

Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems

To obtain a semi-theoretical equation for the excess Gibbs energy of a liquid mixture, Guggenheim's quasi-chemical analysis is generalized through introduction of the local area fraction as the primary concentration variable. The resulting universal quasi-chemical (UNIQUAC) equation uses only two adjustable parameters per binary. Extension to multicomponent systems requires no ternary (or higher) parameters.

The UNIQUAC equation gives good representation of both vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolyte components such as hydrocarbons, ketones, esters, amines, alcohols, nitriles, etc., and water. When well-defined simplifying assumptions are introduced into the generalized quasi-chemical treatment, the UNIQUAC equation reduces to any one of several well-known equations for the excess Gibbs energy, including the Wilson, Margules, van Laar, and NRTL equations.

The effects of molecular size and shape are introduced through structural parameters obtained from pure-component data and through use of Staverman's combinatorial entropy as a boundary condition for athermal mixtures. The UNIQUAC equation, therefore, is applicable also to polymer solutions.

**DENIS S. ABRAMS and
JOHN M. PRAUSNITZ**

Chemical Engineering Department
University of California
Berkeley, California 94720

SCOPE

A significant fraction of chemical process design is concerned with separation of fluid mixtures by diffusional operations. All design methods for such separations require quantitative estimates of fluid-phase equilibria; this work provides a contribution toward making such estimates for liquid-phase mixtures of nonelectrolytes, including polymers, and including those mixtures where nonideality is sufficiently strong to produce two liquid phases.

Activity coefficients in liquid mixtures can be calculated from a model which expresses the excess Gibbs energy of the mixture as a function of the composition. A new model, called UNIQUAC, is presented here. This model is derived from a statistical-mechanical basis extending that used by Guggenheim in his quasi-chemical theory. Unlike Guggenheim's theory, however, UNIQUAC is applicable to mixtures whose molecules differ appreciably in size and shape and, unlike previous attempts to gener-

alize Guggenheim's method, UNIQUAC contains no more than two adjustable parameters per binary.

UNIQUAC is applicable to multicomponent mixtures of nonpolar and polar liquids (including those that participate in hydrogen bonding) as encountered in typical chemical and petrochemical processes. No ternary (or higher) constants are required. Attention is given to vapor-liquid and liquid-liquid equilibria.

When well-defined simplifying assumptions are made, the UNIQUAC model can yield any one of several well-known expressions for the excess Gibbs energy, including the van Laar, Wilson, and NRTL equations. Relative to these well-known equations, the advantage of UNIQUAC is that, for a large variety of multicomponent systems and using only two adjustable parameters per binary, reliable estimates can be made of both vapor-liquid and liquid-liquid equilibria using the same equation for the excess Gibbs energy.

CONCLUSIONS AND SIGNIFICANCE

The UNIQUAC model for liquid-phase activity coefficients provides the process-design engineer with a useful tool for calculating fluid-phase equilibria as required in

the design of distillation, extraction and similar operations. Because of its theoretical basis, the UNIQUAC model is applicable to a wide range of mixtures even though only two adjustable parameters per binary are required. For binary mixtures of moderate nonideality, the two-parameter model can be simplified to yield a one-parameter equation for activity coefficients.

Correspondence concerning this paper should be addressed to J. M. Prausnitz. D. S. Abrams is with African Explosives and Chemical Industries, Johannesburg, South Africa.

The derivation of UNIQUAC shows that the three-parameter NRTL equation is more properly applicable to excess enthalpy than to excess Gibbs energy.

While UNIQUAC provides no major improvement over Wilson's equation for vapor-liquid equilibria in completely

miscible systems, it can, unlike Wilson's equation, also represent liquid-liquid equilibria for multicomponent mixtures using only two adjustable parameters per binary. UNIQUAC provides a versatile model for calculating liquid-phase activity coefficients in multicomponent mixtures using only limited binary data.

The thermodynamics of nonideal liquid mixtures has generated a vast literature. Despite attention for over a century from some of the best scientific minds, the goal of predicting mixture properties from pure-component properties alone remains elusive; failure to reach this goal follows from inadequate fundamental understanding of liquid structure and intermolecular forces. Therefore, to calculate vapor-liquid and liquid-liquid equilibria needed for process design, it is necessary to construct models which, by necessity, are only approximations containing parameters that must be obtained empirically. This work presents such a model and discusses its use for engineering applications.

ACTIVITY COEFFICIENT, EXCESS GIBBS ENERGY AND LATTICE MODELS

Deviations from ideal behavior (Raoult's law) are commonly expressed by activity coefficients as discussed in numerous textbooks. In a mixture, activity coefficient γ_i (for component i) is related to g^E , the excess Gibbs energy per mole of mixture, by

$$n_T g^E = RT \sum_i n_i \ln \gamma_i \quad (1)$$

$$RT \ln \gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i} \right)_{T,P,n_j (j \neq i)} \quad (2)$$

where n_i is the number of moles of component i and n_T is the total number of moles. To obtain activity coefficients, therefore, it is necessary to construct an expression which gives g^E as a function of composition, temperature, and pressure; the most important variable is composition. For liquid mixtures at ordinary pressures, the effect of pressure is negligible. The effect of temperature is not negligible, but often it is not large when consideration is restricted to a moderate temperature range.

When nonelectrolyte liquids are mixed at constant temperature and constant pressure remote from critical conditions, there is little volume change. As shown by Scatchard (1937), even small volume changes can have a significant effect on the entropy of mixing and on the enthalpy of mixing but, to a good approximation, these effects tend to cancel in the excess Gibbs energy. Therefore, when attention is restricted to mixtures of nonelectrolyte liquids at low or modest pressures, we can substitute for the excess Gibbs energy of mixing at constant temperature and pressure, the excess Helmholtz energy of mixing at constant temperature and volume (Hildebrand and Scott, 1950). This substitution very much facilitates construction of a theory which is physically reasonable on the one hand and mathematically (relatively) simple on the other. Such a theory is provided by Guggenheim's quasi-chemical lattice model which, however, in its original form is restricted to small molecules of essentially the same size. Previous attempts to extend it to larger molecules (Barker, 1952; Sweeny and Rose, 1963) have not been useful, primarily because of the excessive number of adjustable parameters required to reduce the theory to practice.

In this work, the theory of Guggenheim is extended to mixtures containing molecules of different size and shape by utilizing the local-composition concept introduced by Wilson (1964). The central idea of this concept is that when viewed microscopically, a liquid mixture is not homogeneous; the composition at one point in the mixture is not necessarily the same as that at another point. In engineering applications and in typical laboratory work only the average, overall (stoichiometric) composition matters, but for constructing liquid-mixture models, it appears that the local composition, rather than the average composition, is a more realistic primary variable.

The extension, or generalization, of Guggenheim's model leads to a result here called the UNIQUAC (universal quasi-chemical) equation. The derivation of this equation is given in the next few sections. Readers concerned only with the engineering application of this equation may proceed directly to the section on Application to Binary and Multicomponent Systems following Equation (24).

Partition Function for a Binary Liquid Mixture

Following Guggenheim (1952), we postulate that a liquid can be represented by a three-dimensional lattice of equi-spaced lattice sites; the volume in the immediate vicinity of a site is called a *cell*. Each molecule in the liquid is divided into attached segments such that each segment occupies one cell. The total number of cells is equal to the total number of segments. [A possible refinement where some cells are unoccupied (holes) is not used here.] The configurational partition function Z is given by

$$Z = Z_{\text{lattice}} \cdot Z_{\text{cell}} \quad (3)$$

where Z_{lattice} refers to the situation where the center of every segment is coincident with a lattice site and where Z_{cell} provides those contributions to Z which are caused by motions of a segment about this central position. In mixtures of nonelectrolyte liquids removed from critical conditions, we assume that for each component Z_{cell} is independent of composition. For a binary mixture containing N_1 molecules of component 1 and N_2 molecules of component 2, the Helmholtz energy of mixing is then given by

$$\Delta A = -kT \ln \frac{Z_{\text{lattice}}(N_1, N_2)}{Z_{\text{lattice}}(N_1, 0) Z_{\text{lattice}}(0, N_2)} \quad (4)$$

where k is Boltzmann's constant. The molar excess Gibbs energy g^E is given by

$$g^E \approx a^E = \frac{\Delta A}{n_1 + n_2} - RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (5)$$

where R is the gas constant, x stands for mole fraction, and n for the number of moles.

Following Guggenheim, the lattice partition function is given by

$$Z_{\text{lattice}} = \sum_{\text{all } \theta} \omega(\theta) \exp[-U_0(\theta)/kT] \quad (6)$$

where ω is the combinatorial factor (number of ways that the molecules can be arranged in space) and U_0 is the potential energy of the lattice, that is, the energy required to remove all molecules from the lattice; U_0 is closely related to the energy of isothermal vaporization from the liquid to the ideal-gas state.

