3, CH_4O) are shown in Table II and columns 1–10 of Table III of the supplementary material. In general, the RMS errors in x_1 are of the order of 1% with maxima of less than 4%. We believe that some of the error comes from inadequate vapor phase equations and the liquid description appears to be very precise. [An example is the H_2-C_6H_6 system, where the present values for γ_i agree better with the values of Connolly (1962) than do values of ϕ_i^V.] The binary parameter values are subjectively chosen to give good agreement, but the results are sufficiently insensitive to k_{ij} that any value within ±0.03 of the value cited would yield comparable correlations. In most cases, variations of up to 0.1 or more would not even double the error. Thus, if only the low-pressure solubility (Henry's constant) had been known, we are confident that conditions for the high-pressure systems could have been predicted successfully using an estimated value of k_{ij}. Note that negative values are used for water, ammonia, and methanol.

Figures 1 and 2 show the results for the systems with hydrogen; the extensive volumetric and phase behavior data of Connolly (1962) allowed us to make detailed analysis of calculated and experimental solution molar volumes. Comparisons with the properties tabulated by Connolly show that most of our error is in the vapor phase. In this case, as shown before (Mathias and O'Connell, 1981), if only the Poynting correction had been included (the Krichevskii-Kasarnovsky method; see Prausnitz et al., 1986), there would be far too positive a correction from the ideal solution.

Figure 3 shows similar results for the system nitrogen-water. The correlated values are within 0.0001 mole fraction for pressures up to 300 bar with a binary constant $k_{12} = 0$, even though the best fit is with $k_{12} = -0.25$.

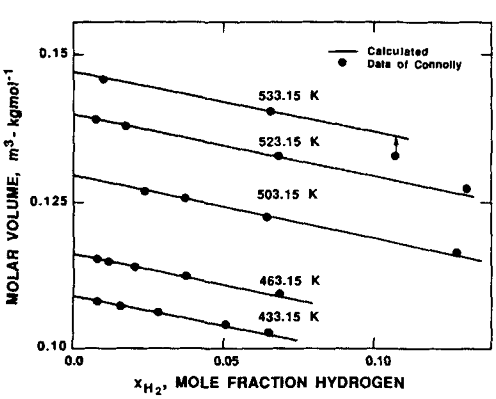

Figure 2. Molar volumes of hydrogen(1)-benzene(2) liquid solutions.

——— calculated
Data of Connolly (1962)

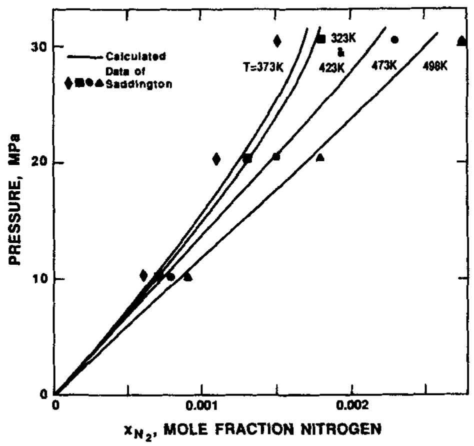

Figure 3. Pressure-liquid composition relations for nitrogen(1) with water(2).

Data of Saddington and Krase (1934)

Application to Binary Systems—Prediction

One use of Eq. 8 is for the variation of solute fugacity from infinite dilution in one solvent (R) to infinite dilution in another (2), that is, prediction of H_{12} knowing H_{1R} at the same temperature. This follows from

$$\begin{aligned}\ln (H_{12}/H_{1R}) &= \lim_{x_2 \to 1} \ln (\hat{f}_1/x_1) - \lim_{x_r \to 1} \ln (\hat{f}_1/x_1) \\ &= \ln \gamma_1^f(T, \rho^f = \rho_2^{sat}, \rho^r = \rho_R^{sat}) \end{aligned} \tag{14}$$

