Activity Coefficients for Binary and Multicomponent Liquid Mixtures from Unary Property Model for Wilson Parameters

A model has been developed for prediction of Wilson parameters from single component properties. Activity coefficients and VLE data for miscible binary or multicomponent systems can be calculated from the standard form of the Wilson equation using these properties. The major advantage of this model is that experimental determinations of binary data are not required. Relevant properties for a fairly large number of chemical species have been provided. This method has been compared with UNIFAC, which is generally used for prediction of activity coefficients and has been found to give comparable results with considerably less computational effort.

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SCOPE

Although the Wilson model (Wilson, 1964) provides a computationally simple and reasonably accurate method for calculation of liquid phase activity coefficients, the two adjustable binary parameters that it contains have to be obtained by fitting experimental binary data. This severely limits the scope of use of the Wilson equation. Several attempts have been made to modify the equation by using a single binary parameter only (Tassios, 1971; Ladurelli et al., 1975; Hiranuma and Honma, 1975; Krumins et al., 1980) or to predict the binary parameters by using empirical correlations (Ghosh and Chopra, 1975; Gothard et al., 1976), but none has been of general utility.

An approximate theoretical model, based on the assumption that the solution is locally regular, has been developed that successfully expresses Wilson parameters in terms of pure compound properties. The model is quite general in nature and uses the solubility parameter, "effective molar volume," and two deviation parameters for pure substances to predict the Wilson parameters. These properties for a number of polar and nonpolar compounds have been obtained. The results obtained by this method for a large number of binary and multicomponent systems have been compared with those predicted by the UNIFAC method.

CONCLUSIONS AND SIGNIFICANCE

The correlation obtained from the proposed model for prediction of Wilson binary parameters uses only three types of single component properties; the solubility parameter, effective molar volume, and the deviation parameter. This has been tested for a large number of binary and multicomponent systems, including hydrocarbons (aliphatic, cyclic, and aromatic), alcohols (primary and secondary), carbonyl compounds, esters, halogenated hydrocarbons, nitriles, and water. The computed average deviation in bubble point pressure and vapor phase composition is small, normally within 2%. The results have also been compared with and found to be as good as those predicted by the UNIFAC method.

The proposed correlations and expressions are remarkably simple and require only pure compound data. The method will considerably simplify and reduce the computational efforts now required to evaluate liquid state activity coefficients without sacrificing accuracy.

The Wilson equation (Wilson, 1964) has been quite satisfactory for correlation of binary vapor-liquid equilibrium (VLE) data and for the prediction of multicomponent VLE behavior from relevant binary data. In his model Wilson used the energies of interaction λ_{ii} and λ_{ij} or λ_{ji} between like and unlike pairs of molecules, but was not successful in attributing precise physical significance to or in obtaining expressions for these quantities. Fortunately, however, the model was so constructed that only the difference terms, $(\lambda_{ij} - \lambda_{ii})$ and $(\lambda_{ji} - \lambda_{jj})$, appeared in the final expressions. Hence, Wilson could use these as adjustable parameters to be obtained from fitting of experimental binary equilibrium data. Wilson had introduced the idea that local volume fraction, rather than the overall volume fraction, would be an important parameter for modeling phase equilibrium but had used the pure compound molar volume directly as a measure of its volume in solution. He also assumed empirically that the Flory-Huggins equation with local volume fraction replacing the volume fraction term would give a reasonable representation of the excess Gibbs energy.

Tassios (1971) proposed a simplification of the Wilson equation on the assumption that the like component interaction parameter λ_{ii} may be equated to the negative of molar energy of vaporization of component i, thus leaving only λ_{ij} as the single adjustable parameter. Several other forms for λ_{ii} in the "single parameter Wilson equation" have been tried by Ladurelli et al. (1975) and Krumins et al. (1980).

Hiranuma and Honma (1975) proposed that the unlike-pair interaction may be correlated to certain basic single component properties like molar dispersion energy and dipole energy. They were not, however, quite successful in this effort, needing at least one binary parameter that has to be obtained from the interaction parameter for a "similar" binary system, thus limiting the applicability of the method.

