in the list of sub-problems with $s_i = 1$ for all i and calculate $\mathbf{J}$ from (11). If this particular solution is feasible, add on costs to give $\bar{J}$; otherwise, use the absolute upper bound. Set $J^0 = \bar{J}$.

2. Take the sub-problem with least lower bound $\mathbf{J}$ from the list. If the list is empty then J^0 is optimal. If J^0 equals the absolute upper bound then no feasible solution exists.

3. If $\mathbf{J} > J^0$ go to step 2.

4. If $\bar{J} < J^0$ set $J^0 = \bar{J}$ and record particular solution.

5. If no more feasible combinations are possible, go to step 2.

6. Select the unspecified measurement i with largest cost (13) that gives a feasible combination when eliminated. Add a sub-problem to the list with $s_i = 1$ (provided that the specified combination is feasible) and with lower bound $\mathbf{J} + s'R_3s$. $\bar{J}$ remains unaltered.

7. Set $s_i = 0$ and calculate $\mathbf{J}$ from (11). If the particular solution is feasible add on measurement cost to give $\bar{J}$, otherwise $\bar{J}$ is set to the absolute upper bound. Go to step 3.

Literature Cited

Kafarov, V. V., et al., *Theor. Found. Chem. Eng.* (*USSR*), **7**, 224–229 (1973).
Kwakernaak, H., Sivan, R., "Linear Optimal Control Systems", Wiley, New York, N.Y., 1972.
Mellefont, D. J., Ph.D. Thesis, University of London, 1977.
Mellefont, D. J., Sargent, R. W. H., "Proceedings of the 8th IFIP Conference on Optimization Techniques, Wurzburg, 1977", J. Stoer, Ed., Vol. I, pp 166–176, Springer-Verlag, Berlin, 1978.
Pollard, G. P., Sargent, R. W. H., *Automatica*, **6**, 59–76 (1970).
Shunta, J. P., Luyben, W. L., *AIChE J.*, **17** (1), 92–97 (1971).
Weber, R., Brosilow, C., *AIChE J.*, **18** (3), 614–623 (1972).

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Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria. 1. Vapor–Liquid Equilibria

T. F. Anderson and J. M. Prausnitz*

Department of Chemical Engineering, University of California, Berkeley, California 94720

Pure-component UNIQUAC parameters have been calculated for 90 fluids and binary parameters have been obtained for 142 binary systems. All binary parameters were found from data reduction using the principle of maximum likelihood. The UNIQUAC equation is modified slightly to yield better results for those binary systems where an alcohol is one of the components. As in all equations for excess Gibbs energy, UNIQUAC parameters are not unique and they are at least weakly temperature dependent. The effects of parameter uncertainty are fortunately not large for typical vapor–liquid equilibria. Illustrative examples are given for a variety of strongly nonideal binary and ternary mixtures.

Because of its importance in design of separation operations, chemical engineers have given much attention to the thermodynamics of phase equilibrium in fluid mixtures. While numerous semiempirical equations have been proposed for calculating activity coefficients in mixtures of nonelectrolytes, a truly satisfactory equation has not as yet been established. However, a particularly useful equation, applicable to a wide variety of liquid mixtures, was given by Abrams and Prausnitz (1975); this equation, called UNIQUAC, uses only two adjustable parameters per binary in addition to pure-component parameters reflecting the sizes and outer surface areas of the molecules. In this work we consider in detail how the UNIQUAC equation can be used to represent binary and multicomponent vapor–liquid equilibria in typical mixtures of nonelectrolytes at low or moderate pressure. Toward that end we briefly review a recently developed method for reduction of experimental data to obtain UNIQUAC parameters; next, we propose an empirical modification in UNIQUAC which significantly improves the ability of UNIQUAC to represent the properties of mixtures containing alcohols, and finally, we present a variety of examples to illustrate how UNIQUAC may be used to correlate binary and predict multicomponent vapor–liquid equilibria. In the second article, immediately following this one, we consider multicomponent liquid–liquid equilibria.

Fundamental Thermodynamic Relations

When a liquid phase is in equilibrium with a vapor phase, the compositions of the two phases are related by a set of equations, one for each component i

$$\phi_i y_i P = \gamma_i x_i f_i^0 \tag{1}$$

where x is the liquid-phase mole fraction, y is the vapor-phase mole fraction, ϕ is the vapor-phase fugacity coefficient, γ is the liquid-phase activity coefficient, P is the total pressure, and f^0 is the standard-state fugacity.

The vapor-phase fugacity coefficients are calculated from an equation of state. At low or moderate pressures we use an equation of state which considers only two-body interactions; for mildly interacting components, this is the virial equation truncated after the second term and for strongly interacting systems (e.g., those containing a carboxylic acid), this is an equation based on a (chemical) dimerization hypothesis. Our method is that given by Hayden and O'Connell (1975) as briefly discussed in Appendix A.

Liquid-phase activity coefficients are related to the molar excess Gibbs energy g^E through

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$$g^E = RT\sum_i x_i \ln \gamma_i \quad (2)$$

and

$$\left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_j} = RT \ln \gamma_i \quad (3)$$

where R is the gas constant, T is the absolute temperature, n_i is the number of moles of component i, n_T is the total number of moles ($n_T = \sum_i n_i$), and $x_i = n_i/n_T$.

The standard-state fugacity is here taken as the fugacity of the pure liquid i at system temperature and pressure. It depends primarily on the pure liquid's vapor pressure as discussed elsewhere (Prausnitz, 1969).

At low or moderate pressure, g^E depends only on x and T since P has little effect. The UNIQUAC equation for g^E consists of two parts

$$g^E = g^E \text{ (combinatorial)} + g^E \text{ (residual)} \quad (4)$$

For a binary mixture

$$\frac{g^E \text{ (combinatorial)}}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_1} + \left(\frac{z}{2}\right)\left(q_1 x_1 \ln \frac{\theta_1}{\Phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2}\right) \quad (5)$$

$$\frac{g^E \text{ (residual)}}{RT} = -q_1' x_1 \ln (\theta_1' + \theta_2'\tau_{21}) - q_2' x_2 \ln (\theta_2' + \theta_1'\tau_{12}) \quad (6)$$

where the coordination number z is set equal to 10 and segment fraction, Φ, and area fractions, θ and θ', are given by

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}; \qquad \Phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \quad (7)$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}; \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \quad (8)$$

$$\theta_1' = \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'}; \qquad \theta_2' = \frac{x_2 q_2'}{x_1 q_1' + x_2 q_2'} \quad (9)$$

The parameters r, q, and q' are pure-component molecular-structure constants depending on molecular size and external surface areas. In the original formulation (Abrams and Prausnitz, 1975) $q = q'$. To obtain better agreement with water or alcohols, q' for water and alcohols has now been obtained empirically to give an optimum fit to a variety of systems containing these components. For alcohols, the surface of interaction q' is smaller than the geometric external surface q, indicating that for alcohols, intermolecular attraction is determined primarily by the OH group. Table I presents values of these structural parameters. A more complete table is available from the authors upon request.