With values of H_{1R}, H_{12}, ρ_R^{sat}, ρ_2^{sat}, and the pure-component parameters, Eq. 14 is a connection of k_{1R} to k_{12}. (We have chosen the particular form of Eq. 14 to ensure symmetry with respect to either solvent as the reference.) This means that once a k_{1R} value is chosen for a solute (1) in a particular solvent (R), the values for that solute in all other solvents (2, 3, . . .) will be fixed by the Henry's constant ratio of Eq. 14. To the degree that the model is successful, the k_{ij} values will be independent of temperature. Over a considerable range this is true for hydrogen, so predictions of entire systems of H_2 in coal oils are described in Table IIISM. The RMS and maximum errors in the predicted values of x_1 are no worse than twice those of the fitted values. Here quinoline is the reference solvent, although its binary parameter is consistent with benzene through their Henry's constants in Eq. 14. The tabulations of Table IISM and the left side of Table IIISM have not been constrained to meet the consistency requirement, so adjustments in k_{12} must be made for the systems in Table IISM before prediction of H_{12} can be made. An example of results when a reference solvent is used is shown in Figure 4, where high-pressure phase behavior for the hydrogen(1)-methanol(2) system (data of Krichevskii et al., 1937) are obtained with benzene as the reference solvent (R). The values from fitting the parameters in Eq. 16 are substantially the same as the predicted values on the graph (RMS deviation in x_1 = 0.0018 predicted vs. 0.0012 fitted). The results are reasonably good considering that k_{12} was obtained by fitting only the methanol Henry's constant data over the temperature range, not the full set of phase equilibria.

The sensitivity of the Henry's constant to the value of k_{12} is the only apparent limitation in this predictive method. It must be specified to about 0.01 to 0.001 to achieve 1% accuracy in H_{12}

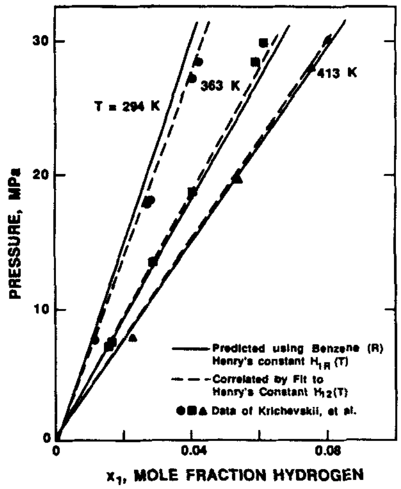

Figure 4. Pressure-liquid composition relations for hydrogen(1) in methanol(2).

Prediction using Henry's constants from hydrogen(1) in benzene(R)
Data of Krichevskii et al. (1937)

from H_{1R} and k_{1R}. It is unlikely that this can be predicted accurately enough, so it may be necessary to measure the low-pressure solubility of solute 1 in solute 2 to find H_{12} and obtain k_{12}. In addition, for many systems constant binary parameters will not completely reproduce the temperature dependence of the Henry's constants even though the solvent densities are used. This appears to be more of a problem for polar solvents and for gases with $T_c > 150$ K.

As expected, nonpolar systems show the best agreement. Figure 5 shows the carbon monoxide(1)–n-octane(2) system (Connolly and Kandalic, 1977) predicted from the carbon monoxide(1)-benzene(R) system. The prediction is effectively as good as the fitting (RMS deviation in $x_1 = 0.00026$ for prediction, 0.00016 for fitting).

A case of particular interest is the phase behavior of hydrogen with heavy aromatic species that appear in coal hydrogenation processes. We have fitted Henry's constant parameters to the data for each binary and correlated the properties of the systems using only Henry's constant for hydrogen(1) in quinoline(R) and k_{1R} while fitting k_{12}. Table IIISM shows the results for several of the systems measured by Chao and coworkers (Sebastian et al., 1981). In the absence of reliable solvent densities and isothermal compressibilities, the characteristic parameters were obtained from their estimated critical values. Table IIISM and the present Figure 6 for the hydrogen–m-cresol system show that the predicted results are nearly as good as the fitted ones, with RMS deviation in x_{H_2} around 1–2%. The resulting deviations in K-factors are less than 5%, but our vapor phase equation probably contributes much of the error.