Few empirical curve-fitting approaches for prediction of λ_{ij} or $(\lambda_{ij} - \lambda_{ii})$ have been reported. Ghosh and Chopra (1975) obtained correlations for λ_{ij} and λ_{ji} in terms of solubility parameters and molar volumes of the components. Gothard et al. (1976) obtained power series expressions for $(\lambda_{ij} - \lambda_{ii})$ and $(\lambda_{ji} - \lambda_{jj})$ for binary hydrocarbon systems in terms of difference of solubility parameters of the components. All these expressions are, however, of limited practical application.

THEORETICAL DEVELOPMENT

In the Wilson model a binary liquid mixture is considered to be made up of two hypothetical fluids—one being cells containing particles of type 1 at the center, the other being cells having particles of type 2 at the center. The compositions of these cells, called local compositions, differ from the macroscopic composition by the Boltzmann factor, that is

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_j} \exp[-(\lambda_{ji} - \lambda_{ii})/RT] \tag{1}$$

The energy difference term $(\lambda_{ji} - \lambda_{ii})$ may be identified with the effective difference in energies of interaction between like and unlike pairs.

The local volume fraction is defined as

$$\Phi_i = \frac{x_{ii} v_i}{x_{ii} v_i + x_{ji} v_j} \tag{2}$$

When these results are introduced in the Flory-Huggins expression for excess free energy, one gets

$$\frac{g^E}{RT} = -\sum x_i \ln[x_i + x_j \Lambda_{ij}] \tag{3}$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \tag{4}$$

In order to obtain an estimate for $(\lambda_{ij} - \lambda_{ii})$ let us consider two cells—the first cell containing a central molecule of type 1 and surrounded by molecules of type 1 only (i.e., pure 1), and the second cell containing a central molecule of type 1, but surrounded by molecules of type 2 only (i.e., an infinitely dilute solution of 1 in 2) (Figure 1). The transfer of the central molecule 1 from the first cell to form the second cell would involve an effective change in internal energy that will obviously be equal to the excess internal energy of mixing per molecule of type 1 for passing from the pure state to the state of infinite dilution. If considered for a mole of 1, this will be directly given by $(\lambda_{12} - \lambda_{11})$; as for the molecule 1 in the second cell only 1–2 interaction is present, while in the first cell only 1–1 interaction is there. Thus we may write

$$\lambda_{12} - \lambda_{11} = u^E \tag{5}$$

Now, to calculate the excess internal energy, it is assumed that the regular solution model holds for these cells, i.e.

$$u^E = g^E = RT \ln\gamma_1^\infty = v_1[(\delta_1 - \delta_2)^2 + 2(1 - K_{12})\delta_1\delta_2] \tag{6}$$

where the modified form of activity coefficient in a binary mixture as suggested by Hildebrand and Scott (1962) has been used.

In the Wilson model molar volume has been used directly to calculate the local volume fractions of the components (Eq. 2), which in turn has been used in the Flory-Huggins expression for excess Gibbs energy to obtain Eq. 3. In the Flory-Huggins model the volume fraction originates from the number of sites occupied by polymer molecules in the lattice. For ordinary molecules, however, the number of occupied sites concept would not be quite appropriate, though the entropy effect due to unequal sizes would still be present. Hence one should rather incorporate an effective molar volume, ϑ_1^*, instead of molar volume in the above expressions.

The new binary interaction parameter K_{12}—considered a "deviation term"—occurs because the regular solution model in its original form does not take into account all types of interactions, particularly those that are not spherically symmetric. These would include dipole type interactions, departure from symmetry because of nonspherical shape of the molecules, specific direction bond formation (like hydrogen bonding), etc. Of these, nonspherical shapes and dipole moments probably are the commonest types of departure.

The intermolecular interactions are likely to be fairly complicated functions of these two effects, and it is unlikely that any simple functional form involving these two quantities would adequately represent the deviation term. However, since two independent properties are involved, one may assume that it should be possible to express the deviation term using two parameters per species.

A reasonable form for K_{12} is thus

$$K_{12} = K_{12}(k_1, k_2, \bar{k}_1, \bar{k}_2) \tag{7}$$

where k and $\bar{k}$ are pure component parameters, which we call the deviation parameters—that describe the extent of deviation from centrally symmetric interactions.