For each binary combination in a multicomponent mixture, there are two adjustable parameters, τ_{12} and τ_{21}. These, in turn are given in terms of characteristic energies Δu_{12} and Δu_{21} by

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) \equiv \exp\left(-\frac{a_{12}}{T}\right) \quad (10)$$

$$\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) \equiv \exp\left(-\frac{a_{21}}{T}\right) \quad (11)$$

Table I. Some Structural Parameters for UNIQUAC Equation[a]

	r	q
carbon tetrachloride	3.33	2.82
chloroform	2.70	2.34
formic acid	1.54	1.48
methanol	1.43	1.43
acetonitrile	1.87	1.72
acetic acid	1.90	1.80
nitroethane	2.68	2.41
ethanol	2.11	1.97
acetone	2.57	2.34
ethyl acetate	3.48	3.12
methyl ethyl ketone	3.25	2.88
diethylamine	3.68	3.17
benzene	3.19	2.40
methylcyclopentane	3.97	3.01
methyl isobutyl ketone	4.60	4.03
n-hexane	4.50	3.86
toluene	3.92	2.97
n-heptane	5.17	4.40
n-octane	5.85	4.94
water[b]	0.92	1.40

size parameter q' for water and alcohols

water	1.00	C_4 alcohols	0.88
CH_3OH	0.96	C_5 alcohols	1.15
C_2H_5OH	0.92	C_6 alcohols	1.78
C_3 alcohols	0.89	C_7 alcohols	2.71

[a] Pure-component parameters for 90 fluids are available upon request to the authors. [b] For convenience, structural parameters for water are those determined by Abrams (1975).

Equations 10 and 11 give the primary effect of temperature on τ_{12} and τ_{21}. Characteristic energies Δu_{12} and Δu_{21} are often weakly dependent on temperature. The activity coefficients γ_1 and γ_2 are given by

$$\ln \gamma_1 = \ln \frac{\Phi_1}{x_1} + \left(\frac{z}{2}\right) q_1 \ln \frac{\theta_1}{\Phi_1} + \Phi_2\left(l_1 - \frac{r_1}{r_2} l_2\right) - q_1' \ln (\theta_1' + \theta_2'\tau_{21}) + \theta_2' q_1'\left(\frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}}\right) \quad (12)$$

$$\ln \gamma_2 = \ln \frac{\Phi_2}{x_2} + \left(\frac{z}{2}\right) q_2 \ln \frac{\theta_2}{\Phi_2} + \Phi_1\left(l_2 - \frac{r_2}{r_1} l_1\right) - q_2' \ln (\theta_2' + \theta_1'\tau_{12}) + \theta_1' q_2'\left(\frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{21}} - \frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}}\right) \quad (13)$$

where

$$l_1 = \left(\frac{z}{2}\right)(r_1 - q_1) - (r_1 - 1) \quad (14)$$

$$l_2 = \left(\frac{z}{2}\right)(r_2 - q_2) - (r_2 - 1) \quad (15)$$

Data Sources

Parameters a_{12} and a_{21} must be found from binary experimental data. Possible sources of data include: (1) vapor–liquid equilibrium data (P, y, x) at constant temperature; (2) total pressure data (P, x or y) at constant temperature; (3) vapor–liquid equilibrium data (T, y, x) at constant pressure; (4) boiling-point (or dew-point) data (T, x or y) at constant pressure; (5) mutual (liquid–liquid) solubilities; (6) azeotropic data; and (7) activity coefficients at infinite dilution.

With the exception of (5) and (7), reduction of such data requires an independent method for calculating vapor-phase fugacity coefficients. Appendix A briefly discusses such a method, applicable to a wide variety of systems at moderate pressure.

Data sources (1–3) are most common. The extensive data compilations and bibliographies by Wichterle et al. (1973), Gmehling and Onken (1977), and others, give literature references for a very large number of binary (and some multicomponent) systems.

Data source (4) is relatively rare and we have not used it in this work.

Data sources (5), (6), and (7) provide only two experimental points per binary. Parameters a_{12} and a_{21} can therefore be obtained by simultaneous solution of two equations. Unfortunately, more than one solution may be possible and judgement must be exercised to choose the physically significant solution.

Extensive azeotropic data are given by Horsley (1962), while mutual solubilities are reported by Stephen and Stephen (1964). Bibliographies for liquid–liquid equilibrium data are given by Francis (1972) and by Himmelblau (1959). When azeotropic or mutual-solubility data are used, small experimental errors can lead to large uncertainties in the binary parameters.

Azeotropic data are of little value when, at the azeotropic composition, the mole fraction of one of the components is close to unity.

Activity coefficient data at infinite dilution provide an excellent method for obtaining binary parameters as shown, for example, by Eckert and Schreiber (1971). Unfortunately, such data are rare.

When no experimental data at all are available, activity coefficients can sometimes be estimated using the UNIFAC method (Fredenslund et al., 1977a, b).

Since the accuracy of experimental data is frequently not high, and since experimental data are hardly ever plentiful, it is important to reduce the available data with care using a suitable statistical method and using a model for the excess Gibbs energy which contains only a minimum of binary parameters. Rarely are experimental data of sufficient quality and quantity to justify more than three binary parameters and, all too often, the data justify no more than two such parameters. When data sources (5), (6), and (7) are used exclusively, it is not possible to use a three (or more)-parameter model without making additional arbitrary assumptions. For typical engineering calculations, therefore, it is desirable to use a two-parameter model such as UNIQUAC.

Data Reduction: Methodology

The most reliable estimates of the parameters are obtained from multiple measurements, usually a series of vapor–liquid equilibrium data (T, P, x, and y). Because the number of data points exceeds the number of parameters to be estimated, the equilibrium equations are not exactly satisfied for all experimental measurements. Exact agreement between theory and experiment is not achieved due to random and systematic errors in the data and "lack of fit" of the model to the data. The optimum parameters must therefore be found by satisfaction of some selected statistical criterion. The criterion used here is based on the maximum likelihood principle which determines the optimum parameters so as to make all the experimental observations appear most likely when taken as a whole (Kreyszig, 1970; Bard, 1974; Fabries and Renon, 1975; Péneloux et al., 1976). With the general application of the method, all the pertinent information is used, including the nature and magnitude of the random errors in all measurements (Anderson et al., 1977).

For binary vapor–liquid equilibrium measurements the optimum parameters are those that minimize the objective functions given by

$$S = \sum_{i}^{N} \left[\frac{(P_i^0 - P_i^e)^2}{\sigma^2_{P_i}} + \frac{(T_i^0 - T_i^e)^2}{\sigma^2_{T_i}} + \frac{(x_{1i}^0 - x_{1i}^e)^2}{\sigma^2_{x_{1i}}} + \frac{(y_{1i}^0 - y_{1i}^e)^2}{\sigma^2_{y_{1i}}} \right] \quad (16)$$

subject to the two equilibrium constraints given by eq 1 for each component. The summation is over all N data points (P, T, x, y). Superscript e indicates an experimentally measured value, and superscript 0 indicates the estimated true value corresponding to each measured point. In eq 16 σ^2 is the estimated variance of each of the measured variables, i.e., pressure, temperature, and liquid and vapor-phase mole fractions. These variances are estimated from probable experimental uncertainties. The important feature to note here is that all the data are used and assumed to have some associated errors. Thus, the true value of each measured variable is also found in the course of the parameter estimation.