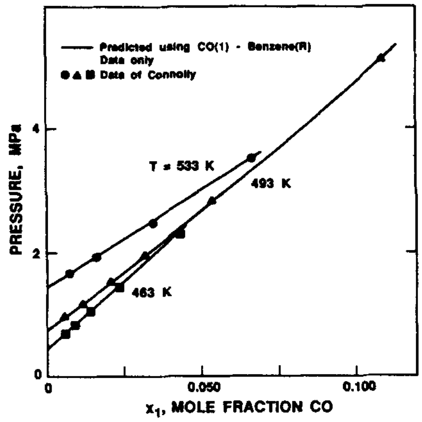

Figure 5. Pressure-liquid composition relations for carbon monoxide(1) in n-octane(2).

Prediction using Henry's constants for carbon monoxide(1) in benzene(R)
Data of Connolly (1977)

Applications—Mixed Solvents

While detailed discussion of the formulation of this problem is given elsewhere (Mathias and O'Connell, 1981), we outline here the basic approach for predicting the vapor-liquid equilibrium in two kinds of systems. In one, the solvent is a mixture of components of approximately the same volatility, so it can be treated as a pseudocomponent. In the second, the properties of the individual solvents $[T^*, V^*, \rho^{sat}(T), P^{sat}(T)]$ and their mixture $[G^E(T, P^r, \underline{x}^{SF}), V^E(T, \underline{x}^{SF})]$ are known and at least one Henry's constant for the supercritical species is available at the temperature of interest. A coal hydrogenation recycle solvent is representative of the former, while a Fischer-Tropsch solvent and mixed solvent absorbers may be typical of the latter.

The first case is most easily treated with the solvent assumed to be a single pseudocomponent. Experimental phase and volumetric behavior and an estimate of the molecular weight of the liquid alone should be measured to obtain P_p^{sat}, ρ_p^r, T_p^*, and V_{pp}^*. Except for the hydrogen systems where the data base of Tables IISM and IIISM can provide an adequate estimate, at least one low-pressure solubility measurement should be made for the supercritical component to obtain k_{1p}. Finally, the calculation of γ_i^f—Eqs. 6 and 8—is made for use in Eq. 3. This has been done successfully for the two "CLPP" Exxon Donor solvent coal oils cited in Table IIISM. It is also possible to mix the parameters, as is done in Eq. 11 with $k_{ij} = 0$, if the solvent components are

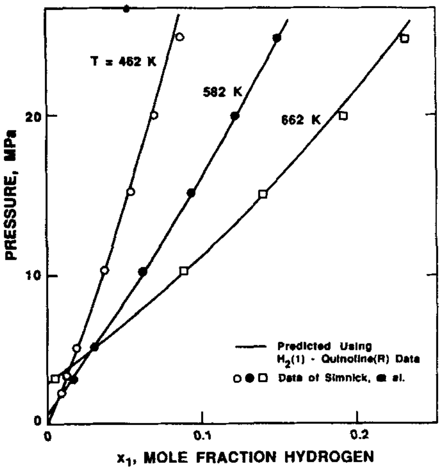

Figure 6. Pressure-liquid composition relations for hydrogen(1) in m-cresol(2).

Prediction using Henry's constants from hydrogen(1) in quinoline(R)
Data of Sebastian et al. (1981)

known. The four-component solvent used by Harrison et al. at BETC (Bartlesville Energy and Technology Center) (1985) was treated in this fashion. Further, Figure 7 shows the results for the bubble pressure of the $CH_4(1)$–n-$C_4H_{10}(2)$–n-$C_{10}H_{22}(3)$ system at $x_2/x_3 = 0.86$ and $T = 310.9$ K when $T_p^* = 559.2$ and $V_p^* = 450.0$. The values of P_p^{sat} and ρ_p^r are experimental, as described elsewhere (Mathias and O'Connell, 1981).