Certain general conditions should be satisfied by the functional form (7). These are

1. Symmetry condition: $K_{12} = K_{21}$
2. Boundary condition: $K_{11} = 1 = K_{22}$

The simplest form that satisfies the above conditions is

$$K_{12} = \exp[|k_1 - k_2| - |\bar{k}_1 - \bar{k}_2|] \tag{8}$$

It may be noted that k and $\bar{k}$ do not correspond to effects due to nonspherical shape and dipole moment separately.

The final expression for Λ_{12} then becomes

$$\begin{aligned}\Lambda_{12} &= \frac{v_2^*}{v_1^*} \exp[-(\lambda_{12} - \lambda_{11})/RT] \\ &= \frac{v_2^*}{v_1^*} \exp[-v_1^*\{(\delta_1 - \delta_2)^2 + 2(1 - K_{12})\delta_1\delta_2\}/RT]\end{aligned} \tag{9}$$

with K_{12} given by Eq. 8.

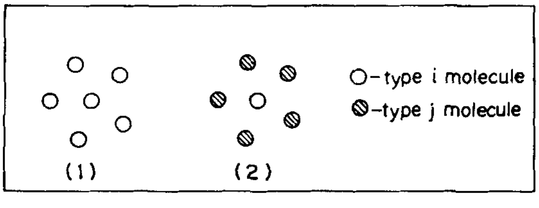

Figure 1. Cell types.

RESULTS AND DISCUSSIONS

The proposed model was tested by using experimental data reported in the literature (Hirata et al., 1975) for 86 binary and 13 multicomponent systems under moderate temperature and pressure. The components included water, hydrocarbons (aliphatic, cyclic, aromatic), alcohols (straight, cyclo-, and branched chain), carbonyl compounds, halogenated hydrocarbons, esters, nitriles, etc.

Λ_{12} and Λ_{21} values for different binaries were obtained by least squares fitting of experimental data. Liquid phase activity coef-

TABLE 1a. COMPUTED AVERAGE DEVIATIONS WITH THE PROPOSED MODEL AND WITH THE UNIFAC (BINARY SYSTEMS)*

Sl. No.	System	N	T, K/P, atm	Proposed Model		UNIFAC	
				AVDP (mm Hg)	AVDy(1)	AVDP (mm Hg)	AVDy(1)
01	*n*-Hexane(1)-ethanol(2)†	19	263 K	2.1	0.0123	2.5	0.0451
02	Chloroform(1)-benzene(2)	19	323 K	2.7	0.004	6.6	0.005
03	*n*-Heptane(1)-*n*-butanol(2)†	10	323 K	6.1	0.016	2.7	0.017
04	Carbon tetrachloride(1)-*n*-propanol(2)	11	343 K	25.6	0.020	28.4	0.012
05	Chloroform(1)-carbon tetrachloride(2)†	13	313 K	20.1	0.024	2.5	0.002
06	Methanol(1)-benzene(2)†	16	293 K	1.9	0.009	1.5	0.012
07	Carbon disulfide(1)-acetone(2)	9	302.2 K	15.6	0.021	3.1	0.017
08	Carbon disulfide(1)-chloroform(2)†	6	293 K	15.5	0.035	10.2	0.005
09	Acetonitrile(1)-benzene(2)†	12	318 K	1.8	0.005	3.1	0.007
10	Methyl acetate(1)-benzene(2)	13	1 atm	28.1	0.005	17.8	0.004
11	Acetone(1)-2,3-dimethylbutane(2)†	7	1 atm	19.3	0.018	5.9	0.017
12	Ethyl ether(1)-acetone(2)	12	293 K	2.7	0.008	4.5	0.006
13	Ethyl ether(1)-ethanol(2)†	19	273 K	2.1	0.004	3.6	0.003
14	Acetone(1)-isopropanol(2)	5	298 K	27.4	0.052	4.5	0.041
15	Methyl acetate(1)-ethyl acetate(2)†	4	312.76 K	6.2	0.003	7.3	0.003
16	Methyl acetate(1)-methanol(2)	7	313 K	6.0	0.012	9.4	0.017
17	Acetonitrile (1)-water(2)†	11	1 atm	28.0	0.014	60.1	0.031
18	Acetone(1)-chloroform(2)†	31	308.17 K	16.4	0.026	1.4	0.004
19	Chloroform(1)-ethanol(2)†	15	318 K	13.4	0.019	12.0	0.010
20	Methyl acetate(1)-chloroform(2)	15	1 atm	4.5	0.002	15.4	0.004
21	Ethanol(1)-isopropanol(2)	13	1 atm	12.6	0.003	29.6	0.005
22	*n*-Propanol(1)-water(2)	18	333 K	3.5	0.019	2.4	0.016
23	*n*-Decane(1)-chlorobenzene(2)†	12	348 K	3.5	0.0154	8.3	0.015
24	Ethanol(1)-benzene(2)†	9	298 K	7.0	0.0154	6.5	0.022
25	Cyclohexane(1)-ethanol(2)†	19	283 K	0.8	0.0063	6.5	0.048
26	Chlorobenzene(1)-bromobenzene(2)†	10	404.7 K	10.6	0.007	—	—
27	Methylcyclopentane(1)-toluene(2)†	27	1 atm	27.7	0.0095	4.2	0.0026