Both ω and U_0 depend on the molecular configuration of the mixture, designated by the variable θ . The summation in Equation (6) is over all possible θ , that is, over all values of θ which are permitted within the constraints of the overall stoichiometry.

Since Guggenheim was concerned with mixtures of spherical molecules having the same size, he used for θ the quantity N_{12} which is the number of nearest neighbors, where one neighbor is a molecule of component 1 and the other a molecule of component 2. N_{12} depends not only on N_1 and N_2 but also on the microscopic structure of the solution; if there is a tendency to segregate, where like molecules want to be near each other, N_{12} is (relatively) small. On the other hand, if there is a tendency for the molecules to mix randomly without regard to identity, N_{12} is (relatively) large.

For mixtures of polysegmented molecules differing in size and shape, N_{12} is not an appropriate variable for describing the micro-composition of the lattice. For such mixtures we propose to use the local area fraction.

LOCAL AREA FRACTION

A molecule of component 1 is represented by a set of bonded segments; the number of segments per molecule is r_1 . While all segments, by definition, have the same size, they differ in their external contact area; for example, in normal pentane, the two methyl end groups have a larger external area than the three methylene groups; in neopentane, the central carbon has no external contact area at all. For a molecule of component 1, the number of external nearest neighbors is given by zq_1 where z is the coordination number of the lattice and q_1 is a parameter proportional to the molecule's external surface area. Similarly, for a molecule of component 2, we have structural parameters r_2 and q_2 .

Let us focus attention on the composition of a region in the immediate vicinity of a molecule 1. The local area fraction θ_{21} is the fraction of external sites around molecule 1 which are occupied by segments of molecule 2. Similarly, local area fraction θ_{11} is the fraction of external sites around molecule 1 which are occupied by segments of (another) molecule 1. When attention is focused on the composition of a region in the immediate vicinity of a molecule 2, similar definitions hold for θ_{12} and θ_{22} . For a binary mixture, therefore, we have four local area fractions which describe the microstructure of the lattice; however, only two of these are independent because

$$\theta_{11} + \theta_{21} = 1 \quad (7)$$

and

$$\theta_{12} + \theta_{22} = 1 \quad (8)$$

The lattice energy U_0 is the sum of all interaction energies between pairs of nonbonded segments

$$-U_0 = \left(\frac{z}{2}\right) q_1 N_1 (\theta_{11} U_{11} + \theta_{21} U_{21}) + \left(\frac{z}{2}\right) q_2 N_2 (\theta_{22} U_{22} + \theta_{12} U_{12}) \quad (9)$$

where U_{ij} characterizes the energy of interaction between sites i and j . For convenience let $u_{ij} = (z/2)U_{ij}$. Equation (9) then becomes

$$-U_0 = q_1 N_1 (\theta_{11} u_{11} + \theta_{21} u_{21}) + q_2 N_2 (\theta_{22} u_{22} + \theta_{12} u_{12}) \quad (9a)$$

The minus sign on the left-hand side of Equations (9) and (9a) follows from the convention that the potential energy of the ideal-gas state (infinite separation between molecules) is taken as zero.

In a given molecule, all segments are not necessarily chemically identical. Energy parameters u_{ij} , therefore, represent averages since subscripts i and j refer to components, that is, molecules of type i and j .

Toward elucidation of the local-area-fraction concept, a two-dimensional example is given in Appendix A.

COMBINATORIAL FACTOR

For a given set of local area fractions, we must calculate the number of possible configurations (microstructures) for a mixture of N_1 molecules of component 1 and N_2 molecules of component 2. There is no exact method available for solving this combinatorial problem; we here use an approximation analogous to that used by Guggenheim.

We assume that

$$\omega = \omega_1 \omega_2 h(N_1, N_2) \quad (10)$$

where ω_i refers to the number of configurations associated with a site occupied by a segment of molecule i ($i = 1, 2$).

The function h depends only on N_1 and N_2 ; it is introduced as a normalization factor to assure that the combinatorial factor ω satisfies a physically reasonable boundary condition. For this boundary condition Guggenheim chose the exact result for mixtures of equi-sized spherical molecules with no attractive forces. For our boundary condition we choose the combinatorial factor of Staverman (1950) for mixtures of molecules with arbitrary size and shape but no attractive forces. Staverman's formula is similar to that of Flory-Huggins. It is not exact but it provides a physically reasonable approximation.

As discussed in several texts on statistical mechanics, the summation in Equation (6) can be replaced by its maximum term.

The number of distinguishable configurations ω_1 and ω_2 are approximated by

$$\omega_1 = \frac{(q_1 N_1 \theta_{11} + q_2 N_2 \theta_{12})!}{(q_1 N_1 \theta_{11})! (q_1 N_1 \theta_{21})!} \quad (11)$$

$$\omega_2 = \frac{(q_2 N_2 \theta_{22} + q_1 N_1 \theta_{21})!}{(q_2 N_2 \theta_{22})! (q_2 N_2 \theta_{12})!} \quad (12)$$

Coordination number z does not appear in Equations (11) and (12) because it is not possible to permute independently all of the nearest neighbors about a lattice site.

To find h , we consider the athermal case (all $u_{ij} = 0$ and therefore $U_0 = 0$). The maximum term in the summation is found by separate differentiations with respect to θ_{11} and θ_{22} , and by setting the results equal to zero. Omitting mathematical details, we find that the average local area fractions for an athermal mixture are given by

$$\theta_{11}^{(0)} = \frac{q_1 N_1}{q_1 N_1 + q_2 N_2} \quad (13)$$

$$\theta_{22}^{(0)} = \frac{q_2 N_2}{q_1 N_1 + q_2 N_2} \quad (14)$$

as illustrated in Appendix A. The superscript (0) denotes zeroth approximation (that is, athermal mixture). Mass-balance constraints give

$$\theta_{12}^{(0)} = \theta_{11}^{(0)} = \theta_1 \equiv \frac{q_1 N_1}{q_1 N_1 + q_2 N_2} \quad (15)$$

$$\theta_{21}^{(0)} = \theta_{22}^{(0)} = \theta_2 \equiv \frac{q_2 N_2}{q_1 N_1 + q_2 N_2} \quad (16)$$

In the zeroth approximation, therefore, the average local area fractions are the same as the average area fractions denoted by θ_1 and θ_2 .

The normalization factor h can now be found by substituting Equations (11) to (14) into Equation (10) yielding

$$h(N_1, N_2) = \frac{\omega^{(0)}(q_1 N_1 \theta_{11}^{(0)})! (q_1 N_1 \theta_{21}^{(0)})! (q_2 N_2 \theta_{22}^{(0)})! (q_2 N_2 \theta_{12}^{(0)})!}{(q_1 N_1 \theta_{11}^{(0)} + q_2 N_2 \theta_{12}^{(0)})! (q_2 N_2 \theta_{22}^{(0)} + q_1 N_1 \theta_{21}^{(0)})!} \quad (17)$$

where $\omega^{(0)}$ is the combinatorial factor given by Staverman (1950).

Having found h as outlined above, we now proceed to find the next approximation for the average local fractions for the nonathermal case, that is, where $u_{ij} \neq 0$.

AVERAGE LOCAL AREA FRACTIONS IN NONATHERMAL MIXTURES

The summation in Equation (6) is replaced by its maximum term. Equations (10), (11), and (12) are used again but in this approximation U_0 [Equation (9)] is not set equal to zero. Equation (17) is retained. The resulting expression for Z_{lattice} is separately differentiated with respect to θ_{11} and θ_{22} and the results are set equal to zero. Again using the constraining Equations (7) and (8) but omitting mathematical details, we now find that the average local area fractions are given by

$$\theta_{11}^{(1)} = \frac{\theta_1}{\theta_1 + \theta_2 \exp \frac{-(u_{21} - u_{11})}{RT}} \quad (18)$$

and

$$\theta_{22}^{(1)} = \frac{\theta_2}{\theta_2 + \theta_1 \exp \frac{-(u_{12} - u_{22})}{RT}} \quad (19)$$

where u_{ij} is expressed in units of calories per mole and where superscript (1) denotes first approximation and θ_1 and θ_2 are average area fractions defined by Equations (15) and (16).

In mixtures that are not athermal, therefore, the average local area fractions are not the same as the average area fractions. Relations similar to Equations (18) and (19) were previously suggested by Wilson (1964).

TABLE 1. TYPICAL VALUES OF SIZE AND SURFACE PARAMETERS*

Fluid	r	q
Water	0.92	1.40
Carbon dioxide	1.30	1.12
Acetaldehyde	1.90	1.80
Ethane	1.80	1.70
Dimethyl amine	2.33	2.09
Methyl acetate	2.80	2.58
Furfural	2.80	2.58
Benzene	3.19	2.40
Toluene	3.87	2.93
Aniline	3.72	2.83
Triethyl amine	5.01	4.26
<i>n</i> -Octane	5.84	4.93
<i>n</i> -Decane	7.20	6.02
<i>n</i> -Hexadecane	11.24	9.26
Acetone	2.57	2.34
Chloroform	2.87	2.41

* Parameters are evaluated as shown in Appendix B.