The second case involves a more complex process but does allow determination of the volatilities of all of the components. First, it must be understood that the method of this paper is not satisfactory to describe activity coefficients of systems with only subcritical species, because such values are too sensitive to small errors in the corresponding states correlation of the C_{ij} (Mathias and O'Connell, 1981; Campanella, 1984). Therefore, the reference state must be chosen as the mixed solvent at T with the fugacities of the solvents known. The solute reference fugacity is H_{lm}, while for solvent-components, j, it is

$$(\hat{f}_j/x_j)^r = \gamma_i^{SF}(T, \underline{x}^{SF})\phi_j^{Vsat}(T)P_j^{sat}(T) \qquad j = \text{solvents only} \quad (15)$$

with $\gamma^{SF}(T, \underline{x}^{SF})$ from an excess Gibbs energy model $G^E \cdot (T, P^r, \underline{x}^{SF})$. Although Henry's constant, H_{lm}, could be measured in the mixed solvent, as shown below, the method predicts this adequately, particularly if the solvent mixture density [or $V^E(\mathrm{T}, \underline{x}^{SF})$] is known. This is necessary because Eq. 6 does not work for mixtures of subcritical components. Here, Eq. 14 becomes

$$\ln(\hat{f}_1/x_1)^r = \ln H_{lm} = \ln H_{1R} + \ln \gamma_1(T, \rho^f = \rho_m^{sat}, \rho^r = \rho_R^{sat}) \qquad 1 = \text{solute} \quad (16)$$

where

$$\rho_m^{sat} = \frac{1}{\sum_{j=2}^{M} \frac{x_j^{SF}}{\rho_j^{sat}} + V^E(T, \underline{x}^{SF})} \quad (17)$$

The binary constants k_{1j} should be determined from k_{1R} and data on H_{1j} and H_{1R}, if available, to ensure consistency in the limit $x_j \rightarrow 1$. Otherwise, the value of k_{1j} must be predicted, resulting in a predicted H_{1j} value. Finally, Eq. 8 can be used as before to obtain deviations from ideality with the mixed solvent reference state. In most cases, the value of k_{ij} for Eqs. 8 and 16 is the same, but different values can be used in the equations if available data indicate that the model needs adjustment. Note that the present method avoids the difficulties encountered by Prausnitz and Chueh (Abrams et al., 1975).

We explore here in detail Henry's constants in mixed solvents since this appears to be the dominant error in phase equilibria in systems with supercritical components at conditions not too near the critical state. As discussed several times before (Nitta and Katayama, 1975; O'Connell, 1971, 1981; Zeck and Knapp, 1985) these properties are among the most challenging problems in physical property prediction because all correlations appear to be unreliable for certain systems, such as those with water. Much of this may be experimental error, but it is clear that all models can make large errors. Our treatment includes comparisons with many systems and methods, similar to that of Kung et al., (1984).

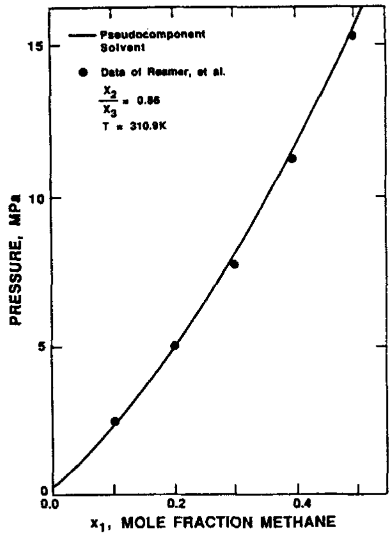

Figure 7. Bubble pressure for $CH_4(1)$–n-butane(2)–n-decane(3) system.

Prediction at $x_2/x_3 = 0.86$, $T = 310.9$ K, treating solvent mixture as a pseudocomponent.
Data of Sage and Lacey (1950).

$$T_{pp}^* = \sum_{i=2}^{3}\sum_{j=2}^{3} x_i x_j T_{ij}^* \qquad V_{pp}^* = \sum_{i=2}^{3}\sum_{j=2}^{3} x_i x_j V_{ij}^*$$

$$T_{23}^* = (T_2^* T_3^*)^{1/2} \qquad V_{23}^* = \frac{(V_{22}^{*\,1/3} + V_{33}^{*\,1/3})^3}{8}$$

$$k_{1p} = 0.12$$

The basic expression we use is Eq. 16. We fix the binary parameter k_{12} to be consistent with k_{1R}, H_{12}, and H_{1R} through Eq. 14. We show the results of predicting binary-solvent H_{1m} in Table IVSM for 56 nonaqueous systems and Table VSM for 24 aqueous systems. We also show the results for a ternary aqueous solvent in Table VISM. Also given are comparisons with other methods. One is based on simple weighting functions of pure-solvent Henry's constants.