N = number of data points. AVDP = average deviation in computed bubble pressure = $1/N\ \Sigma_{i=1}^{N}|P_{i,\mathrm{cal}} - P_{i,\mathrm{exp}}|$. AVDy(1) = average deviation in computed vapor phase composition of component 1 = $1/N\ \Sigma_{i=1}^{N}|y_{i,\mathrm{cal}}^{(1)} - y_{i,\mathrm{exp}}^{(1)}|$.

* Experimental data from Hirata et al. (1975).

† These were among the systems used in evaluation of v^* and K_{12}.

SI Conversion: kPa = mm Hg × 0.133.

TABLE 1b. COMPUTED AVERAGE DEVIATIONS WITH THE PROPOSED MODEL AND WITH THE UNIFAC (MULTICOMPONENT SYSTEMS)

Sl. No.	System	T, K/P, atm	Model	AVDP (mm Hg)	AVDy (1)*	AVDy (2)	AVDy (3)	AVDy (4)	AVDy (5)
01	Methylcyclopentane(1)-ethanol(2)-benzene(3)	1 atm	Proposed	42.7	0.019	0.026	0.013	—	—
	(Sinor and Weber, 1960)		UNIFAC	79.0	0.032	0.045	0.021		
02	Methyl acetate(1)-chloroform(2)-benzene(3)	1 atm	Proposed	2.9	0.004	0.004	0.003	—	—
	(Nagata, 1962)		UNIFAC	11.1	0.005	0.006	0.004	—	—
03	Acetone(1)-chloroform(2)-dimethylbutane(3)	1 atm	Proposed	19.7	0.010	0.026	0.032	—	—
	(Garrett and van Winkle, 1969)		UNIFAC	48.0	0.023	0.010	0.029	—	—
04	Water(1)-*n*-propanol(2)-*n*-butanol(3)	1 atm	Proposed	143.5	0.050	0.039	0.044	—	—
	(Dawe et al., 1973)		UNIFAC	22.1	0.015	0.023	0.012	—	—
05	*n*-Hexane(1)-methylcyclopentane(2)-	1 atm	Proposed	7.8	0.014	0.007	0.006	0.007	0.004
	cyclohexane(3)-benzene(4)-toluene(5)		UNIFAC	10.6	0.002	0.006	0.003	0.003	0.003
	(Weatherford and van Winkle, 1970)								

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* Number in parentheses indicates the corresponding component.

ficients were calculated by considering the vapor phase nonideality

$$\gamma_i = \frac{\varphi_i y_i P}{\varphi_i^s x_i P_i^s \exp[\vartheta_i (P - P_i^s)/RT]} \tag{10}$$

The vapor phase fugacity coefficients were calculated by using the virial equation of state truncated after the second term. The self- and cross-viral coefficients were computed, where necessary, by the Pitzer and Curl (Pitzer, 1955, 1957) method. The fugacity coefficient of saturated vapor, φ_i^s, was computed by standard procedure (Prausnitz et al., 1967).

Liquid molar volumes of the pure components were required for calculation of solubility parameters and the Poynting correction factor. These were obtained from a quadratic fitting (Prausnitz et al., 1967) of liquid molar volumes at different temperatures available in the literature. For a few components these were calculated by using the correlation of Hankinson and Thomson (1979) as data were not available in the literature. Molar heats of vaporization as reported by Reid et al. (1977) were used.