A similar method using combined P–T–x–y measurements has been proposed by Kemény and Manczinger (1978), although it is not based on the maximum likelihood principle and does not yield estimates of the true values of each measured variable.

The commonly used method of Barker (1953) assumes the liquid-composition and temperature measurements to be error free; the total pressure is calculated as a function of the estimated parameters. Then the sum of the squared differences between the calculated and measured pressures is minimized to give a best estimate of the parameters. In addition to neglecting errors in the independent variables, Barker's method also ignores information contained in the vapor-phase mole fraction measurements. The maximum likelihood method used here reduces to Barker's method when a single constraint is used, giving the total pressure as a function of temperature and liquid composition, and when σ_P^2 is very large relative to σ_T^2 and σ_x^2.

Using the criterion given by eq 12, binary parameters have been obtained for 130 distinct binary systems. Parameters for an additional 12 binary systems were estimated from azeotropic and mutual solubility data as discussed above. Table II lists a number of parameters for representative systems. A supplement listing all parameters obtained to date is available upon request from the authors.

Data Reduction: Illustrative Examples

Earlier experience with the UNIQUAC equation indicated that the original formulation of UNIQUAC ($q' = q$) gave only fair results for highly nonideal mixtures containing water and alcohols. The empirical modification, where area parameter q has a different value in the residual contribution to g^E, has introduced an additional unicomponent parameter. However, that parameter is only adjustable to the extent that a single value is chosen after examining a representative number of binary systems. The value of q', once fixed, is independent of binary (or multicomponent) data.

Figure 1 compares data reduction using the modified UNIQUAC equation with that using the original UNIQUAC equation. The data are those of Boublikova and Lu (1969) for ethanol and n-octane. The dashed line indicates results obtained with the original equation (q'

Table II. Some Binary Parameters for UNIQUAC Equation[a]

system (1)-(2)	temp, K	energy parameters, K a_{12}	a_{21}	data reference
acetonitrile-benzene	318	-40.70	229.79	Brown (1955)
n-hexane-nitroethane	318	230.64	-5.86	Edwards (1962)
acetone-chloroform	323	-171.71	93.96	Severns (1955)
ethanol-*n*-octane	348	-123.57	1354.92	Boublikova (1969)
formic acid-acetic acid	374-387	-144.58	241.64	Conti (1960)
propionic acid-methyl isobutyl ketone	390-411	-78.49	136.46	Wisniak (1976)
acetone-acetonitrile	330-353	-176.38	261.53	Pratt (1947)
acetone-water	331-368	530.99	-100.71	Reinders (1947)
acetonitrile-water	350-364	294.10	61.92	Pratt (1947)
acetic acid-water	373-389	530.94	-299.90	Ito (1963)
formic acid-water	374-380	924.01	-525.85	Ito (1963)
methylcyclopentane-ethanol	333-349	1383.93	-118.27	Sinor (1960)
methylclopentane-benzene	344-352	56.47	-6.47	Myers (1956)
ethanol-benzene	340-351	-138.90	947.20	Wehe (1955)
n-hexane-methylcyclopentane	333	-138.84	162.13	Beyer (1965)
n-hexane-ethanol	331-349	1441.57	-108.93	Sinor (1960)
n-hexane-benzene	341-350	62.19	-20.14	Prahlov (1963)
methyl ethyl ketone-*n*-heptane	350-369	-75.13	242.53	Steinhauser (1949)
methyl ethyl ketone-toluene	352-383	-82.85	123.57	Steinhauser (1949)
n-heptane-toluene	371-383	108.24	-72.96	Steinhauser (1949)
methanol-carbon tetrachloride	328	-29.64	1127.95	Scatchard (1946)
methanol-benzene	528	-56.35	972.09	Scatchard (1946)
carbon tetrachloride-benzene	313	-37.52	43.39	Scatchard (1940)
methanol-diethylamine	330-340	-374.88	676.42	Nakanishi (1967)
chloroform-ethanol	323	934.23	-208.50	Abbott (1975)
chloroform-*n*-heptane	323	-19.26	88.40	Abbott (1975)
ethanol-*n*-heptane	323	-105.23	1380.30	Abbott (1975)
acetone-methanol	323	379.31	-108.42	Severns (1955)
chloroform-methanol	323	1018.86	-152.44	Severns (1955)
chloroform-ethyl acetate	336-350	24.16	-119.49	Nagata (1970)
methanol-ethyl acetate	335-347	-107.54	579.61	Nagata (1970)
chloroform-methanol	326-336	926.31	-143.50	Nagata (1970)

[a] Binary parameters for 142 binary systems are available upon request to the authors.

= q for ethanol) and the continuous line shows results obtained with the modified equation. The original equation predicts a liquid-liquid miscibility gap, contrary to experiment. The modified UNIQUAC equation, however, represents the alcohol/*n*-octane system with good accuracy.

The statistically-based data reduction method used here provides confidence ellipses for the two binary parameters. (These are only approximate because certain linear assumptions which have been made.) Since the maximum-likelihood method is not limited to the UNIQUAC equation but may be used with any equation for excess Gibbs energy, we present some confidence ellipses using the Wilson and van Laar equations: Wilson equation

$$\frac{g^E}{RT} = -x_1 \ln (x_1 + x_2\Lambda_{12}) - x_2 \ln (x_2 + x_1\Lambda_{21})$$

where

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(-\frac{\Delta\lambda_{12}}{RT}\right); \Lambda_{21} = \frac{v_1}{v_2} \exp\left(-\frac{\Delta\lambda_{21}}{RT}\right)$$

van Laar equation

$$\frac{g^E}{RT} = (A_{12}A_{21}x_1x_2)/(A_{12}x_1 + A_{21}x_2)$$

These equations were fitted to isothermal data for the system ethyl acetate(1) and 1-propanol(2) reported by Murti and Van Winkle (1958). Figure 2 shows the optimum parameters for each model as well as the estimated confidence ellipses; these are determined from the eigenvalues and eigenvectors of the variance-covariance matrix (Bryson and Ho, 1969). The regions shown represent areas within which the parameter values can be expected to lie at a confidence level associated with the ellipse (here 0.39, 0.87, and 0.99). Large confidence regions are obtained from the parameters because of random error in the data. When a suitable equation is chosen for g^E, the regions become vanishingly small as the random error becomes small or as the number of experimental measurements become large.

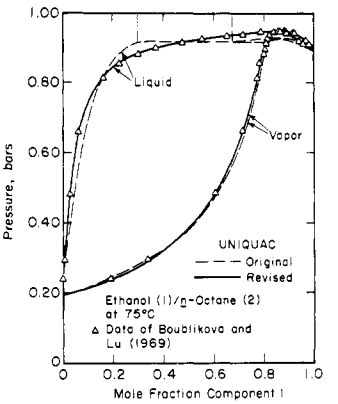

Figure 1. Effect of UNIQUAC equation modification for an alcohol-hydrocarbon system.

The parameters for the van Laar equation are partially correlated; the correlation coefficient is -0.611. The Wilson equation parameters, however, are strongly correlated; the correlation coefficient is -0.983 as emphasized by the highly elongated ellipses. For such highly correlated parameters it is not possible to specify unique values from a given set of data. As discussed by Fabries and Renon (1973), non-uniqueness is a common difficulty for models that have only two parameters representing energy differences.