$$\ln H_{1m} = \sum_{j=2}^{M} \theta_j \ln H_{ij} \qquad j = \text{solvents} \quad (18)$$

where in the ideal solution case, θ_j is the solute-free mole fraction

$$\theta_j \equiv x_j^{SF} = N_j \Big/ \sum_{k=1}^{M} N_k \quad (19a)$$

We examined the volume fraction, the "area" (volume raised to ⅔ power) fraction, the r fraction using the UNIQUAC "r" parameters (Prausnitz et al., 1980), and the q fraction using the UNIQUAC "q" parameters. The last was consistently better than all the others so the results from it are the only ones reported

$$\theta_j \equiv q_j \Big/ \sum_{k=2}^{m} q_k \quad (19b)$$

Other techniques include a solvent-dependent term subtracted from Eqs. 18 plus 19a. The simplest form of this was written by Kehiaian (1966) and O'Connell and Prausnitz (1964) and used by Prausnitz and Chueh (1968) where the solvent G^E/RT was subtracted. O'Connell (1971) and Kung et al. (1984) show that this is less satisfactory than their methods. At this time, the comparisons of Kung et al. imply that their method is probably the most accurate for nonaqueous solvents. However, they needed a different expression to get agreement within 15% for aqueous systems.

For nonaqueous binary solvents, the present method is as good as that of Kung et al., and relatively little accuracy is sacrificed when V^E is ignored in Eq. 17. Thus, for 267 data of 56 systems, the average error is 5% with nonzero V^E and 7% with zero V^E. For the 124 data of 30 systems we could compare with Kung et al., their error was 5% while the present method gave 5% error with nonzero V^E and 6% with zero V^E. For aqueous solvents the present method works well only if the excess volume is included. This is because the large negative V^E is significant compared to the small water molar volume. Thus, for 598 data of 67 systems, the average error was 8% with nonzero V^E and 24% for zero V^E. For the 346 data on 33 systems where the special method of Kung et al. achieved 11% error, the present model gave 7% errors for nonzero V^E and 22% error with zero V^E. While agreement for these systems is probably not within experimental error, the trends are generally followed to a greater accuracy and reliability than with other models. Figure 8 shows comparisons for two systems that show average deviations for the methods used. Table VISM shows that the agreement for the ternary aqueous solvent of Zeck and Knapp (1985) is the same as for the binary aqueous solvents.

Improvements and Computational Aspects

Despite the extensive comparisons we have made, there are several aspects that have been incompletely covered. These include other components of interest, convergence characteristics of our calculations, consistency of binary parameters between Henry's constant and nonideality correlations, excess volumes and mixed solvent Henry's constants, multiple solutes, and utilization to generate data for other correlations. We discuss these here.

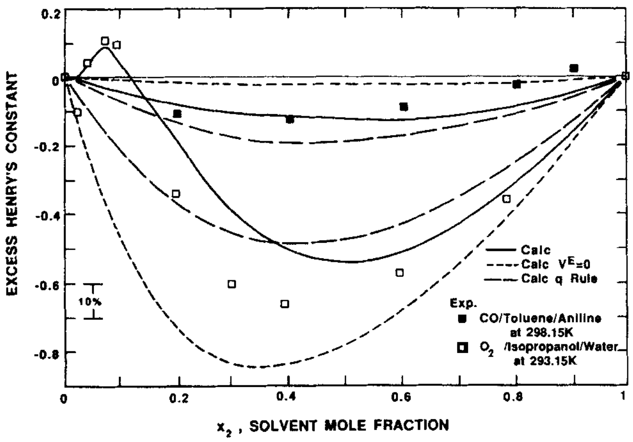

Figure 8. Excess Henry's constant for "average" systems.