The systems tested include 24 components in all. The results show that the model is quite efficient in predicting VLE data at moderate temperature and pressure. The deviations in bubble pressure and vapor phase concentration have been calculated for a good number of data points, and the average deviations have been obtained. A partial list of the systems studied and the computed average deviations are presented in Tables 1a and 1b, along with the corresponding deviations calculated by the UNIFAC method (Fredenslund et al., 1977).

Typical computed results for four binary and two ternary systems containing both polar and nonpolar species have been plotted in Figures 2 and 3. The components also vary reasonably in size. Three of the binaries—acetone-chloroform, acetonitrile-water, and

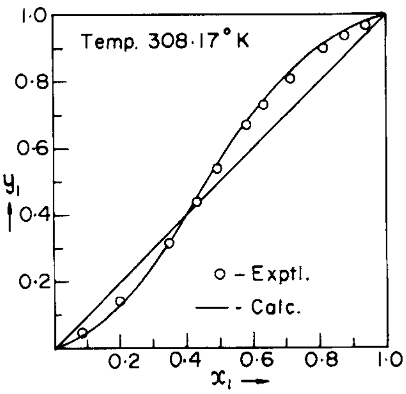

Figure 2a. Acetone(1), chloroform(2) system.

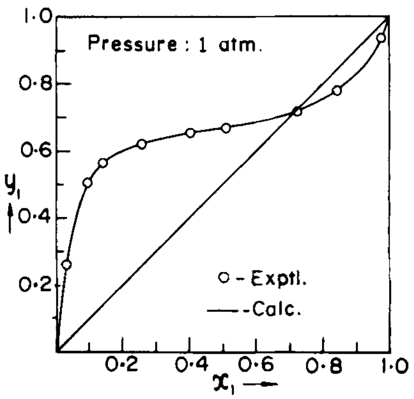

Figure 2b. Acetonitrile(1), water(2) system.

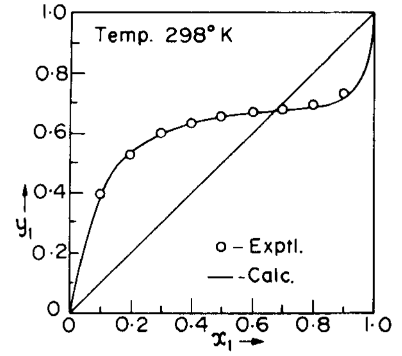

Figure 2c. Benzene(1), ethanol(2) system.

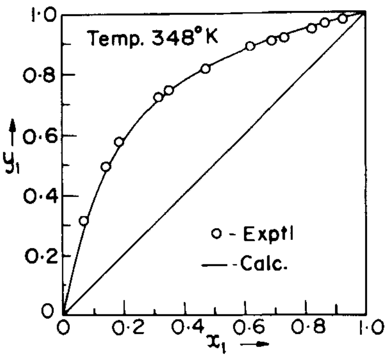

Figure 2d. *n*-Decane(1), chlorobenzene(2) system.

benzene-ethanol—are azeotropic, the first one being a maximum boiling azeotrope. The system decane-chlorobenzene contains components of sufficiently different molecular size. The agreement between computed and experimental results is quite satisfactory.

Computed values of effective molar volume, v^*, which is considerably less than molar volume in most cases, and the deviation parameters k and $\bar{k}$ for the compounds are presented in Table 2. These values were obtained by using VLE data for 45 binary systems in two stages. First the v^* values of individual components and K_{12} values for binaries were obtained by a three-parameter fit of VLE data. The values of k and $\bar{k}$ were then obtained from the K_{12} values thus determined, initially starting with binaries constituted from seven compounds (Table 2) and then using those values to determine k and $\bar{k}$ for the remaining compounds. Finally the values of v^*, k, and $\bar{k}$ of the compounds were used to compute the VLE data for all 86 binaries and 13 multicomponent systems. No multicomponent system data were used for evaluation or refinement of the values of the parameters. These parameters are assumed to be independent of temperature following the Wilson concept and also because the temperature ranges involved in the data were not large. Some preliminary work has indicated that these are probably related to other fundamental molecular properties, though no definite correlation has yet been obtained.