Table III. Temperature Dependence of UNIQUAC Parameters for Ethanol (1)/Cyclohexane (2) Isothermal Data (5-65 °C) of Scatchard (1964)

no. of parameters	α_{12}	α_{21}	β_{12}	β_{21}	σ_F^2 [a]
2	-85.67	1187.36	-	-	53.33
3	-87.87	1659.25	-	9.245×10^5	24.67
3	-331.75	1304.33	7.392×10^4	-	4.44
4	-296.05	259.28	6.278×10^4	3.352×10^5	3.46

[a] σ_F^2 = (sum of squared, weighted residuals)/(number of degrees of freedom); $a_{ij} = \alpha_{ij} + \beta_{ij}/T$; $a_{ij} = \Delta u_{ij}/R$.

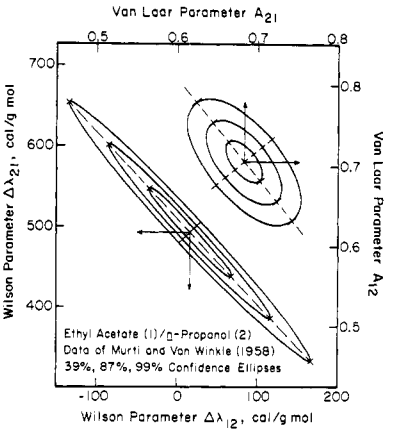

Figure 2. Binary parameters are partially correlated. Binary parameters and their approximate confidence regions in two models for excess Gibbs energy.

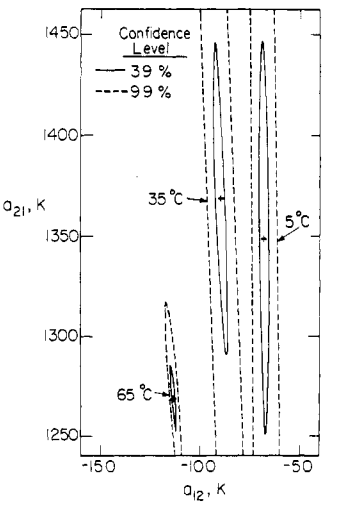

Figure 3. UNIQUAC parameters and their approximate confidence regions for the ethanol-cyclohexane system for three isotherms. Data of Scatchard and Satkiewicz (1964).

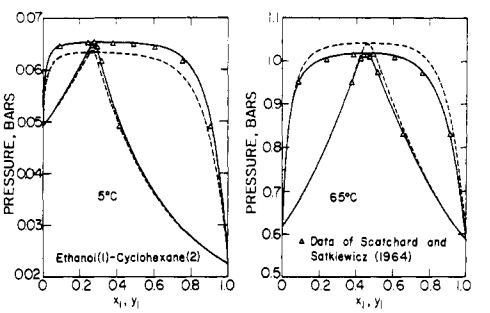

Figure 4. Calculated and experimental vapor-liquid equilibria: ---, calculated with temperature-independent UNIQUAC parameters; —, calculated with temperature-dependent UNIQUAC parameters.

Highly correlated binary parameters are encountered in the UNIQUAC equation as well as in the Wilson equation, NRTL equation, etc. Such correlation is primarily responsible for different estimated binary parameters when different data reduction methods are used (Kemény and Manczinger, 1978). The main advantage of the UNIQUAC equation, relative to that of Wilson, is that unlike Wilson's equation, UNIQUAC is applicable to partially miscible systems as discussed in the second paper of this series.

A high degree of correlation can also be beneficial. Since it implies that the parameters are strongly related, it is possible that some linear combination of the two parameters could represent the data as well as the individual parameters. In that event it may be possible to eliminate one of the parameters giving a single-parameter equation to represent vapor-liquid equilibrium data (Tassios, 1971; Wong and Eckert, 1971; Schreiber and Eckert, 1971, and Hiranuma and Honma, 1975).

When there are sufficient data at different temperatures, the temperature dependence of the parameters is reflected in the confidence ellipses. To illustrate, UNIQUAC parameters were obtained for the ethanol/cyclohexane system using the extensive isothermal data of Scatchard and Satkiewicz (1964). Figure 3 shows parameters for 5, 35, and 60 °C along with the confidence ellipses. These regions indicate that it is possible to choose a single value of a_{21} appropriate for all temperatures; a single value of a_{21} (e.g., 1300) can be included in all three confidence ellipses, implying that in the range 5–65 °C parameter a_{21} is temperature independent. For a_{21}, however, there is no single value which can intercept all three confidence ellipses. Therefore, parameter a_{12} must be represented by a function of temperature as shown in Table III, where the estimated variance of the fit, σ_F^2, provides a measure of how well the data are represented. The first line shows results obtained when fitting two UNIQUAC parameters, a_{12} and a_{21}, independent of temperature. The next two lines show the results of three-parameter fits: first a_{21} and then a_{12} are functions of temperature. Finally, four parameters were determined: both UNIQUAC parameters are now functions of temperature. Substantial improvement is obtained when only a_{12} is temperature dependent, supporting the conclusions drawn from Figure 3. Finally, Figure 4 shows agreement between observed and calculated equilibria when the three-parameter fit is used.

Results: Binary Systems

An adequate prediction of multicomponent vapor-liquid equilibria requires an accurate description of the phase equilibria for the binary systems. We have reduced a large body of binary data including a variety of systems containing, for example, alcohols, ethers, ketones, organic acids, water, and hydrocarbons with the UNIQUAC equation. Experience has shown it to do as well as any of the other common models. When all types of mixtures are considered, including partially miscible systems, the modified UNIQUAC equation performs as well as or better than any other two-parameter equation for excess Gibbs energy g^E. Below we present examples of representative

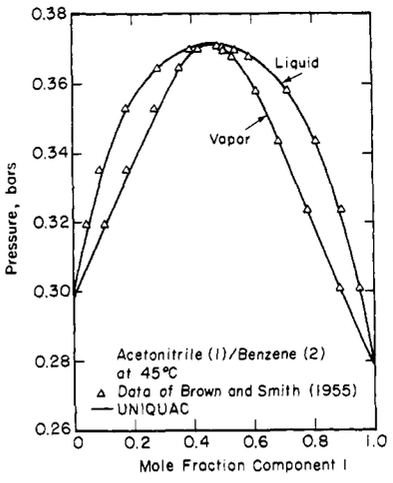

Figure 5. Representation of vapor–liquid equilibria for a binary system showing strong positive deviations from Raoult's law.

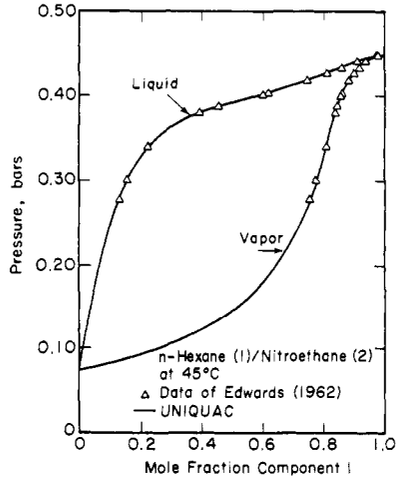

Figure 6. Representation of vapor–liquid equilibria for a binary system showing strong positive deviations from Raoult's law.

sets of binary data which we have correlated.