Excess Henry's constant: $H^E_{1m} = \ln H_{1m} - \sum_{j=2}^{3} x_j^{SF} \ln H_{1j}$

Systems: CO(1) in tolunene(2)/aniline mixtures at 298.15 K and O_2(1) in isopropanol(2)/water mixtures at 293.15 K

1. The pure-component parameters in Table ISM are only a few of those for which the correlation could be used. The greatest source of liquid compression data is the work of Huang (1986), which collects data on over 250 substances and fits them to a more accurate form than Eq. 6. However, his correlation could also be used to generate data to obtain values of T^* and V^* for the present model. Obviously many other supercritical substances and solvents are of interest; Tables IISM and IIISM are only intended to assist users in judging the potential utility of the correlation for their purposes. It should be noted that as T^* of the solute increases, sensitivity to k_{12} values increases. Since we ignored reactions, the possibility of partial solute dissociation will also affect the accuracy of the results.

2. Some of the systems cited in Tables IISM and IIISM had a few more data points than we were able to use. In most cases, we were limited by the validity of the vapor equation of state chosen and the convergence in calculating x_1 and y_1 from T and P. In general, we could obtain good results up to solute amounts where y/x of the solvent component went through its minimum (50–90% of critical solute mole fraction). Such information might be useful to guide complete equations of state closer to the critical point. They certainly would not have the convergence problems of the present treatment. Also, in some of the high-pressure systems, we found that the best fit k_{12} depended on initial guess, primarily because of scatter in the data and insensitivity to the k_{12} value.

3. The optimal k_{12} value for binary high-pressure data is often different from that to predict consistent Henry's constants; that is, Table IISM gives different values than used for Tables IVSM and VSM. Since the results for γ are less sensitive to k_{12}, the values from Henry's constants are to be preferred. The most accurate results would be found by using different k_{12} values for γ and H_{12} in Eq. 12a when H_{12} is found from Eq. 14 and γ from Eq. 7. In this case, even though the k_{12} for H_{12} may depend on temperature when k_{1R} is fixed, a constant k_{12} can be used for γ. Table VIISM shows the binary parameters we have found.

4. Solvent excess volume data can be difficult to obtain. As Table IVSM shows, they may not be necessary for nonaqueous systems, but Table VSM shows that water systems must include such input. We have found as a rule of thumb that each 0.1% change in solution density changes H_{1m} by 1%. If density data are not available but H_{1m} data are, it is possible to obtain V^E as a function of composition and then construct a correlation such as Handa and Benson (1979) used. For ternary and higher order solvents, the additivity of binary V^E values seem adequate. We have compared experimental results for acetone-chloroform-benzene (Campbell et al., 1966), benzene–cyclohexane–*n*-hexane (Ridgway and Butler, 1967) and several ternaries with naphthenic, aromatic and pyridinic rings, and halogenated paraffins (Singh and Sharma, 1985), and water, methanol, and acetone (Zeck and Knapp, 1985) with the equation

$$V^E_{123} = \sum_{i=1}^{3} \sum_{j=1}^{3} V^E_{ij} \tag{20}$$

where V^E is the binary *i-j* solution excess volume calculated from the ternary mole fractions x_i and x_j in model expressions such as those of Handa and Benson (1979). (Note that $x_i + x_j \neq 1$.) The errors are rarely over 0.1 cm³/gmol.

5. For multiple solutes, the only modification to the above formulation involves Eqs. 6 and 7, with ρ_i^r for all solutes equal to zero. Comparisons with data for the system H_2-CH_4-tetralin (Simnick et al., 1980) and H_2-CO-methanol (Krichevskii et al., 1937) show good results and essentially complete insensitivity to the value of solute-solute binary constants.

6. New equations of state are sufficiently powerful that it is usually not necessary to choose separate models for the vapor and liquid to achieve good results as we have done here. However, such equations often require extensive data in order to choose proper mixing rules and values of the binary parameters for accuracy in the region of interest. Because of its reliability for the liquid, the present model may provide a basis to use a minimum of more readily accessible information (principally pure-solvent densities, vapor pressures, and low-pressure solubilities) to generate such data for fitting to a desired equation of state form.