The limitations of the proposed model are similar to those of the Wilson equation. It fails to represent satisfactorily VLE in systems where phase splitting may occur (e.g., water-*n*-butanol). Since this model does not take into account specific interactions, it may not be able to predict satisfactorily solution behavior where such interactions are prominent (e.g., acetone-water system). Also, a good

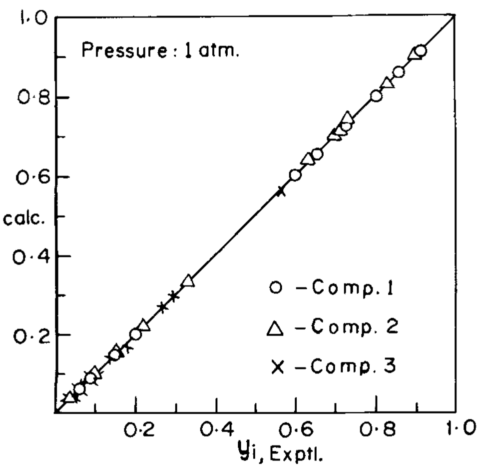

Figure 3a. Methyl acetate(1), chloroform(2), benzene(3) system.

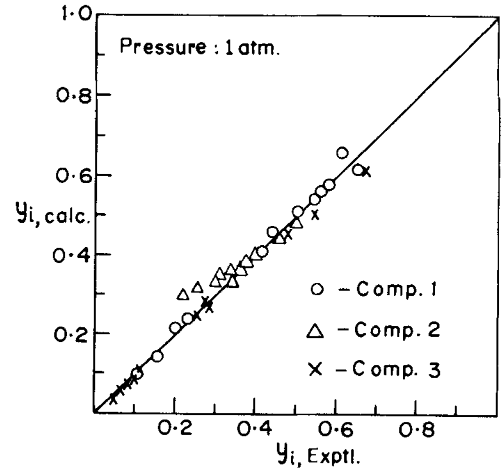

Figure 3b. Methylcyclopentane(1), ethanol(2), benzene(3) system.

TABLE 2. VALUES OF v^*, k, AND $\bar{k}$

Component	v^*, cm^3/g-mole	k	$\bar{k}$
Acetone*	57.5670	0.9980	0.9950
Acetonitrile	39.2945	0.9590	1.0220
Benzene*	39.7151	0.9800	1.0520
Bromobenzene	55.0128	0.9350	1.0140
n-Butanol	69.9732	1.0060	0.9780
Carbon disulfide	50.2393	1.0100	1.0700
Carbon tetrachloride*	35.7106	0.9780	1.0470
Chlorobenzene	55.3174	0.9370	1.0150
Chloroform*	30.4862	1.0440	0.9980
Cyclohexane	43.7878	0.9760	1.0430
n-Decane	55.2877	1.0270	0.9600
2,3-Demethylbutane	49.9291	0.9880	1.0600
Ethanol*	62.6226	1.0300	0.9630
Ethyl acetate	68.0613	0.9580	1.0150
Ethyl ether	48.1538	0.9760	0.9590
n-Heptane	32.6681	1.0060	1.0800
n-Hexane*	50.1702	0.9430	1.0070
Methanol*	53.2313	1.0675	0.9905
Methyl acetate	46.9239	0.9780	1.0350
Methylcyclopentane	38.8234	0.9840	1.0675
iso-Propanol	54.3928	1.0100	0.9500
n-Propanol	66.0437	1.0060	0.9560
Toluene	40.6905	0.9780	1.0555
Water	33.5495	1.2720	0.8900

* k and $\bar{k}$ values of these compounds were initially determined.

deal of computation indicates that it cannot predict excess enthalpy more effectively than the original Wilson equation.

CONCLUSION

The proposed model yields a simple expression for the interaction energy difference $(\lambda_{12} - \lambda_{11})$ in the Wilson equation. Of the four single component parameters required, solubility parameter data are easily available. The other three properties of a component—v^*, k, $\bar{k}$—have to be determined from experimental VLE data of any binary system containing that component. The method gives results comparable to that obtained by using UNIFAC but requires much less computational effort.

