$$V_o = \frac{V_s}{1 - X} \qquad (6)$$

is more nearly constant than V_s. Examination of the present holdup data, data of Gayler, Roberts, and Pratt (1953), and data from an earlier study of Gayler and Pratt (1951) reveals that neither V_s nor V_o is a satisfactory parameter for correlating holdup over a wide range of fluid properties and flow rates. Both our data and that of Gayler and Pratt (1951) contained primarily high values of holdup (> 10%), and in such cases V_s appears to be the preferred correlating parameter. This is illustrated in Figure 2 of Watson and McNeese (1973). The data of Gayler, Roberts, and Pratt (1953) contained lower values of holdup (most values were < 10%), and V_o was shown to be more nearly constant. At low values of holdup, there is little difference between V_o and V_s. Generally, V_s is believed to be a more useful correlating parameter over a wide range of holdup values. However, neither of the parameters is as accurate as one may desire, and improved correlations, especially those with a theoretical basis, are needed.

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NOTATION

a = cm^2 of packing surface/cm^3 of packing volume
d_p = diameter of packing, cm
V_c = superficial velocity of the continuous phase, cm/s
V_d = superficial velocity of the dispersed phase, cm/s
$V_{c,f}$ = superficial continuous phase velocity at flooding, cm/s
$V_{d,f}$ = superficial dispersed phase velocity at flooding, cm/s
V_o = characteristic velocity defined by Equation (6), cm/s
V_s = superficial slip velocity, cm/s

Greek Letters

$\Delta\rho$ = difference in densities of dispersed and continuous phases, g/cm^3
ϵ = void fraction of the packing, dimensionless
μ = viscosity, poise
$\Delta V_{c,o}^{1/2}$ = defined by Equation (5)
$\Delta V_{d,o}^{1/2}$ = defined by Equation (5)

Subscripts

c, d = continuous and dispersed phases, respectively
o = intercept value; flow rate of other phase approaching zero

LITERATURE CITED

Ballard, J. H., and E. L. Piret, "Limiting Flow Phenomena in Packed Liquid-Liquid Extraction Columns," *Ind. Eng. Chem.*, **42**, 1088 (1950).

Breckenfeld, R. R., and C. R. Wilke, "Limited Flows in Packed Extraction Columns," *Chem. Eng. Progr.*, **46**, 187 (1950).

Crawford, J. W., and C. R. Wilke, "Limited Flows in Packed Extraction Column; Correlations for Larger Packing," *ibid.*, **47**, 423 (1951).

Dell, F. R., and H. R. C. Pratt, "Liquid-Liquid Extraction, Part I. Flooding Rates for Packed Columns," *Trans. Inst. Chem. Engrs.*, **29**, 39 (1951).

Gayler, R., and H. R. C. Pratt, "Liquid-Liquid Extraction, Part II. Holdup and Pressure Drop in Packed Columns," *ibid.*, p. 110.

Gayler, R., N. W. Roberts, and H. R. C. Pratt, "Liquid-Liquid Extraction, Part IV: A Further Study of Hold-up in Packed Columns," *ibid.*, **31**, 57 (1953).

Hannaford, B. A., J. S. Watson, C. W. Kee, and H. D. Cochran, Jr., "Hydrodynamics and Mass Transfer in Packed Columns," paper presented at the National Meeting of AIChE, St. Louis, Mo. (1972).

Johnson, T. R., R. D. Pierce, F. G. Tents, and E. F. Johnson, "Behavior of Countercurrent Liquid-Liquid Columns with a Liquid Metal," *AIChE J.*, **17**, 14 (1971).

Watson, J. S., and L. E. McNeese, "Holdup, Flooding, and Pressure Drop in Packed Columns During Countercurrent Flow of Mercury and Water," *ibid.*, **19**, 230 (1973).