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Notation

a_0, a_1, a_2 = parameters in Henry's constant correlation, Eq. 13
$\tilde{B}$ = reduced second virial coefficient, Eq. A7
B^{hs} = hard-sphere second virial coefficient, Eq. A10
C_{ij} = integral of direct correlation function for species i and j
$\hat{f}_i$ = fugacity of component i, bar
G^E = excess Gibbs energy, J/gmol
H_i = Henry's constant, Eq. 2, bar
k_{ij} = binary constant, Eqs. 11b and A8
M = number of components in system
N = number of moles
P = absolute pressure, bar
q = UNIQUAC parameter
R = universal gas constant = 83.143 cm³ · bar/gmol · K
r = UNIQUAC parameter
SM = supplementary material
T = absolute temperature, K
V = molar volume, cm³/gmol
$\bar{V}_i$ = partial molar volume of component i, cm³/gmol
V^E = excess volume, cm³/gmol
x_i = liquid mole fraction of component i

Greek letters

γ_i = activity coefficient of component i
δ_{ij} = Kronecker delta; = 1 if $i = j$, = 0 if $i \neq j$
θ_i = solute-free composition, Eqs. 18–19
κ_T = isothermal compressibility, bar^{-1}
μ_i = chemical potential of component i, J/gmol
ξ_α = reduced density, Eq. A5, $\alpha = 0, 1, 2, 3$
ρ = molar density of solution, gmol/cm³
ρ_i = molar density of component i, g/mol/cm³ = $x_i\rho$
σ_i = hard sphere diameter, Eq. A10
ϕ_i^V = vapor fugacity coefficient of component i

Subscripts

c = critical property
m = mixed solvent
p = pseudocomponent species (mixed solvent)
R = reference solvent
$\underline{\quad}$ = (underline) set of values for all components

Superscripts

calc = calculated value using theory
exp = experimental value
f = final state
hs = hard sphere expression
r = reference state
sat = saturated liquid condition
SF = solute-free solvent mixture
$*$ = characteristic property
$\tilde{}$ = reduced property

Appendix

Listed below are the expressions for the quantities used in Eqs. 4–9. The thermodynamic property differences are calculated from

$$\frac{P^f - P^r}{RT} = \frac{P^{hs}(T, \underline{\rho}^f)}{RT} - \frac{P^{hs}(T, \underline{\rho}^r)}{RT} + \sum_{i=1}^{M}\sum_{j=1}^{M} [\rho_i^f \rho_j^f - \rho_i^r \rho_j^r][\tilde{B}_{ij} V_{ij}^* - B_{ij}^{hs}] \quad \text{(A1)}$$

$$\frac{P^{hs}}{RT}(T, \underline{\rho}) = \frac{6}{\pi}\left[\frac{\xi_0}{(1 - \xi_3)} + \frac{3\xi_1\xi_2}{(1 - \xi_3)^2} + \frac{\xi_2^3(3 - \xi_3)}{(1 - \xi_3)^3}\right] \quad \text{(A2)}$$

$$\ln \gamma_i^f = \frac{\mu_i^{hs}(T, \underline{\rho}^f)}{RT} - \frac{\mu_i^{hs}(T, \underline{\rho}^r)}{RT} + 2\sum_{j=1}^{M} (\rho_j^f - \rho_j^r)(\tilde{B}_{ij} - \tilde{B}_{ij}^{hs}) \quad \text{(A3)}$$

$$\frac{\mu_i^{hs}}{RT}(T, \underline{\rho}) = \ln \rho - [\ln (1 - \xi_3)]\left[1 - \left(\frac{\xi_2\sigma_i}{\xi_3}\right)^2 \cdot \left(3 - 2\frac{\xi_2\sigma_i}{\xi_3}\right)\right] + [3(\xi_2\sigma_i + \xi_1\sigma_i^2) - (\xi_2\sigma_i)^3(2 - \xi_3)/\xi_3^2]/(1 - \xi_3) + \frac{3}{\xi_3}\left(\frac{\xi_2\sigma_i}{1 - \xi_3}\right)^2 + \frac{\pi}{6}\sigma_i^3 \frac{P^{hs}(T, \underline{\rho})}{RT} \quad \text{(A4)}$$

where

$$\xi_\alpha = \frac{\pi}{6}\sum_{i=1}^{M} \rho_i N_o(\sigma_i)^\alpha \quad \alpha = 0, 1, 2, 3 \quad \text{(A5)}$$

with $\rho_i = x_i\rho$. ρ is the molar density, N_o is Avogadro's number, and σ_i is the molecular diameter.