Substituting Equations (4), (6), (9a), (10) to (12), and (17) to (19) into Equation (5) we obtain the desired result

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \quad (20)$$

where

$$\frac{g^E(\text{combinatorial})}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2}$$

$$+ (z/2) \left(q_1 x_1 \ln \frac{\theta_1}{\Phi_1} + q_2 x_2 \ln \frac{\theta_2}{\Phi_2} \right) \quad (21)$$

and

$$\frac{g^E(\text{residual})}{RT} = -q_1 x_1 \ln [\theta_1 + \theta_2 \tau_{21}] - q_2 x_2 \ln [\theta_2 + \theta_1 \tau_{12}] \quad (22)$$

where

$$\tau_{21} \equiv \exp \left\{ - \left[\frac{u_{21} - u_{11}}{RT} \right] \right\},$$

$$\tau_{12} \equiv \exp \left\{ - \left[\frac{u_{12} - u_{22}}{RT} \right] \right\} \quad (23)$$

In Equation (21) Φ is the average segment fraction:

$$\Phi_1 \equiv \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \text{and} \quad \Phi_2 \equiv \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \quad (24)$$

Equations (20) to (22) contain pure-component structural parameters r_1 , r_2 , q_1 , and q_2 ; these are evaluated from bond angles and bond distances as discussed in Appendix B.

Note that the expression for $g^E(\text{combinatorial})$ contains two composition variables: the average area fraction θ and the average segment fraction Φ . However, the expression $g^E(\text{residual})$ contains only one composition variable: the average area fraction θ . There are no adjustable binary parameters in Equation (21), but there are two adjustable binary parameters in Equation (22): $(u_{21} - u_{11})$ and $(u_{12} - u_{22})$. From the derivation of Equations (20) to (22) it follows that $u_{21} = u_{12}$.

APPLICATION TO BINARY AND MULTICOMPONENT SYSTEMS

Equations (20) to (22) give the excess Gibbs energy for a binary mixture in terms of two adjustable binary parameters and two pure-component structural parameters per component, r and q . Table 1 gives these structural parameters for some representative nonelectrolyte molecules; a more complete list is available from the authors upon request.

Activity coefficients are readily found by differentiation as indicated by Equation (2). For a binary mixture, activity coefficient γ_1 is given by

$$\ln \gamma_1 = \ln \Phi_1/x_1 + (z/2) q_1 \ln \frac{\theta_1}{\Phi_1} + \Phi_2 \left(l_1 - \frac{r_1}{r_2} l_2 \right) - q_1 \ln (\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) \quad (25)$$

where

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

and

$$(26)$$

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

For component 2, γ_2 can be found by interchanging subscripts 1 and 2.

Numerical results for $\ln \gamma$ are insensitive to the choice of coordination number z provided a reasonable value ($6 \leq z \leq 12$) is chosen. However, adjustable parameters τ_{21} and τ_{12} depend on that choice. In this work we have consistently used $z = 10$.

The derivation of Equation (20) is readily extended to mixtures containing three or more components without additional assumptions. For the multicomponent case Equations (21) and (22) become

$$\frac{g^E(\text{combinatorial})}{RT} = \sum_i x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} \quad (21a)$$

$$\frac{g^E(\text{residual})}{RT} = - \sum_i q_i x_i \ln \left(\sum_j \theta_j \tau_{ji} \right) \quad (22a)$$

where

$$\tau_{ji} \equiv \exp - \left\{ \left[\frac{u_{ji} - u_{ii}}{RT} \right] \right\} \quad (23a)$$

and the activity coefficient for component i becomes

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \left(\frac{z}{2}\right) q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j - q_i \ln \left(\sum_j \theta_j \tau_{ji} \right) + q_i - q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \quad (25a)$$

where

$$l_j = \left(\frac{z}{2}\right) (r_j - q_j) - (r_j - 1) \quad (26a)$$

and where the average area fraction θ and the average segment fraction Φ are defined by

$$\theta_i \equiv \frac{q_i N_i}{\sum_j q_j N_j} = \frac{q_i x_i}{\sum_j q_j x_j} \quad (27)$$

$$\Phi_i \equiv \frac{r_i N_i}{\sum_j r_j N_j} = \frac{r_i x_i}{\sum_j r_j x_j} \quad (28)$$

where x is the mole fraction. The summations in Equations (25a), (27), and (28) are over all components, including component i . From Equation (23a) it follows that $\tau_{ii} = \tau_{jj} = 1$.

Since the derivation of Equation (25) is based on a generalization (or extension) of Guggenheim's quasi-chemical model, we refer to that equation by the name UNIQUAC (universal quasi-chemical).

The UNIQUAC equation is not only a generalization of Guggenheim's model; it also provides a generalization of nearly all commonly-used expressions for the excess Gibbs energy. When clearly-defined simplifications are made in Equations (21) and (22), the UNIQUAC equation reduces to any one of several well-known equations, as indicated in Table 2.

The main advantage of the UNIQUAC equation is that, with only two adjustable parameters per binary, it gives good representation of both vapor-liquid and liquid-liquid equilibria for a variety of nonelectrolyte liquid mixtures. Some typical results are shown in Tables 3 and 4 and in Figures 5 to 11.

To test the applicability of the UNIQUAC equation, experimental vapor-liquid equilibrium data from the literature were reduced for 220 typical binary systems including those where the components differ appreciably in molecular size and shape. Optimum parameters ($u_{21} - u_{11}$) and ($u_{12} - u_{22}$) were obtained by a new fitting technique (Abrams and Grens, 1974) wherein probable experimental uncertainties were used to determine relative weighting factors for individual data points. In reducing the data, the coordination number z was set equal to ten.

When both vapor-liquid and liquid-liquid equilibrium data are used to obtain UNIQUAC parameters for a fixed binary system, the results appear to be smooth functions of temperature as indicated in Figure 1.

Vapor-liquid equilibrium data reduction was also performed using the two-parameter Wilson equation and the three-parameter NRTL equation. For binary vapor-liquid

TABLE 2. SIMPLIFICATIONS IN UNIQUAC EQUATION TO OBTAIN WELL-KNOWN RELATIONS FOR THE EXCESS GIBBS ENERGY

Simplifying assumptions		Resulting relation for $g^E(a)$
Equation (21)	Equation (22)	
$q_1 = r_1$ $q_2 = r_2$	$(u_{21} - u_{11}) = 0$ $(u_{12} - u_{22}) = 0$	Athermal Flory-Huggins
$q_1 = r_1$ $q_2 = r_2$	$q_1 = q_2 = 1$	Two-parameter Wilson
$q_1 = r_1$ $q_2 = r_2$	$q_1 = q_2 = c$	Three-parameter Wilson
Equals zero	$q_1^{-1} = q_2^{-1} = \alpha_{12}$ $g^E_{\text{residual}} = h^E$	NRTL
Equals zero	Expand terms in $\left(\frac{\Delta u}{RT}\right)$ truncating after linear term	van Laar with $A = (-2u_{12} + u_{11} + u_{22})q_1^{-1}$ $B = (-2u_{12} + u_{11} + u_{22})q_2^{-1}$
Equals zero	Expand terms in $\left(\frac{\Delta u}{RT}\right)$ truncating after quadratic term	Scatchard-Hamer with $q_1 = v_1$ $q_2 = v_2$
Equals zero	Expand terms in $\left(\frac{\Delta u}{RT}\right)$ truncating after quadratic term	Three-suffix Margules
Equals zero	Expand terms in $\left(\frac{\Delta u}{RT}\right)$ truncating after linear term	Scatchard-Hildebrand with $\delta_1^2 = u_{11}$ $\delta_2^2 = u_{22}$
$q_1 = r_1$ $q_2 = r_2$	$u_{12} = \sqrt{u_{11}u_{22}}$ Expand terms in $\left(\frac{\Delta u}{RT}\right)$ truncating after linear term	Flory-Huggins with $q_1 = v_1$ $q_2 = v_2$ $\chi = \frac{(-2u_{12} + u_{11} + u_{22})}{RT}$

(a) Unit inconsistencies are only apparent because r and q are dimensionless. The parameter u_{ij} is proportional to the interaction energy per pair of $i-j$ contact sites. It is expressed in units of calories per mole.

equilibria, the goodness-of-fit is about the same for all three equations. Further, when binary parameters alone are used to predict ternary vapor-liquid equilibria, all three equations are essentially similar in prediction accuracy. (See Table 5.) The important advantages of the UNIQUAC equation follow from its applicability to both vapor-liquid and liquid-liquid equilibria using only two adjustable parameters per binary.