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Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures

A group-contribution method is presented for the prediction of activity coefficients in nonelectrolyte liquid mixtures. The method combines the solution-of-functional-groups concept with a model for activity coefficients based on an extension of the quasi chemical theory of liquid mixtures (UNIQUAC). The resulting UNIFAC model (*UNI*QUAC *F*unctional-group *A*ctivity *C*oefficients) contains two adjustable parameters per pair of functional groups.

By using group-interaction parameters obtained from data reduction, activity coefficients in a large number of binary and multicomponent mixtures may be predicted, often with good accuracy. This is demonstrated for mixtures containing water, hydrocarbons, alcohols, chlorides, nitriles, ketones, amines, and other organic fluids in the temperature range 275° to 400°K.

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SCOPE

Chemical process design typically includes units for the separation of liquid mixtures. Design methods for such units require quantitative estimates of fluid phase equilibria. While these estimates can often be made from limited experimental mixture data or from empirical correlations, in many cases no experimental data at all are available. In that event, the design engineer can do little more than make a reasonable guess, often with large uncertainty. To reduce the uncertainty, this work provides a rational method for predicting activity coefficients in nonelectrolyte liquid mixtures.

The solution-of-groups concept is combined with a recently developed model for activity coefficients (UNIQUAC) derived from an extension of Guggenheim's quasichemical theory of liquid mixtures. The resulting UNIFAC method provides a simple procedure for calculating activity coefficients in terms of constants reflecting the sizes and surface areas of individual functional groups, and parameters representing energetic interactions between groups.

Size and area parameters for groups were evaluated from pure-component, molecular structure data. Group-interaction parameters were evaluated from phase equilibrium data for mixtures containing paraffins, olefins, aromatic hydrocarbons, water, alcohol, ketones, amines, esters, ethers, aldehydes, chlorides, nitriles, and other organic liquids.

CONCLUSIONS AND SIGNIFICANCE

The UNIFAC method for predicting liquid-phase activity coefficients provides the process design engineer with a useful tool for calculating vapor-liquid equilibrium compositions in the frequently encountered situation where no binary (or higher) experimental information is available. The UNIFAC method is applicable to a wide range of mixtures exhibiting either positive or negative deviations from Raoult's law. Parameters are given for eighty-three different group interactions in the temperature region 275° to 400°K.

Prediction of liquid-phase activity coefficients is demonstrated for a variety of binary and ternary mixtures including those containing alcohols, water, or other polar liquids. Predicted activity coefficients agree well with those obtained from experimental vapor-liquid equilibrium data not included in the determination of group-interaction parameters. In most typical cases, predicted activity coefficients at infinite dilution deviate less than 20% from measured results. These measured results, however, are often subject to appreciable experimental uncertainties.

While the present range of applicability is already much larger than that of any other correlation, this range can readily be expanded as new experimental results become available for data reduction.

Since chemical process design is often concerned with separation of fluid mixtures, design engineers must frequently estimate liquid-phase activity coefficients. In those fortunate cases where phase equilibrium data are at hand, such estimates can usually be made with ease. In many other cases, however, where the required experimental data are not available, it is difficult to make even rough estimates on a rational basis. This work is a contribution toward alleviating this common problem in chemical process design.

The method presented here is based on the well-known group-contribution concept which has been successful for estimating a variety of pure-component properties such as liquid densities, heat capacities, and critical constants. The basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups which constitute these compounds is much smaller. Therefore, if we assume that a physical property of a fluid is the sum of contributions made by the molecule's functional groups, we obtain a possible technique for correlating the properties of a very large number of fluids in terms of a much smaller number of parameters which characterize the contributions of individual groups.

Any group-contribution method is necessarily approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule. The fundamental assumption of a group-contribution method is additivity; the contribution made by one group is assumed to be independent of that made by another group. This assumption is valid only when the influence of any one group in a molecule is not affected by the nature of other groups within that molecule.