We have also defined

$$V_{ij}^* = (V_{ii}^{*1/3} + V_{jj}^{*1/3})^3/8 \quad \text{(A6)}$$

$$\tilde{B}_{ij} = 0.3625065 - \frac{0.7140666}{\tilde{T}_{ij}} - \frac{1.7543882}{\tilde{T}_{ij}^2} + \frac{0.470750}{\tilde{T}_{ij}^3} - \frac{0.0041793}{\tilde{T}_{ij}^8} \quad \text{(A7)}$$

where

$$\tilde{T}_{ij} = T/(1 - k_{ij})(T_{ii}^* T_{jj}^*)^{1/2} \quad \text{(A8)}$$

Further,

$$B_{ij}^{hs} = (\tilde{B}_{ii}^{hs} V_{ii}^* + \tilde{B}_{jj}^{hs} V_{jj}^*)/2 \tag{A9}$$

where $\tilde{B}_{ii}^{hs}$ and σ_i are related to reduced temperature and V_{ii}^*

$$\tilde{B}_{ii}^{hs} = \frac{\frac{2\pi}{3} N_o \sigma_i^3}{V_{ii}^*} = 0.65386227/(T/T_{ii}^*)^{0.16067976}$$

$$T/T_{ii}^* \geqq 0.73 \tag{A10a}$$

$$= 0.807662393 \exp\left[-0.22010926(T/T_{ii}^*)\right]$$

$$T/T_{ii}^* \leqq 0.73 \tag{A10b}$$

From Eq. 4

$$C_{ij}(T, \rho) = C_{ij}^{hs} - 2\rho[\tilde{B}_{ij} V_{ij}^* - B_{ij}^{hs}] \tag{A11}$$

with

$$\begin{aligned} -\frac{C_{ij}^{hs}}{\xi_0} = {} & (\sigma_i + \sigma_j)^3/(1 - \xi_3) \\ & + \{3\sigma_i\sigma_j\xi_2[(\sigma_i + \sigma_j)^2 + \sigma_i\sigma_j] \\ & + 3\xi_1(\sigma_i\sigma_j)^2(\sigma_i + \sigma_j) + \xi_0(\sigma_i\sigma_j)^3\}/ \\ & \cdot (1 - \xi_3)^2 + 9(\sigma_i\sigma_j\xi_2)^3/(1 - \xi_3)^4 \\ & + \xi_2(\sigma_i\sigma_j)^2/(1 - \xi_3)^3 \times \big(9\xi_2(\sigma_i + \sigma_j) \\ & + 6\xi_1\sigma_i\sigma_j + [6 + \xi_3(-15 + 9\xi_3)]/\xi_3 \\ & - (\sigma_i + \sigma_j)\xi_2[6 + \xi_3(-15 + 12\xi_3)]/\xi_3^2 \\ & + \xi_2^2\sigma_i\sigma_j\{6 + \xi_3[-21 \\ & + \xi_3(26 - 14\xi_3)]\}/\xi_3^3(1 - \xi_3)\big) \\ & + 6\xi_2(\sigma_i\sigma_j)^2 \ln(1 - \xi_3)[\xi_3 \\ & - (\sigma_i + \sigma_j)\xi_2 + \xi_2^2\sigma_i\sigma_j/\xi_3]/\xi_3^3 \end{aligned} \tag{A12}$$

In the limiting case of a pure fluid, Eq. A12 reduces to

$$-C^{hs} = 2\xi_3(4 - \xi_3)/(1 - \xi_3)^4 \tag{A13}$$

Fortran computer subprograms for evaluating the pressure-density relation of Eqs. A1 and A2 and the activity coefficient-density relation of Eqs. A3 and A4 are available from J. P. O'Connell.

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