ONE-PARAMETER FORM OF UNIQUAC EQUATION

The UNIQUAC equation contains two adjustable parameters per binary: $(u_{21} - u_{11})$ and $(u_{12} - u_{22})$. As suggested by Bruin (1971), it is possible to eliminate one of these by assuming

$$-u_{11} = \frac{\Delta u_1^{\text{vap}}}{q_1} \quad \text{and} \quad -u_{22} = \frac{\Delta u_2^{\text{vap}}}{q_2} \quad (29)$$

where Δu_i^{vap} is the energy required to vaporize one mole of pure liquid i isothermally from the saturated liquid to the ideal gas. To a zeroth approximation the adjustable parameter u_{12} is given by the geometric mean of u_{11} and u_{22} . For a first approximation we write

$$u_{12} = u_{21} = (u_{11}u_{22})^{1/2} [1 - c_{12}] \quad (30)$$

where c_{12} is the single adjustable parameter. Optimum values of c_{12} are shown in Table 4 for some representative binary systems. For mixtures of nonpolar liquids c_{12} is positive and small compared to unity. For mixtures containing one polar component (1) and one nonpolar component (2), c_{12} is also positive but no longer small because only the nonpolar part of u_{11} contributes to u_{12} . For mixtures of polar liquids no general rule can be observed; however, it is clear that if there is a preferential attraction (solvation) between the unlike molecules (for example,

TABLE 3. TYPICAL REPRESENTATION OF BINARY VAPOR-LIQUID EQUILIBRIA BY UNIQUAC EQUATION

System	Temp., °C or pressure, mm Hg	No. of data points	σ^2 , Variance of Fit $\times 10^{3\dagger}$		Reference
			One parameter	Two parameter	
Methylcyclopentane-benzene	760	29	8.4	8.7	Myers (1956)
Benzene- <i>iso</i> -octane	760	11	4.1	4.5	Chu (1956)
Isooctane-nitroethane	35°	19	0.4	0.2	Edwards (1962)
Nitromethane-benzene	45°	12	0.4	0.5	Brown (1957)
Hexane-nitroethane	45°	12	1.3	0.1	Edwards (1962)
Methanol-benzene	55°	9	197.2	3.2	Scatchard (1946)
Ethanol- <i>iso</i> -octane	50°	13	103.4	6.3	Kretschmer (1948)
Ethanol-hexane	760	16	196.3	8.8	Sinor (1960)
Ethanol-water	70°	13	126.1	0.55	Mertl (1972)
Ethylacetate-ethanol	70°	15	18.2	0.69	Mertl (1972)
Water-methylethyl ketone	760	8	1.7	1.3	Othmer (1945)
Acetone-benzene	45°	11	2.7	0.5	Brown (1957)
Carbon tetrachloride-acetonitrile	45°	13	147.8	7.1	Brown (1954)
Methylacetate-ethanol	45°	11	8.6	9.3	Nagata (1962)
Acetone-chloroform	50°	29	23.5	4.2	Severns (1953)
Methylacetate-methanol	50°	15	41.6	4.2	Severns (1953)

† The variance of the fit σ^2 is given by

$$\sigma^2 = \frac{1}{D-L} \left[\left\{ \sum_i \frac{1}{\sigma_{z_i}^2} (x_i^o - x_i^M)^2 + \frac{1}{\sigma_{y_i}^2} (y_i^o - y_i^M)^2 + \frac{1}{\sigma_{P_i}^2} (P_i^o - P_i^M)^2 + \frac{1}{\sigma_{T_i}^2} (T_i^o - T_i^M)^2 \right\} \right]$$

where the superscript M denotes the measured value of the variable and the superscript o denotes the estimate of the true value of the variable. D is the number of data points and L is the number of parameters and the σ 's are the variances in the measured variables.

TABLE 4. BINARY PARAMETERS IN TWO-PARAMETER OR ONE-PARAMETER UNIQUAC EQUATION FOR REPRESENTATIVE BINARY SYSTEMS

System (1)-(2)	Temp., °C or pressure, mm Hg	Two-parameter		One parameter c_{12}	Reference
		$(u_{21} - u_{11})$ cal/mole	$(u_{12} - u_{22})$ cal/mole		
Methylcyclopentane-benzene	760	-36.9	138.1	0.092	Myers (1956)
Benzene- <i>iso</i> -octane	760	182.1	-76.5	0.078	Chu (1956)
Isooctane-nitroethane	35°	5.3	492.3	0.412	Edwards (1962)
Nitromethane-benzene	45°	309.1	35.45	0.218	Brown (1957)
Hexane-nitroethane	45°	-36.3	471.6	0.351	Edwards (1962)
Methanol-benzene	55°	1355.8	-417.4	0.182	Scatchard (1946)
Ethanol- <i>iso</i> -octane	50°	968.2	-357.6	0.229	Kretschmer (1948)
Ethanol-hexane	760	940.9	-335.0	0.308	Sinor (1960)
Water-ethanol	70°	258.4	378.1	0.272	Mertl (1972)
Ethylacetate-ethanol	70°	-292.3	446.5	0.034	Mertl (1972)
Water-methylethyl ketone	760	622.3	222.2	0.419	Othmer (1945)
Acetone-benzene	45°	331.0	-208.9	0.059	Brown (1957)
Carbon tetrachloride-acetonitrile	45°	-100.1	953.4	0.494	Brown (1954)
Methylacetate-ethanol	45°	-40.5	426.5	0.229	Nagata (1962)
Acetone-chloroform	50°	149.8	-315.5	-0.183	Severns (1955)
Methylacetate-methanol	50°	-233.1	622.1	0.156	Severns (1955)

hydrogen bonding in acetone-chloroform) then c_{12} must be negative.

Table 3 shows that for mixtures of nonpolar liquids the one-parameter UNIQUAC equation represents the data

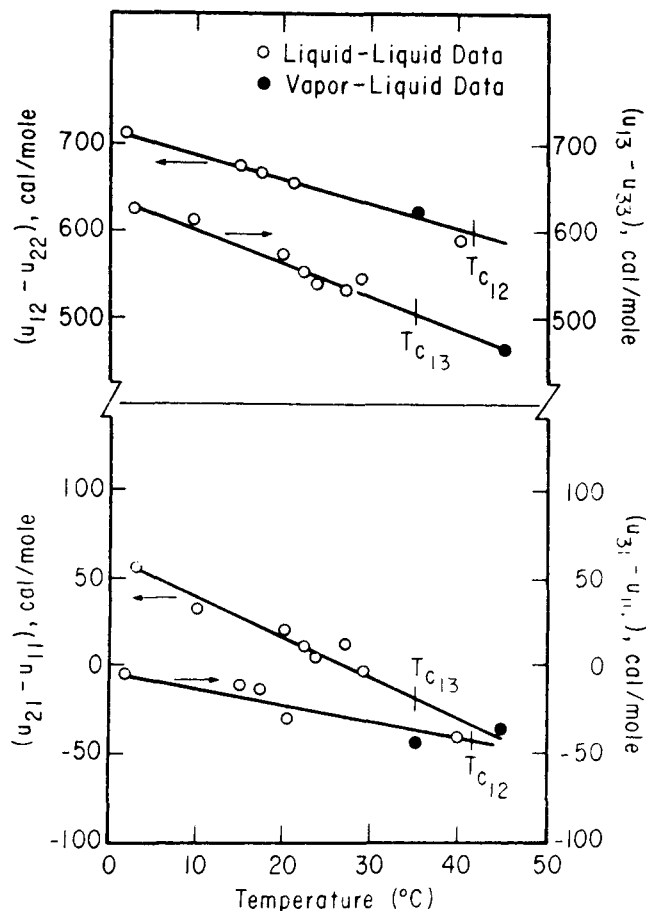


Fig. 1. UNIQUAC parameters for nitroethane (1), octane (2); and nitroethane (1), hexane (3) calculated from vapor-liquid and liquid-liquid data. The upper consolute temperature is T_c .

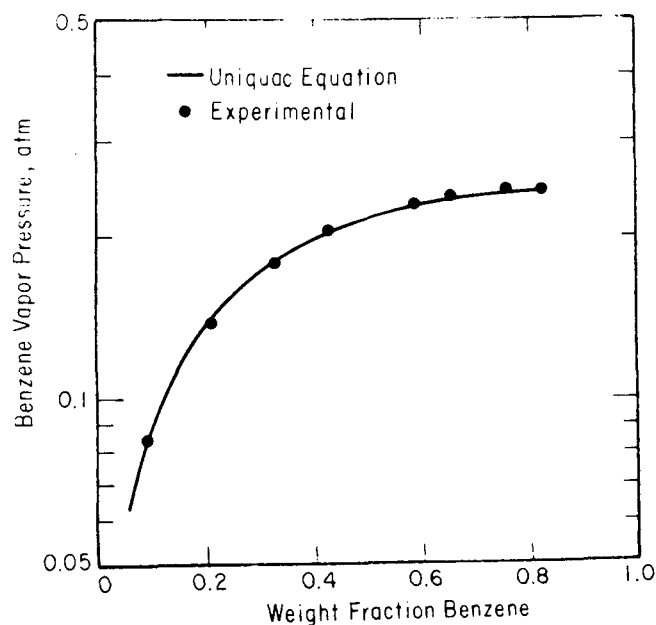


Fig. 2. Vapor pressure of benzene in solutions of polyisobutylene (molecular weight 10^5) at 40°C .

essentially as well as the two-parameter UNIQUAC equation. However, for other mixtures two parameters, rather than one, are required to obtain satisfactory representation.