For example, we would not expect the contribution of a carbonyl group in a ketone (say, acetone) to be the same as that of a carbonyl group in an organic acid (say, acetic acid). On the other hand, experience suggests that the contribution of a carbonyl group in, for example, acetone, is close to (although not identical with) the contribution of a carbonyl group in another ketone, say, 2-butanone.

Accuracy of correlation improves with increasing distinction of groups; in considering, for example, aliphatic alcohols, in a first approximation no distinction is made between the position (primary or secondary) of a hydroxyl group, but in a second approximation such distinction is desirable. In the limit, as more and more distinctions are made, we recover the ultimate group, namely, the molecule itself. In that event, the advantage of the group-contribution method is lost. For practical utility, a compromise must be attained. The number of distinct groups must remain small but not so small as to neglect significant effects of molecular structure on physical properties.

Extension of the group-contribution idea to mixtures is extremely attractive because, while the number of pure fluids in chemical technology is already very large, the number of different mixtures is still larger, by many orders of magnitude. Thousands, perhaps millions, of multicomponent liquid mixtures of interest in the chemical industry can be constituted from perhaps twenty, fifty, or at most one hundred functional groups.

Estimation of thermodynamic properties of liquid mixtures from group contributions was first suggested by Langmuir (1925). This suggestion, however, received little attention until Derr and co-workers (Redlich, Derr and Pierotti, 1959; Derr and Papadopoulos, 1959) used

group contributions to correlate heats of mixing, followed by Wilson and Deal (1962) who developed the solution-of-groups method for activity coefficients. This work was expanded by Derr and Deal (1969) with their Analytical-Solution-of-Groups (ASOG) method and by Ratcliff and co-workers (Ronc and Ratcliff, 1971).

The success of this earlier work encouraged us to attempt a correlation which, in principle but not in detail, is similar to the ASOG method. Our efforts were much facilitated by recent development of what appears to be a particularly useful model based on an extension of Guggenheim's quasi-chemical theory of liquid mixtures. This extension, the universal quasi-chemical (UNIQUAC) equation (Abrams and Prausnitz, 1975), is particularly appropriate for establishing a group-contribution correlation where the important independent variables are the concentrations of the functional groups rather than those of the molecules themselves. Upon combining the concept of functional groups with the analytical results of the universal quasi-chemical theory, we arrive at the UNIFAC (*UNI*QUAC Functional-group Activity Coefficients) method.

THE UNIFAC METHOD

The fundamental idea of a solution-of-groups model is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no experimental data are available. In concept, the UNIFAC model follows Derr and Deal's (1969) ASOG model, wherein activity coefficients in mixtures are related to interactions between structural groups. The method entails the following: suitable reduction of experimentally obtained activity-coefficient data to obtain parameters characterizing interactions between pairs of structural groups in nonelectrolyte systems, and use of these parameters to predict activity coefficients for other systems which have not been studied experimentally but which contain the same functional groups.

Derr and Deal (1969) separate the molecular activity coefficient into two parts: one part provides the contribution due to differences in molecular size and the other provides the contribution due to molecular interactions. The first part is arbitrarily estimated by using the athermal Flory-Huggins equation, and the Wilson equation, applied to functional groups, is chosen to estimate the second part. Much of the arbitrariness is removed by combining the solution-of-groups concept with the UNIQUAC equation. First, the UNIQUAC model per se contains a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions. Second, functional group sizes and interaction surface areas are introduced from independently obtained pure-component, molecular structure data.