Figure 5 shows experimental and predicted phase equilibria for the acetonitrile/benzene system at 45 °C. This system exhibits moderate positive deviations from Raoult's law. The high-quality data of Brown and Smith (1955) are very well represented by the UNIQUAC equation.

Figure 6 shows the isothermal data of Edwards (1962) for *n*-hexane and nitroethane. This system also exhibits positive deviations from Raoult's law; however, these deviations are much larger than those shown in Figure 5. At 45 °C the mixture shown in Figure 6 is only 15° above its critical solution temperature. Again representation with the UNIQUAC equation is excellent.

The acetone/chloroform system, shown in Figure 7, exhibits strong negative deviations from Raoult's law because of hydrogen bonding between the single hydrogen atom of chloroform and the carbonyl oxygen of acetone. The data of Severns et al. (1955) are well represented by the UNIQUAC equation.

Figure 8 shows a fit of the UNIQUAC equation to the isobaric data of Nakanishi et al. (1967) for the methanol–diethylamine system; this system also exhibits strong negative deviations from Raoult's law. The UNIQUAC equation correctly reproduces a weak minimum in the activity coefficient of methanol. Agreement with experiment is not as good as that in previous examples because the data are badly scattered, particularly near the azeotrope.

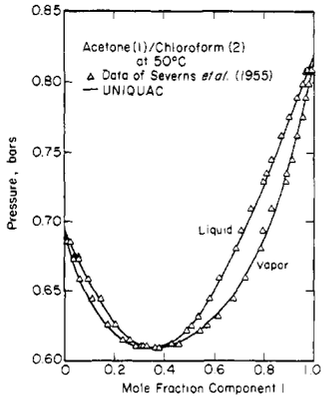

Figure 7. Representation of vapor–liquid equilibria for a binary system showing strong negative deviations from Raoult's law.

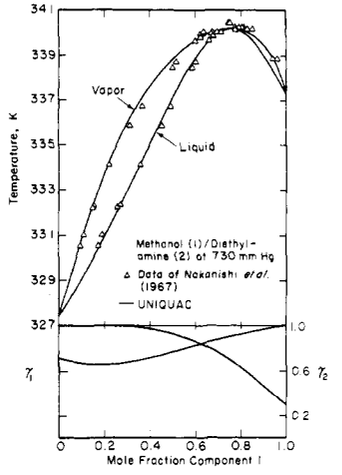

Figure 8. Vapor–liquid equilibria and activity coefficients in a binary system showing a weak minimum in the activity coefficient of methanol.

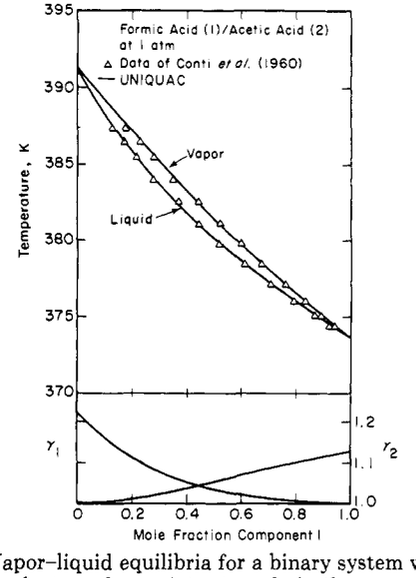

Figure 9. Vapor–liquid equilibria for a binary system where both components solvate and associate strongly in the vapor phase.

At moderate pressures, vapor-phase nonideality is usually small in comparison to liquid-phase nonideality. However, when associating carboxylic acids are present, vapor-phase nonideality may dominate. These acids dimerize appreciably in the vapor phase even at low pressures; fugacity coefficients are well removed from unity. To illustrate, Figures 9 and 10 show observed and calculated vapor–liquid equilibria for two systems containing an associating component. In the first, both components

Table IV. Prediction of Multicomponent Vapor-Liquid Equilibria

system	no. of data points	press., mmHg (temp, °C)	dev in temp or % dev in press., av (max)	dev in vapor compn, mol %, av (max)	data ref
methylcyclopentane ethanol benzene	48	760 (60-71)	0.25 (0.31) °C	0.51 (−3.03) 0.55 (2.99) 0.35 (−1.25)	Sinor (1960)
acetic acid formic acid water	40	760 (102-110)	0.55 (−1.80) °C	1.00 (−2.08) 1.60 (3.77) 2.18 (−5.36)	Conti (1960)
acetone acetonitrile water	30	762 (63-92)	1.13 (−3.67) °C	1.22 (3.24) 1.27 (−3.45) 1.53 (−4.68)	Pratt (1947)
methanol carbon tetrachloride benzene	8	665-717 (55)	0.11 (−0.27)%	0.44 (0.99) 0.39 (−0.89) 0.09 (0.17)	Scatchard (1952)
methyl ethyl ketone *n*-heptane toluene	39	760 (77-103)	0.17 (−0.63) °C	0.79 (2.00) 0.52 (−1.31) 0.38 (−1.18)	Steinhauser (1949)
chloroform ethanol *n*-heptane	92	262-501 (50)	1.57 (−3.03)%	*a*	Abbott (1975)
chloroform acetone methanol	29	463-645 (50)	1.10 (−3.12)%	0.86 (1.03) 0.77 (2.68) 0.81 (1.03)	Severns (1955)
chloroform methanol ethyl acetate	72	760 (56-72)	0.36 (1.77) °C	0.74 (2.06) 1.11 (2.40) 0.80 (2.47)	Nagata (1962)
n-hexane methylcyclopentane ethanol benzene	10	760 (60-65)	0.38 (−0.45) °C	0.31 (0.60) 0.44 (0.95) 0.55 (−1.13) 0.44 (0.96)	Sinor (1960)

[a] *P-T-x* data only.

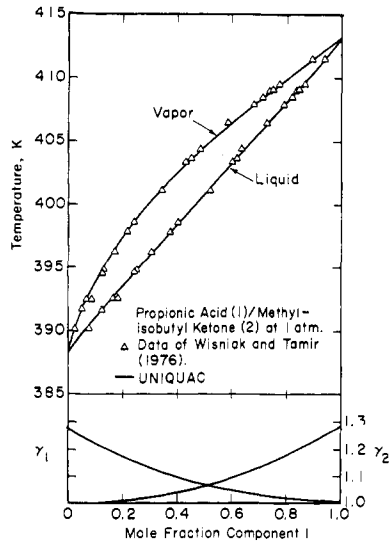

Figure 10. Vapor-liquid equilibria for a binary system where one component dimerizes in the vapor phase. Activity coefficients show only small deviations from liquid-phase ideality.

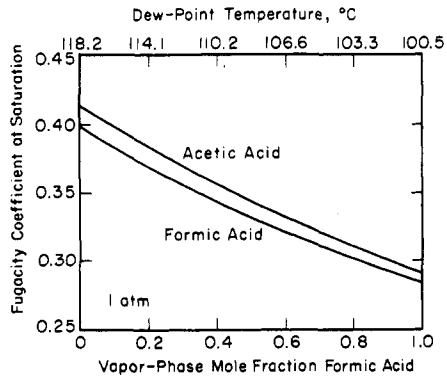

Figure 11. Fugacity coefficients for saturated mixtures containing two carboxylic acids: formic acid(1) and acetic acid(2). Calculations based on chemical theory show large deviations from ideal behavior.