POLYMER SOLUTIONS

Since the combinatorial contribution to the excess Gibbs energy [Equation (21)] is applicable to mixtures containing very large molecules (polymers) and molecules of normal size (monomers), the UNIQUAC equation may also be used to represent the properties of polymer solutions. Illustrative results are shown in Figures 2 and 3. All results shown in Figure 3 were obtained with only two adjustable parameters.

LIQUID-LIQUID EQUILIBRIA

Well-known equations of thermodynamic stability can be applied to the UNIQUAC equation to determine whether one or two liquid phases exist at equilibrium. Whenever the magnitude of u_{12} is low compared to that of u_{11} or u_{22} , a single phase is unstable and two liquid phases are formed. However, in addition to energetic effects, differences in molecular size and shape may also affect phase stability. To illustrate, Figure 4 shows the molar Gibbs energy of mixing as a function of composition. For simplicity, a symmetric system has been chosen; for each of the three curves shown $r_1 = r_2 = 3.3$ and $(u_{21} - u_{11}) = (u_{12} - u_{22}) = 0.45 RT$. Further, for all three curves $q_1 = q_2$. The lowest line, with $q = 2$, indicates phase stability; the middle line, with $q = 2.5$, indicates incipient instability and the top line, with $q = 3$, indicates

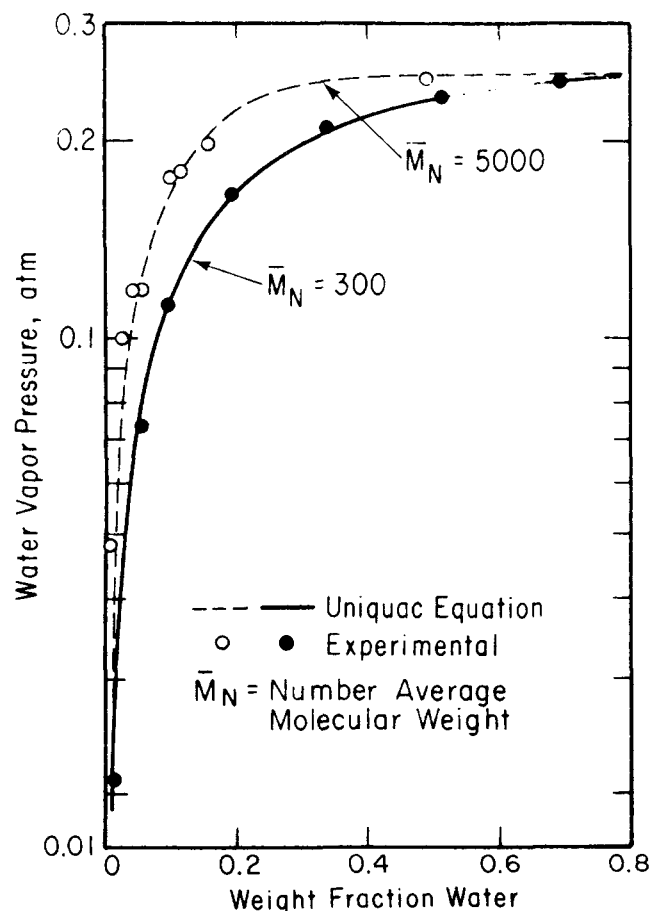


Fig. 3. Vapor pressure of water in solutions of polyethylene glycol at 65°C .

that two phases coexist. Figure 4, therefore, shows that the tendency for phase-splitting depends not only on differences in potential energy but also on molecular geometry: when $q = 2$, the external molecular surface area is insufficient to produce phase instability but when $q = 3$ the molecular area available for interaction is sufficiently large to produce two liquid phases.

The effect illustrated in Figure 4 is observed in experimental results for the systems methanol-*n*-octane and methanol-*iso*-octane. In these two binaries, the energetic parameters are essentially identical and parameter r for octane is almost independent of chain branching. However, q for *iso*-octane is smaller than that for *n*-octane; the external surface area of a branched chain is always lower

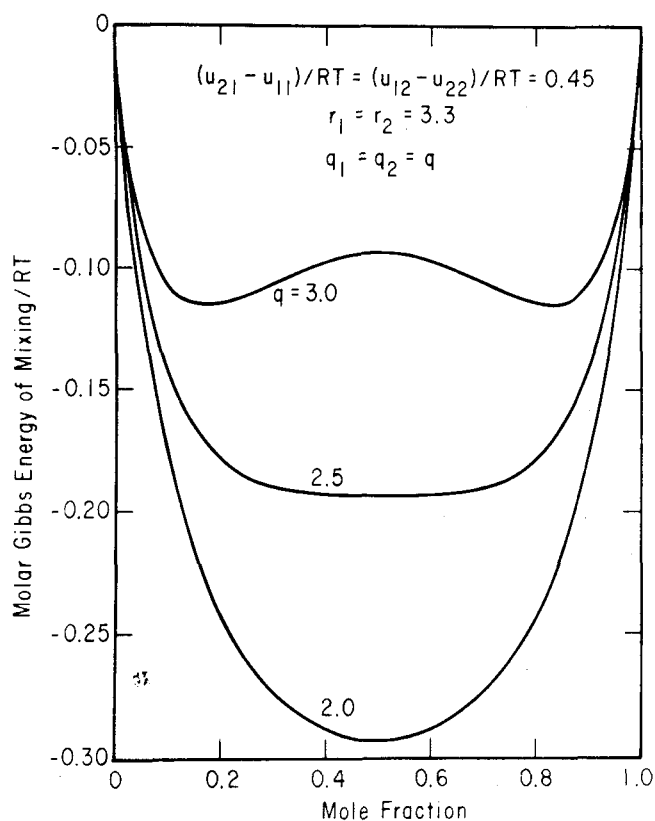


Fig. 4. Effect of surface-area parameter q on Gibbs energy of mixing for a symmetric system according to UNIQUAC.

than that of an unbranched chain having the same number of segments. Therefore, we expect methanol-*n*-octane to show phase instability more readily than does methanol-*iso*-octane, in agreement with experiment: the upper consolute temperature for methanol-*n*-octane is 66.7°C while that for methanol-*iso*-octane is 42.5°C (Francis, 1961).

When binary data alone are used, representation of multicomponent liquid-liquid equilibria is much more difficult than representation of multicomponent vapor-liquid equilibria. For vapor-liquid equilibria for mixtures of normal molecular weight, Raoult's law often gives a reasonable zeroth or first approximation; activity coefficients provide corrections, but the main influence on vapor-liquid equilibria is given by the pure-component vapor pressures. However, this influence plays no role at all in liquid-liquid equilibria. Small changes in activity coefficients usually produce large qualitative changes in the shape of the connodal curve and the slopes of the tie lines, especially near the plait point. Therefore, for any empirical or semi-empirical expression for the excess Gibbs energy, ternary liquid-liquid equilibria provide a much stricter test than ternary vapor-liquid equilibria.

The two-parameter Wilson equation which is so successful for multicomponent vapor-liquid equilibria, fails completely for liquid-liquid equilibria (Wilson, 1964), even in binary systems. While Wilson has suggested a three-parameter form of his equation which is applicable to binary liquid-liquid systems (Wilson, 1964), it is not possible to generalize it to ternary (and higher) systems without additional simplifying assumptions (Renon and Prausnitz, 1969). The two-parameter equations of van Laar and Margules are applicable to liquid-liquid equilibria but usually give poor representation of such equilibria.

The three-parameter NRTL equation, proposed in 1968, provides a large improvement in representation of ternary liquid-liquid equilibria using only binary parameters. However, calculated results are sensitive to the choice of the binary parameters α_{12} , α_{23} , and α_{13} , especially to α_{12} in plait-point systems where 1 and 2 are the partially miscible components. Mutual solubility data for the 1-2 binary can be used to fix two of the 1-2 binary parameters, but the all-important choice of α_{12} remains elusive. Empirical rules originally suggested (Renon and Prausnitz, 1968) appear to be inadequate for consistently reliable results. Therefore, as shown by Renon et al. (1971), good representation for ternary systems can only be obtained with extensive ternary data used to fix the nine

TABLE 5. REPRESENTATION OF TERNARY VAPOR-LIQUID EQUILIBRIA BY UNIQUAC EQUATION

System	Temperature °C or pressure, mm Hg	No. of data points	Root mean square deviation in vapor mole fraction $\times 10^3$	Root mean square relative deviation in pressure $\times 10^3$	Reference
Ethanol			9		
Ethyl acetate	70°	9	10	12	Mertl (1972)
Water			8		
Methyl acetate			5		
Chloroform	760	91	4	8	Nagata (1962)
Benzene			7		
Ethanol			15		
Benzene	760	19	8	11	Morachevskii (1963)
Cyclohexane			9		
Chloroform			8		
Methanol	760	13	9	10	Hudson (1969)
Methyl acetate			9		
Acetone			8		
Methanol	50°	30	10	12	Severns (1955)
Chloroform			10		

binary NRTL parameters.