NOTATION

g = molar Gibbs energy
K_{ij} = binary interaction parameter for components i and j, Eq. 6
$k,\bar{k}$ = deviation parameters, Eq. 7
P = total pressure
P^s = saturation pressure
R = universal gas constant
T = absolute temperature
u = molar internal energy
v = liquid molar volume
v^* = effective molar volume
x = liquid phase mole fraction
x_{ij} = local mole fraction of molecule i in the immediate neighborhood of molecule j
y = vapor phase mole fraction

Greek Letters

γ = liquid phase activity coefficient
γ^∞ = liquid phase activity coefficient in infinite dilution
δ = solubility parameter
Λ_{ij} = Wilson parameter for i–j binary
λ_{ij} = energy of interaction for i–j binary
Φ = local volume fraction
φ = fugacity coefficient of vapor phase
φ^s = fugacity coefficient of saturated vapor

Subscripts

E = excess function
i,j = components i and j

LITERATURE CITED

Dawe, R. A., D. M. T. Newsham, and S. B. Ng, "Vapor-Liquid Equilibrium in Mixture of Water, *n*-Propanol and *n*-Butanol," *J. Chem. Eng. Data*, **18**, 75 (1973).

Fredenslund, A., J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam (1977).

Garrett, G. R., and M. van Winkle, "Vapor-Liquid Equilibria of the Ternary System Acetone-Chloroform-2,3-Dimethylbutane," *J. Chem. Eng. Data*, **14**, 303 (1969).

Ghosh, S. K., and S. J. Chopra, "Activity Coefficients from the Wilson Equation," *Ind. Eng. Chem. Process Design Develop.*, **14**, 304 (1975).

Gothard, F. A., et al., "Predicting the Parameters in the Wilson Equations for Activity Coefficients in Binary Hydrocarbon Systems," *Ind. Eng. Chem. Process Design Develop.*, **15**, 333 (1976).

Hankinson, R. W., and G. H. Thomson, "A New Correlation for Saturated Densities of Liquids and Their Mixtures," *AIChE J.*, **25**, 653 (1979).

Hildebrand, J. M., and R. L. Scott, *Regular Solutions*, Prentice-Hall, Englewood Cliffs, NJ (1962).

Hiranuma, M., and K. Honma, "Estimation of Unlike-Pair Potential Parameter in Single-Parameter Wilson Equation," *Ind. Eng. Chem. Process Design Develop.*, **14**, 221 (1975).

Hirata, M., S. Ohe, and K. Nagahama, *Computer Aided Data Book of Vapor-Liquid Equilibria*, Kodansha, Tokyo (1975).

Krumins, A. E., A. K. Rastogi, M. E. Rusak, and D. Tassios, "Prediction of Binary Vapor-Liquid Equilibrium from One-Parameter Equations," *Can. J. Chem. Eng.*, **58**, 663 (1980).

Ladurelli, A. J., C. H. Eon, and G. Guiochon, "Fallabilities Inherent in the Wilson Equation Applied to Systems Having a Negative Excess Gibbs Energy," *Ind. Eng. Chem. Process Design Develop.*, **14**, 291 (1975).

Nagata, I., "Vapor-Liquid Equilibrium at Atmospheric Pressure for Ternary System, Methyl Acetate-Chloroform-Benzene," *J. Chem. Eng. Data*, **7**, 360 (1962).

Prausnitz, J. M., C. A. Eckert, R. V. Orye, and J. P. O'Connell, *Computer Calculations for Multicomponent Vapor-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1967).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York (1977).

Sinor, J. E., and J. H. Weber, "Vapor-Liquid Equilibria at Atmospheric Pressure Systems Containing Ethyl Alcohol, *n*-Hexane, Benzene and Methylcyclopentane," *J. Chem. Eng. Data*, **5**, 243 (1960).

Tassios, D., "A Single-Parameter Equation for Isothermal Vapor-Liquid Equilibrium Correlations," *AIChE J.*, **17**, 1367 (1971).

Weatherford, R. M., and M. van Winkle, "Vapor-Liquid Equilibria of the Quinary System Hexane, Methylcyclopentane, Cyclohexane, Benzene and Toluene," *J. Chem. Eng. Data*, **15**, 387 (1970).

Wilson, G. M., "Vapor-Liquid Equilibrium: XI. A New Expression for Excess Free Energy of Mixing," *J. Am. Chem. Soc.*, **86**, 127 (1964).

Manuscript received July 12, 1983; revision received Jan. 19, 1984, and accepted Apr. 1.