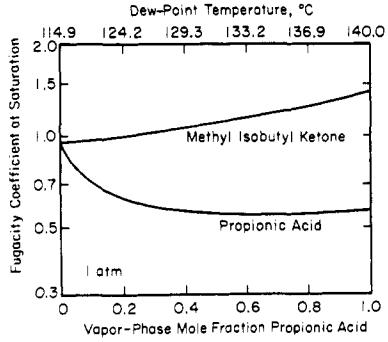

Figure 12. Fugacity coefficients for saturated mixtures of propionic acid(1) and methyl isobutyl ketone(2). Calculations based on chemical method show large deviations from ideal behavior.

strongly associate with themselves and with each other. In the second, only one of the components associates strongly. For both systems, representation of the data is very good. However, the interesting quality of these systems is that whereas the fugacity coefficients are significantly remote from unity, the activity coefficients show only minor deviations from ideal solution behavior. Figures 11 and 12 indicate that the fugacity coefficients show marked departure from ideality. In these systems, the major contribution to nonideality occurs in the vapor phase. Failure to take into account these strong vapor-phase nonidealities would result in erroneous activity-coefficient parameters, a_{12} and a_{21}, leading to poor pre-

diction of multicomponent equilibria.

Multicomponent Systems

The procedure for calculating multicomponent vapor–liquid equilibria has been outlined elsewhere (Prausnitz, 1969; Prausnitz et al., 1967). Equation 1 is applied to every component i and activity coefficient i is found from eq 3 using some convenient expression for the excess Gibbs energy. For a multicomponent mixture, for example, the UNIQUAC equation is

$$\frac{g^E \text{ (combinatorial)}}{RT} = \sum_i x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2}\sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \quad (17)$$

$$\frac{g^E \text{ (residual)}}{RT} = -\sum_i q_i' x_i \ln \left(\sum_j \theta_j' \tau_{ji}\right) \quad (18)$$

where segment fraction Φ and area fractions θ and θ' are given by

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (19)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (20)$$

$$\theta_i' = \frac{q_i' x_i}{\sum_j q_j' x_j} \quad (21)$$

For any component i, the activity coefficient is given by

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \left(\frac{z}{2}\right) q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j x_j l_j - q_i' \ln \left(\sum_j \theta_j' \tau_{ji}\right) + q_i' - q_i' \sum_j \frac{\theta_j' \tau_{ij}}{\sum_k \theta_k' \tau_{kj}} \quad (22)$$

where

$$l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1) \quad (23)$$

Equation 22 requires only pure-component and binary parameters.

Using UNIQUAC, Table IV summarizes vapor–liquid equilibrium predictions for several representative ternary mixtures and one quaternary mixture. Agreement is good between calculated and experimental pressures (or temperatures) and vapor-phase compositions.

The largest errors in predicted compositions occur for the systems acetic acid–formic acid–water and acetone–acetonitrile–water where experimental uncertainties are significantly greater than those for other systems.

Moderate errors in the total pressure calculations occur for the systems chloroform–ethanol–n-heptane and chloroform–acetone–methanol. Here strong hydrogen bonding between chloroform and alcohol creates unusual deviations from ideality; for both alcohol–chloroform systems, the activity coefficients show well-defined extrema. Since extrema are generally not well reproduced by the UNIQUAC equation, these binaries are not well represented. The overall ternary deviations are of the order of those for the worst fitting binaries, methanol–chloroform and ethanol–chloroform. In spite of the relatively large deviations in calculated pressure, the predicted vapor compositions agree well with the experimental data of Severns (1955).

Predictions for the other isobaric systems (experimental data of Sinor, Steinhauser, and Nagata) show good agreement. Excellent agreement is obtained for the system carbon tetrachloride–methanol–benzene, where the binary data are of superior quality.

The results shown in Table IV indicate that UNIQUAC can be used with confidence for multicomponent systems including those that exhibit large deviations from ideality.

Conclusions

Design of common separation processes requires quantitative information on multicomponent fluid-phase equilibria. Often these mixtures are highly nonideal, either in vapor or liquid phase. The scarcity of multicomponent data and the time-consuming nature of multicomponent experimental measurements demand a predictive method. When binary data are reduced with care, the UNIQUAC equation for the excess Gibbs energy provides a suitable model for correlation of binary vapor–liquid equilibrium data; these, in turn, provide a reliable basis for prediction of multicomponent vapor–liquid equilibria.

Acknowledgment

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Appendix A. Vapor-Phase Nonidealities and Pure-Component Reference Fugacities

Vapor-Phase Nonidealities. At low to moderate pressures, the truncated volume-explicit form of the virial equation may be used to represent the vapor phase

$$\frac{Pv}{RT} = 1 + \frac{BP}{RT} \quad (1A)$$

where B is the second virial coefficient of the mixture of m components. B is calculated from the pure-component and cross-virial coefficients, B_{ij}, by

$$B = \sum_{i=1}^{m}\sum_{j=1}^{m} y_i y_j B_{ij} \quad (2A)$$

The fugacity coefficient ϕ_i is obtained by substituting the equation of state into the appropriate thermodynamic relation as discussed elsewhere (Prausnitz, 1969). For eq 1A we obtain

$$\ln \phi_i = \frac{P}{RT}\left[2\sum_{j=1}^{m} y_j B_{ij} - B\right] \quad (3A)$$

In the generalized correlation of Hayden and O'Connell (1975), the pure-component and cross-virial coefficients are sums of contributions from free pairs of molecules, metastable pairs, physically bound pairs, and chemically bound pairs

$$B_{ij} = (B_{\text{free}})_{ij} + (B_{\text{metastable}})_{ij} + (B_{\text{bound}})_{ij} + (B_{\text{chem}})_{ij} \quad (4A)$$

Correlating equations are presented by Hayden and O'Connell for each contribution.

For mixtures containing one or more strongly interacting components, such as carboxylic acids, the calculation of the fugacity coefficients is based on a (chemical) dimerization equilibrium constant. In such cases the fugacity coefficient is given by

$$\phi_i = (z_i/y_i) \exp\left[\frac{P(B_{\text{free}})_{ii}}{RT}\right] \quad (5A)$$

where z is the true mole fraction of species i (monomer i or dimer ij) at equilibrium. The true mole fraction z differs from y which represents the stoichiometric mole fraction as if no dimerization occurs. The calculation of z's for a

mixture requires a knowledge of the dimerization constants for all the molecular species, K_{ij} as discussed by Nothnagel (1973). Dimerization constants are conveniently given in terms of the various contributions to the second virial coefficients

$$K_{ij} = \frac{YPB_{ij}^{D}}{RT} \exp\left[\frac{P}{RT}(B_{free})_{ii} + (B_{free})_{jj} + (B_{free})_{ij}\right] \quad (6A)$$

where $Y = 1$ when $i = j$ and $Y = 2$ when $i \neq j$.