The advantage of the UNIQUAC equation is that it is applicable to partially miscible systems using only two adjustable parameters per binary. Not only does this mean that fewer experimental points are needed to fix the parameters but, what is more important, the mutual-solubility data for a partially miscible binary uniquely fix the two parameters needed for that binary.

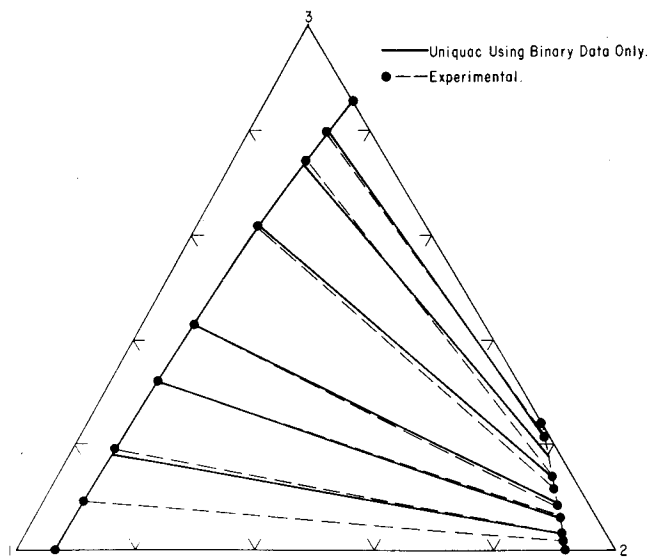


Fig. 5. Liquid-liquid equilibria in the system: hexane (1) aniline (2), and methylcyclopentane (3) at 25°C. Concentrations are in mole fractions.

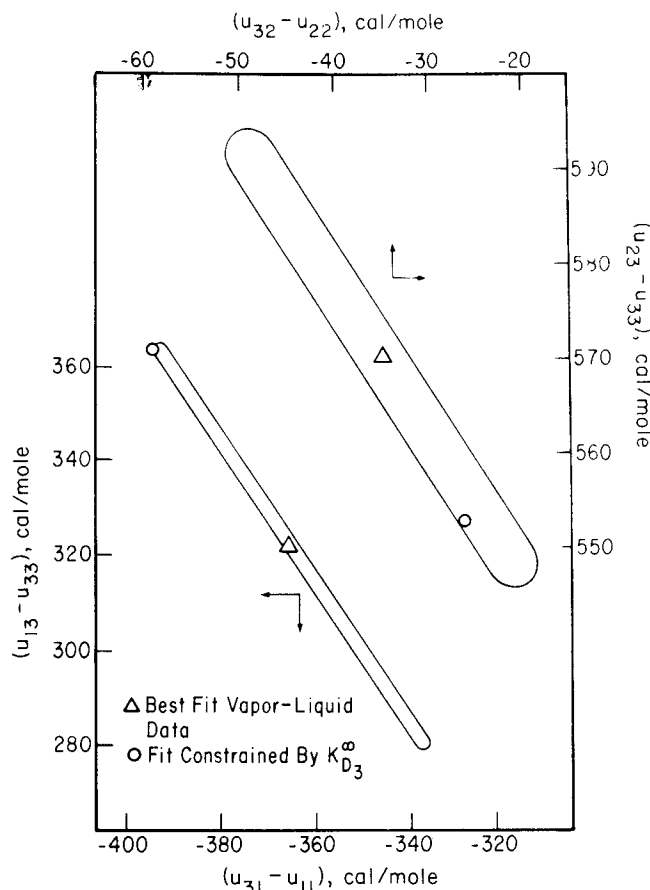


Fig. 6. Confidence ellipses for the UNIQUAC binary parameters in the systems: chloroform (1), acetone (3), and water (2), acetone (3).

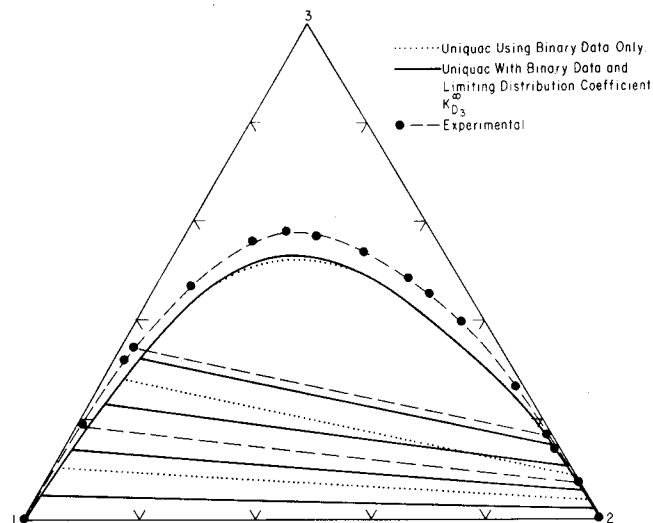


Fig. 7. Liquid-liquid equilibria in the system: chloroform (1), water (2), and acetone (3) at 60°C. Concentrations are in weight fractions.

In most common ternary liquid-liquid systems there are either one or two partially-miscible binaries. If there are two, it is a relatively simple matter to construct the equilibrium diagram when mutual-solubility data are available for both partially miscible binaries. Results are not strongly sensitive to the binary parameters of the completely miscible pair. To illustrate, Figure 5 shows excellent agreement between calculated and experimental results for the system hexane-aniline-methylcyclopentane.

However, if the ternary diagram has a plait point (only one partially-miscible pair), accurate representation using binary data only becomes much more difficult. Binary parameters for the partially-miscible pair are determined uniquely from mutual-solubility data, but calculated results are now sensitive to the choice of binary parameters for the two miscible pairs.

It has been pointed out by several authors (Tierney, 1958; Nagahama et al., 1971) that reduction of vapor-liquid equilibrium data cannot yield unique binary parameters unless the accuracy of the data is extremely high, much higher than usually encountered in typical experimental studies. Within the experimental error, many sets of binary parameters can equally well reproduce the binary vapor-liquid equilibrium data. The two parameters are strongly correlated such that if one of them is chosen arbitrarily, the other is fixed.

To illustrate the difficulties encountered in calculating ternary equilibria in a plait-point system, consider the ternary chloroform (1), water (2), acetone (3) at 60°C. Parameters τ_{12} and τ_{21} are uniquely fixed by mutual solubility data. Vapor-liquid equilibrium data for the 1-3 and 2-3 binaries yield parameters shown in Figure 6; for each binary, any point within the area shown can reproduce the experimental vapor-liquid equilibrium data within the experimental uncertainty.

When ternary calculations are based on the best binary parameters shown by triangle-points in Figure 6, we obtain results shown by the dotted lines in Figure 7 and by the dashed lines in Figure 8 which show the distribution coefficient and the selectivity defined by

$$K_{D3} \equiv \frac{x_3'}{x_3''} \quad (31)$$

$$\beta_{3,1} \equiv K_{D3}/K_{D1} = \frac{x_3' x_1''}{x_3'' x_1'} \quad (32)$$

where ' and '' designate the equilibrium liquid phases. Similar results were obtained for the system furfural (1), *iso*-octane (2), benzene (3) at 25°C shown in Figures 9 and 10. The calculated results are in poor agreement with the ternary data. In these calculations the best binary parameters are those which give the best representation of the binary vapor-liquid equilibria.