Coefficient B_{ij}^{D} stands for the bound, metastable, and chemical contributions for the second virial coefficient for the i–j interaction. Anderson (1978) discusses the implementation of the Hayden and O'Connell method to multicomponent mixtures. Input to the correlation for second virial coefficients consists of: (a) pure-component information: critical temperature and critical pressure, Thompson's mean radius of gyration, dipole moment, and association factor, which depends only upon the type of associating group (for example, hydroxyl, amine, carboxylic acid, etc.); (b) binary mixture information: solvation factor; and (c) the system temperature. Hayden and O'Connell give input parameters, including association and solvation factors, for a large number of systems.

Pure-Component Reference Fugacities. The standard-state, liquid-phase fugacities used here were calculated from

$$f_i^0 = f_i^{(PO)} \exp\frac{v_i P}{RT} \quad (7A)$$

$$f_i^{(PO)} = \phi_i^s P_i^s \exp\left[\frac{-v_i P_i^s}{RT}\right] \quad (7B)$$

where superscript PO refers to zero pressure, P_i^s is the saturation (vapor) pressure of i, and ϕ_i^s is the fugacity coefficient at P_i^s. Whereas f_i^0 is a function of temperature and pressure, $f_i^{(PO)}$ is a function only of temperature. To reduce computational effort in multicomponent vapor–liquid equilibrium calculations, Hsieh and Eckert (1976) correlated $f_i^{(PO)}$ as a function of temperature for 90 fluids. This correlation uses the Hayden–O'Connell method to calculate ϕ's and Lyckman's method (1965) to calculate reference fugacities for reduced temperatures larger than 0.85. The correlation of Hsieh and Eckert is used here in eq 1 for binary data reduction and for predictions of multicomponent vapor–liquid equilibria.

Nomenclature

a_{ij} = UNIQUAC binary interaction parameter related to Δu_{ij} and τ_{ij}
A_{ij} = van Laar equation parameter
B = second virial coefficient of a mixture
B_{ij} = second virial coefficient for i–j interaction
$(B_{free})_{ij}$, $(B_{metastable})_{ij}$, $(B_{bound})_{ij}$, $(B_{chem})_{ij}$ = free, metastable, bound, and chemical contributions to the second virial coefficient for i–j interaction
B_{ij}^{D} = sum of metastable, bound, and chemical contributions to second virial coefficient for i–j interaction
f_i^0 = pure-component reference fugacity of component i
$f_i^{(PO)}$ = pure-component reference fugacity of component i corrected to zero pressure
g^E = excess molar Gibbs energy
K_{ij} = equilibrium dimerization constant for i–j pair
l_i = pure-component constant defined by eq 23
m = number of components
P = total pressure
P_i^s = vapor pressure of pure component i
q_i = molecular-geometric area parameter for component i
q_i' = molecular-interaction area parameter for component i
r_i = molecular volume parameter for pure component i
R = gas constant
T = absolute temperature
Δu_{ij} = UNIQUAC binary interaction parameter
v_i = molar liquid volume of component i
x_i = liquid-phase mole fraction of component i
y_i = vapor-phase mole fraction of component i
z = lattice coordination number, here equal to 10
z_i = true vapor-phase mole fraction of species i at equilibrium

Greek Letters

γ_i = activity coefficient of component i
θ_i = area fraction of component i in combinatorial contribution to the activity coefficient
θ_i' = area fraction of component i in residual contribution to the activity coefficient
$\Delta\lambda_{ij}$ = Wilson binary parameter related to Λ_{ij}
Λ_{ij} = Wilson binary parameter
σ_P^2, σ_T^2, σ_x^2, σ_y^2 = error variances for the pressure, temperature, liquid composition, and vapor composition measurements, respectively
τ_{ij} = UNIQUAC binary parameter
ϕ_i = fugacity coefficient of component i
ϕ_i^S = fugacity coefficient of pure component i at its saturation pressure
Φ_i = segment fraction of component i

Literature Cited

Abbott, M. M., Van Ness, H. C., *AIChE J.*, **21**, 62 (1975).
Abrams, D. S., Prausnitz, J. M., *AIChE J.*, **21**, 116 (1975).
Anderson, T. F., Ph.D. Thesis, University of California, Berkeley, 1978.
Anderson, T. F., Abrams, D. S., Grens, E. A., Prausnitz, J. M., Paper presented at 69th Annual AIChE Meeting, Chicago, Ill., 1976.
Anderson, T. F., Abrams, D. S., Grens, E. A., *AIChE J.*, **24**, 20 (1978).
Bard, Y., "Nonlinear Parameter Estimation", Academic Press, New York, N.Y., 1974.
Barker, J. A., *Aust. J. Chem.*, **6**, 207 (1953).
Beyer, W., Schuberth, H., Leibnitz, E., *J. Prakt. Chem.*, **27**, 276 (1965).
Boublikova, L., Lu, B. C. Y., *J. Appl. Chem. (London)*, **19** (3), 89 (1969).
Brown, I., Smith, F., *Aust. J. Chem.*, **8**, 62 (1955).
Bryson, A. E., Ho, Y. B., "Applied Optimal Control; Optimization, Estimation, and Control", Blaisdell Publishing, Waltham, Mass., 1969.
Conti, J. J., Othmer, P. F., Gilmont, R., *J. Chem. Eng. Data*, **5**, 301 (1960).
Edwards, J. B., Ph.D. Dissertation, Georgia Institute of Technology, 1962.
Fabries, J., Renon, H., *AIChE J.*, **21**, 735 (1975).
Francis, A. W., "Handbook for Components in Solvent Extraction", Gordon and Breach Publishers, New York, N.Y., 1972.
Fredenslund, Aa., Gmehling, J., Michelsen, M., Rasmussen, P., Prausnitz, J. M., *Ind. Eng. Chem. Process. Des. Dev.*, **16**, 450 (1977).
Fredenslund, A., Gmehling, J., Rasmussen, P., "Vapor–Liquid Equilibiria Using UNIFAC, A Group-Contribution Method", Elsevier, Amsterdam, 1977.
Gmehling, J., Onken, U., "Vapor-Liquid Equilibrium Data Collection", DECHEMA Chem. Data Ser., Vol. 1 (Parts 1–10), Frankfurt, 1977.
Gothard, F. A., Codrea Ciobano, M. F., Breban, D. G., Bucur, C. I., Sorescu, G. V., *Ind. Eng. Chem. Process Des. Dev.*, **15**, 333 (1976).
Himmelblau, D. M., Brady, B. L., McKetta, J. J., "Survey of Solubility Diagrams for Ternary and Quaternary Liquid Systems", Bureau of Engineering Research, Special Publication No. 30, University of Texas, Austin, Texas, 1959.
Hayden, J. G., O'Connell, J. P., *Ind. Eng. Chem. Process Des. Dev.*, **14**, 204 (1975).
Hiranuma, M., Honma, K., *Ind. Eng. Chem. Process Des. Dev.*, **14**, 221 (1975).
Hsieh, R., Eckert, C. A., University of Illinois, Urbana, Ill., private communication, 1976.
Ito, T., Yoshida, F., *J. Chem. Eng. Data*, **8**, 315 (1963).
Kemény, S., Manczinger, J., *Chem. Eng. Sci.*, **33**, 71 (1978).
Kreyszig, E., "Introductory Mathematical Statistics", Wiley, New York, N.Y., 1970.
Lyckman, E., Eckert, C. A., Prausnitz, J. M., *Chem. Eng. Sci.*, **20**, 685 (1965).
Murti, P. S., Van Winkle, M., *Chem. Eng. Data Ser.*, **3**, 73 (1958).
Myers, H. S., *Ind. Eng. Chem.*, **48**, 1104 (1956).
Nagata, I., Hayashida, H., *J. Chem. Eng. Jpn.*, **3**, 161 (1970).
Nakanishi, K., Shirai, H., Minamiyama, T., *J. Chem. Eng. Data*, **12**, 591 (1967).
Nothnagel, K., Abrams, D. S., Prausnitz, J. M., *Ind. Eng. Chem. Process Des. Dev.*, **12**, 25 (1973).
O'Connell, J. P., University of Florida, Gainesville, Fla., private communication, 1974.
Péneloux, A., Deyrieux, R., Canals, E., Neau, E., *J. Chim. Phys.*, **73**, 706 (1976).
Prahbu, P. S., Van Winkle, M., *J. Chem. Eng. Data*, **8**, 210 (1963).
Pratt, H. R. C., *Trans. Inst. Chem. Eng. (London)*, **25**, 43 (1947).
Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1969.
Prausnitz, J. M., Eckert, C. A., Orye, R. V., O'Connell, J. P., "Computer Calculations of Multicomponent Vapor–Liquid Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1967.
Reinders, W., De Minjer, C. H., *Recl. Trav. Chim.*, **66**, 573 (1947).
Scatchard, G., Wood, S. E., Mochel, J. M., *J. Am. Chem. Soc.*, **62**, 712 (1940).
Scatchard, G., Wood, W. E., Mochel, S. M., *J. Am. Chem. Soc.*, **68**, 1960 (1946).
Scatchard, G., Ticknor, L. B., *J. Am. Chem. Soc.*, **74**, 3724 (1952).
Scatchard, G., Satkiewicz, F. G., *J. Am. Chem. Soc.*, **86**, 130 (1964).