Significant improvement (especially in K_D and β) can be obtained by choosing the best binary parameters in such a way that, first, the binary vapor-liquid equilibrium data are reproduced within the experimental uncertainty and, second, the calculated limiting distribution coefficient K_D^∞ is in agreement with the experimental value as determined from the ternary data:

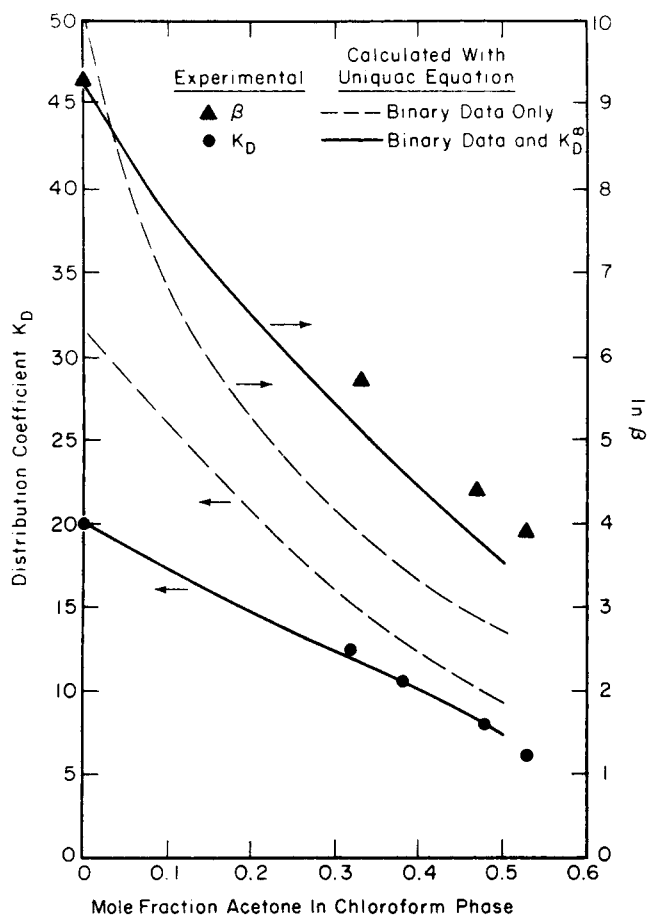


Fig. 8. Distribution coefficient of acetone and β , selectivity of chloroform for acetone relative to water, at 60°C.

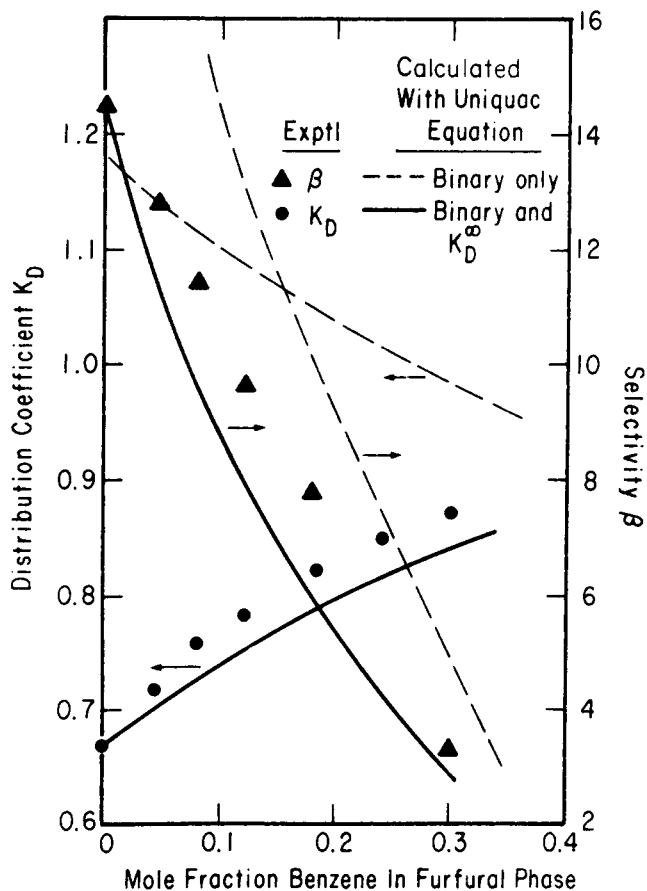


Fig. 10. Distribution coefficient of benzene and selectivity of furfural for benzene relative to iso-octane.

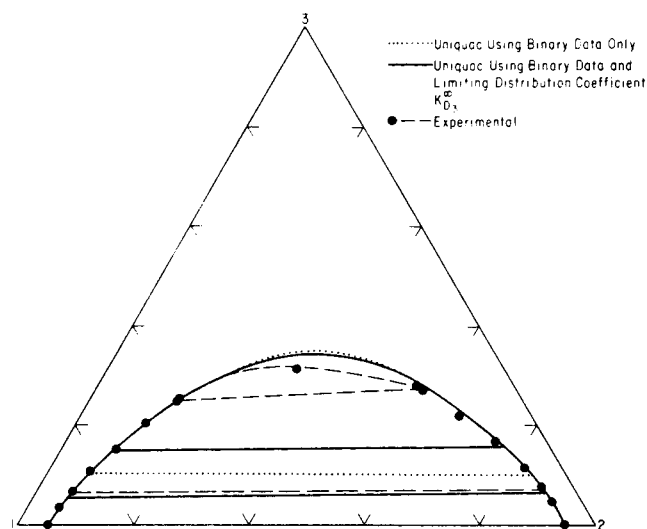


Fig. 9. Liquid-liquid equilibria in the system: furfural (1), *iso*-octane (2), and benzene (3) at 25°C. Concentrations are in weight fractions.

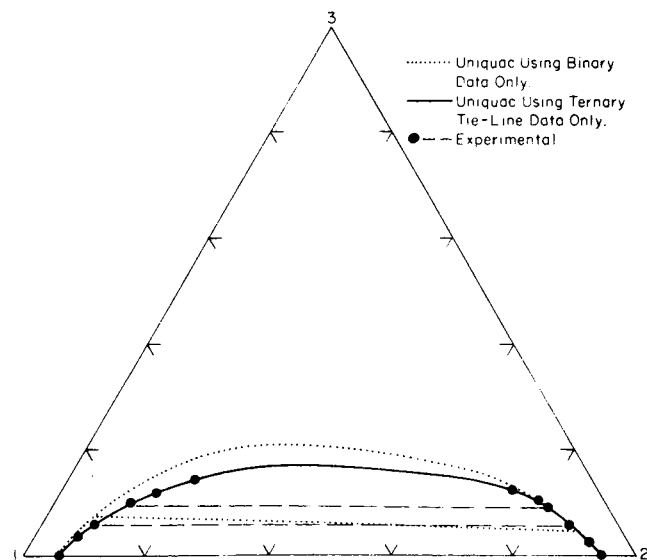


Fig. 11. Liquid-liquid equilibria in the system: ethyl acetate (1), water (2), and ethanol (3). Concentrations are in weight fractions.

$$K_{D_3}^{\infty} = \text{Limit } K_{D_3} \quad (33)$$

$$\begin{matrix} x_3' \rightarrow 0 \\ x_3'' \rightarrow 0 \end{matrix}$$

Ternary results based on these calculations are shown by the continuous lines in Figures 7 through 10. Agreement with experiment is now very much better. Binary parameters used in the calculations are shown by circle-points in Figure 6.

FITTING OF BINARY PARAMETERS FROM TERNARY DATA

Instead of fitting the binary parameters from binary data, it is, of course, possible to ignore vapor-liquid binary data and, with a suitable computer program, to obtain all binary parameters from the ternary connodal-line and tie-line data. This procedure, as discussed by Renon (1971), necessarily produces excellent results. We too have performed such a calculation for the system water, ethanol, ethyl acetate with splendid results, as shown in Figure 11. However, we find that the six binary parameters obtained by such brute-force fitting fall far outside the contour lines obtained from fitting binary vapor-liquid equilibria; in other words, these brute-force binary parameters, obtained from ternary liquid-liquid data alone, cannot predict vapor-liquid equilibria for the binaries within experimental error.

If interest is restricted to a particular ternary liquid-liquid system, then brute-force fitting of parameters for that system may serve a useful purpose. But such a procedure is likely to produce poor results for the case, commonly encountered in industry, where there are four, five, or more components present and experimental data for the multicomponent system are unavailable or, at best, fragmentary. In that case forcefitting one of the ternaries locks-in parameters for three of the binaries, leaving insufficient freedom for accurate calculation of the multicomponent equilibrium diagram. For example, consider the quaternary system benzene (1), furfural (2), cyclohexane (3), iso-octane (4). We can easily force-fit the 1-2-3 ternary and obtain a fine representation of the ternary data. We have thereby fixed the 1-2, 1-3, and 2-3 binary parameters. If we now want to fit the 1-2-4 ternary we can vary the 1-4 and 2-4 binary parameters. But we still have to fit two additional ternaries (1-3-4 and 2-3-4) and to do so we have available for adjustment only one set (3-4) of binary parameters. Unless data are plentiful and the computer program is very large, force-fitting is not useful for representing liquid-liquid equilibria for systems containing more than three components.

CONCLUSION

A new model has been established for the excess Gibbs energies of multicomponent liquid mixtures of nonelectrolytes. This model, using only two adjustable parameters per binary, gives good representation of vapor-liquid and liquid-liquid equilibria for a wide variety of mixtures. The utility of this model follows from its semitheoretical basis which gives consideration to molecular size and shape through structural parameters and to deviations from random mixing through application of the local-composition concept.