Schreiber, L. B., Eckert, C. A., *Ind. Eng. Chem. Process Des. Dev.*, **10**, 572 (1971).
Severns, W. H., Sesonske, A., Perry, R. H., Pigford, R. L., *AIChE J.*, **1**, 401 (1955).
Sinor, J. E., Weber, J. H., *J. Chem. Eng. Data*, **5**, 243 (1960).
Spencer, C. F., Danner, R. P., *J. Chem. Eng. Data*, **17**, 236 (1972).
Steinhauser, H. H., White, R. R., *Ind. Eng. Chem.*, **41**, 2912 (1949).
Stephen, H., Stephen, T., Ed., "Solubilities of Inorganic and Organic Compounds", MacMillan Co., New York, N.Y., 1964.
Wehe, A. H., Coates, J., AIChE *J.*, **1**, 241 (1955).
Wichterle, I., Linek, J., Hala, E., "Vapor-Liquid Equilibrium Data Bibliography", Elsevier Publishing Co., New York, N.Y., 1973.
Wisniak, J., Tamir, A., *J. Chem. Eng. Data*, **21**, 88 (1976).
Wong, K. F., Eckert, C. A., *Ind. Eng. Chem. Fundam.*, **10**, 20 (1971).

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Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria. 2. Liquid–Liquid Equilibria

T. F. Anderson and J. M. Prausnitz*

Department of Chemical Engineering, University of California, Berkeley, California 94720

Calculation of ternary (and higher) liquid–liquid equilibria is based on a model for the excess Gibbs energy using only binary parameters. Since these are not unique, meticulous care must be taken to obtain optimum binary parameters for yielding reliable multicomponent results. In many cases binary data are not sufficient to fix optimum binary parameters; limited ternary tie-line data are often also required. The principle of maximum likelihood provides a convenient data-reduction method for obtaining optimum binary parameters. Using UNIQUAC, illustrative examples are given for a variety of ternary (and higher) systems.

In recent years, increasing attention has been given to calculation of multicomponent, liquid–liquid–vapor equilibria for three-phase distillation and to liquid–liquid equilibria for extraction (Leach, 1977; Block and Hegner, 1976; Peng and Robinson, 1976; Bender and Block, 1975; Bouvard, 1974; and Guffey and Wehe, 1972). Although several computing techniques for such calculations have been proposed, there is a lack of methods for calculating the necessary phase equilibria. While much effort and an abundance of data have led to successful ways for calculating multicomponent vapor–liquid equilibria, comparatively little is known for successful calculation of liquid–liquid equilibria. In this paper we discuss application of the UNIQUAC equation for calculation of such equilibria.

We address ourselves primarily to one key question: For liquid–liquid equilibrium calculations, what are the minimum experimental data needed and how are they most effectively reduced to obtain the required model parameters? While our discussion uses the UNIQUAC equation for the excess Gibbs energy, the general procedure which we have developed is not limited to that equation since other expressions for the excess Gibbs energy, if preferred, may also be used.

Prediction of Ternary Liquid-Liquid Equilibria from Binary Data Alone

As indicated by Treybal (1963), the technical literature contains several empirical and/or graphical proposals for predicting or correlating the distribution of a solute between two partially miscible solvents. For example, Hand (1930), Hildebrand (1936), Treybal (1944), Scheibel and Friedland (1947), and more recently, Ishida (1971), have suggested estimation methods for ternary systems; these, however, suffer the disadvantage of not being generalizable to mixtures containing four (or more) components. Often these methods provide only a qualitative description of the desired equilibria.

A thermodynamic procedure, based on excess Gibbs energy coupled with a liquid-phase model, is more useful for quantitative results. (See, for example, Kenny, 1957; Hwa, 1969; Renon and Prausnitz, 1968a, b; Joy and Kyle, 1963; Renon et al., 1971; Marina and Tassios, 1973; and Heinrich, 1975.)

When two liquid phases are in equilibrium, the compositions of the two phases are related by a set of equations, one for each component i

$$(x_i\gamma_i)^\alpha = (x_i\gamma_i)^\beta \qquad (1)$$

where x is the liquid-phase mole fraction, γ is the liquid-phase activity coefficient, and α and β indicate equilibrium phases. As discussed in part 1, the activity coefficients are immediately related to the molar excess Gibbs energy, here given by the UNIQUAC equation.

In ternary systems we can distinguish between two common types. In type II, two binaries are partially miscible and the third binary is completely miscible; in type I, only one binary is partially miscible. (A third type, where all three binaries are only partially miscible, is only rarely of interest in chemical engineering.)

For systems of type II, if the mutual binary solubility (LLE) data are known for the two partially miscible pairs, and if reasonable vapor–liquid equilibrium (VLE) data are known for the miscible pair, it is relatively simple to predict the ternary equilibria as shown previously by several authors. For systems of type I, which has a plait point, reliable calculations are much more difficult. However, sometimes useful quantitative predictions can be obtained for type I systems with binary data alone provided that: (1) reliable, preferably isothermal, VLE data are used for the two miscible binaries; (2) a suitable model is chosen which accurately represents the excess Gibbs energy of each constituent binary; (3) mutual solubility data are used for the partially miscible binary pairs. In addition, if other data are available for these pairs, those data may also be useful (Heinrich, 1975).

Best ternary predictions are usually obtained for mixtures having a very broad two-phase region, i.e., where the two partially miscible liquids have only small mutual solubilities. Fortunately, this is the type of ternary that

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