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NOTATION

A	= Helmholtz energy
a^E	= excess Helmholtz energy per mole
c	= third parameter in Wilson's equation
c_{12}	= deviation from geometric mean in Equation (30)
D	= number of data points (Table 3)
g^E	= excess Gibbs energy per mole
h	= normalizing factor in Equations (10) and (17)
h^E	= excess enthalpy per mole (Table 2)
k	= Boltzmann constant
K_D	= distribution coefficient
L	= number of parameters (Table 3)
l	= see Equation (26)
n	= number of moles
N	= number of molecules
P	= pressure
q	= pure-component area parameter
r	= pure-component volume parameter
T	= temperature
U_0	= potential energy of a lattice containing $N_1 + N_2 + \dots$ molecules
U_{ij}	= potential energy characterizing ij interaction
u_{ij}	= UNIQUAC binary interaction parameter
u^{vap}	= energy of vaporization to ideal gas per mole
x	= liquid-phase mole fraction
y	= vapor-phase mole fraction
Z	= configurational partition function
z	= lattice coordination number, a constant here set equal to 10

Greek Letters

α_{12}	= parameter in NRTL equation
β	= selectivity
γ_i	= activity coefficient of component i
σ	= variance (Table 3)
Φ_i	= segment fraction
θ_i	= area fraction
θ_{ij}	= local area fraction of sites belonging to molecule i around sites belonging to molecule j
θ	= molecular configuration. See Equation (6)
τ	= see Equation (23)
ω	= combinatorial factor

Superscripts

0	= zeroth approximation
1	= first approximation
M	= measured variable (Table 3)
o	= estimated true value of variable (Table 3)
' or ''	= equilibrium liquid phase in two-liquid system
∞	= infinite dilution

Subscripts

i	= component i
j	= component j
T	= total

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APPENDIX A. LOCAL AREA FRACTION

To illustrate the concept of local area fraction, we consider a binary system containing six molecules of type 1 and six molecules of type 2 on a two-dimensional lattice as enclosed by the boxes in Figure A1. Each 1-molecule occupies three sites and each 2-molecule occupies two sites; thus $r_1 = 3$ and $r_2 = 2$. The coordination number z of the two-dimensional

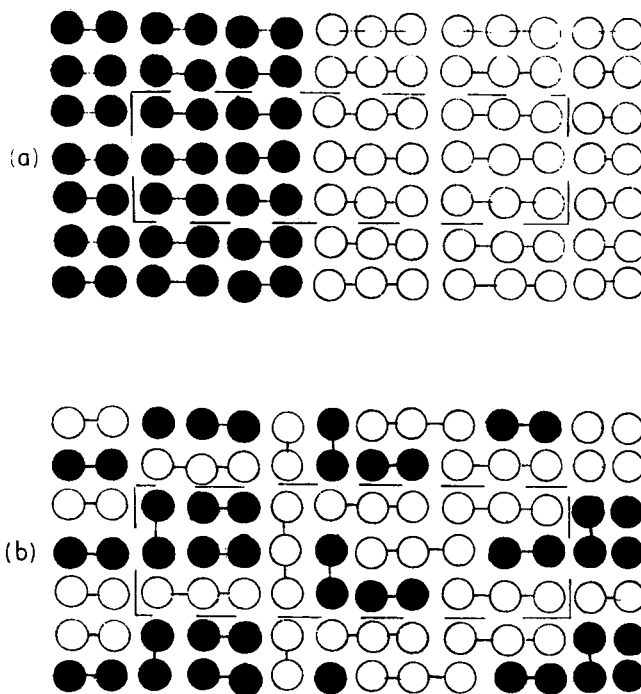


Fig. A1. Two possible arrangements (within box) of six black and white molecules. Black molecules contain two segments each and white molecules contain three segments each.

lattice is four. Each 1-molecule has eight external contacts; thus $q_1z = 8$ and $q_2z = 6$.

The average segment fraction Φ_1 is given by

$$\Phi_1 = \frac{x_1r_1}{x_1r_1 + x_2r_2} = \frac{\frac{1}{2} \times 3}{\frac{1}{2} \times 3 + \frac{1}{2} \times 2} = \frac{3}{5}$$

and similarly $\Phi_2 = 2/5$.

The average area fraction of 1-molecules is given by

$$\theta_1 = \frac{x_1q_1}{x_1q_1 + x_2q_2} = \frac{x_1q_1z}{x_1q_1z + x_2q_2z} = \frac{\frac{1}{2} \cdot 8}{\frac{1}{2} \cdot 8 + \frac{1}{2} \cdot 6} = \frac{4}{7}$$

and similarly $\theta_2 = 3/7$.

Two possible arrangements of the molecules are illustrated in Figure A1. In the first figure the molecules are segregated in an ordered fashion, whereas in the second the molecules are distributed in a more random fashion. The average segment fractions and the average area fractions are the same in both figures. However, the local area fractions are different. The number of 1 segments about 1 segments differ in the two arrangements, also there are differences in the number of 1 segments about 2 segments, the number of 2 segments about 1 segments, and the number of 2 segments about 2 segments. In Figure A1b there are forty-five 1-about-1 neighbors but there are only three 2-about-1 neighbors. Thus the local area fraction θ_{11} is 45/48 and the local area fraction θ_{21} is 3/48.

By contrast in Figure A1a there are twenty-four 1-about-1 interactions and twenty-four 2-about-1 interactions; thus $\theta_{11} = 24/48$ and $\theta_{21} = 24/48$. Further, in Figure A1a, $\theta_{22} = 33/36$ and $\theta_{12} = 3/36$, whereas in Figure A1b $\theta_{22} = 12/36$ and $\theta_{12} = 24/36$.

This two-dimensional example illustrates the multiple number of ways in which molecules in a binary mixture can arrange themselves in space. This multiplicity (also called degeneracy) is reflected in the combinatorial factor of the partition function. The combinatorial factor, in turn, is the primary quantity which determines the thermodynamic properties of a mixture.

APPENDIX B. EVALUATION OF PURE-COMPONENT STRUCTURAL PARAMETERS r AND q

The structural parameters r and q are, respectively, the van der Waals volume and area of the molecule relative to those of a standard segment.

$$r_i = V_{wi}/V_{ws} \quad (B1)$$

$$q_i = A_{wi}/A_{ws} \quad (B2)$$

where V_{wi} and A_{wi} are the van der Waals volumes and areas of the molecule given by Bondi (1968) and where V_{ws} and A_{ws} are the van der Waals volume and area of a standard segment. The choice of a standard segment is somewhat arbitrary. Here it is defined as a sphere such that for a linear polymethylene molecule of infinite length the identity

$$(z/2)(r - q) = r - 1 \quad (B3)$$

is satisfied. The coordination number z is set equal to 10. The volume of the standard sphere in terms of its radius R_{ws} is given by

$$V_{ws} = 4/3 \pi R_{ws}^3 \quad (B4)$$

and the area by

$$A_{ws} = 4 \pi R_{ws}^2 \quad (B5)$$

The van der Waals volume and area of an n -mer of polymethylene are n times the volume and area of a methylene group as given by Bondi; that is

$$V_{wi} = n(10.23) \text{ cm}^3/\text{mole} \quad (B6)$$

$$A_{wi} = n(1.35) \times 10^9 \text{ cm}^2/\text{mole} \quad (B7)$$

Substitution of Equations (B1), (B2), and (B4) to (B7) into (B3) as n tends to infinity yields an equation which fixes $R_{ws} = 10.95 \times 10^{15} \text{ cm}/\text{mole}$.[†] Substitution into Equations (B4) and (B5) yields a standard segment volume of $15.17 \text{ cm}^3/\text{mole}$ and a standard segment area of $2.5 \times 10^9 \text{ cm}^2/\text{mole}$. Equations (B1) and (B2) then become

$$r_i = V_{wi}/15.17 \quad (B1a)$$

$$q_i = A_{wi}/(2.5 \times 10^9) \quad (B2a)$$

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[†] Per molecule $R_w = \frac{10.95 \times 10^{15}}{6.023 \times 10^{23}} \text{ cm}/\text{molecule}$. This number is substituted into Equations (B4) and (B5).

Two Kinds of Self-Preserving Size Spectra of a Cloud of Particles

The population balances describing the time dependence of the size distribution can, under some conditions, be transformed by means of a similarity transformation into an ordinary integro-differential equation containing two instead of three variables. If there is compatibility between the transformed equation and the constraints given by the total mass conservation equation and the equation for the total number of particles, a self-preserving spectrum of the first kind can be obtained. There are, however, many situations such as the sintering controlled aging of supported metal catalysts, coagulation of colloidal particles in laminar shear flow, and coagulation of colloidal particles in a turbulent flow when the particles are smaller than the size of the smallest eddy for which, although a similarity transformation is possible, the transformed equation has no solution because of incompatibility with the above mentioned constraints. A second kind of self-preserving spectrum is suggested for these situations. The new variables are induced from a particular case for which an analytical result is available. A detailed presentation of the sintering controlled aging of supported metal catalysts is presented.

B. PULVERMACHER

Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

and

E. RUCKENSTEIN

Faculty of Engineering and Applied Sciences
State University of New York at Buffalo
Buffalo, New York 14214

Correspondence concerning this paper should be addressed to E. Ruckenstein.