Abrams and Prausnitz (1975) show that the UNIQUAC equation gives good representation of both vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolytes such as hydrocarbons, ketones, esters, water, amines, alcohols, nitriles, etc. In a multicomponent mixture, the UNIQUAC equation for the activity coefficient of (molecular) component i is

$$\ln \gamma_i = \underbrace{\ln \gamma_i^C}_{\text{combinatorial}} + \underbrace{\ln \gamma_i^R}_{\text{residual}} \qquad (1)$$

where

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \Sigma_j x_j l_j \qquad (2)$$

and

$$\ln \gamma_i^R = q_i[1 - \ln (\Sigma_j \theta_j \tau_{ji}) - \Sigma_j (\theta_j \tau_{ij} / \Sigma_k \theta_k \tau_{kj})] \qquad (3)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1); \quad z = 10$$

$$\theta_i = \frac{q_i x_i}{\Sigma_j q_j x_j}; \quad \Phi_i = \frac{r_i x_i}{\Sigma_j r_j x_j}$$

$$\tau_{ji} = \exp - \left[\frac{u_{ji} - u_{ii}}{RT} \right]$$

In these equations, x_i is the mole fraction of component i, and the summations in Equations (2) and (3) are over all components, including component i; θ_i is the area fraction, and Φ_i is the segment fraction which is similar to the volume fraction. Pure component parameters r_i and q_i are, respectively, measures of molecular van der Waals volumes and molecular surface areas.

The two adjustable binary parameters τ_{ij} and τ_{ji} appearing in Equation (3) must be evaluated from experimental phase equilibrium data. As indicated by Abrams and Prausnitz (1975), no ternary (or higher) parameters are required for systems containing three or more components.

In the UNIFAC method, the combinatorial part of the UNIQUAC activity coefficients, Equation (2), is used directly. Only pure component properties enter into this equation. Parameters r_i and q_i are calculated as the sum of the group volume and area parameters, R_k and Q_k, given in Table 1:

$$r_i = \Sigma_k \nu_k^{(i)} R_k \quad \text{and} \quad q_i = \Sigma_k \nu_k^{(i)} Q_k \qquad (4)$$

where $\nu_k^{(i)}$, always an integer, is the number of groups of type k in molecule i. Group parameters R_k and Q_k are obtained from the van der Waals group volume and surface areas V_{wk} and A_{wk} given by Bondi (1968):

$$R_k = V_{wk}/15.17 \quad \text{and} \quad Q_k = A_{wk}/(2.5 \cdot 10^9) \qquad (5)$$

The normalization factors 15.17 and $2.5 \cdot 10^9$ are those given by Abrams and Prausnitz (1975).

The residual part of the activity coefficient, Equation (3), is replaced by the solution-of-groups concept. Instead of Equation (3), we write

$$\ln \gamma_i^R = \sum_{\text{all groups}} \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \qquad (6)$$

where Γ_k is the group residual activity coefficient, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i. In Equation (6) the term $\ln \Gamma_k^{(i)}$ is necessary to attain the normalization that activity coefficient γ_i becomes unity as $x_i \to 1$. The activity coefficient for group k in molecule i depends on the molecule i in which k is situated. For example, $\Gamma_k^{(i)}$ for the COH group (see Table 1) in ethanol refers to a solution containing fifty group percent COH and fifty group percent CH_3 at temperature of the mixture, whereas $\Gamma_k^{(i)}$ for the COH group in n-butanol refers to a solution containing twenty-five group percent COH, fifty group percent CH_2, and twenty-five group percent CH_3.

The group activity coefficient Γ_k is found from an expression similar to Equation (3):

$$\ln \Gamma_k = Q_k[1 - \ln (\Sigma_m \Theta_m \Psi_{mk}) - \Sigma_m (\Theta_m \Psi_{km} / \Sigma_n \Theta_n \Psi_{nm})] \qquad (7)$$

Equation (7) also holds for $\ln \Gamma_k^{(i)}$. In Equation (7), Θ_m is the area fraction of group m, and the sums are over all different groups. Θ_m is calculated in a manner similar to that for θ_i:

TABLE 1. GROUP VOLUME AND SURFACE AREA PARAMETERS

Group number and name				R_k	Q_k	Sample group assignment
1	CH_2	Alkane group				
	Subgroups:					
	1A	CH_3	end group of hydrocarbon chain	0.9011	0.848	Ethane: $2CH_3$
	1B	CH_2	middle group in hydrocarbon chain	0.6744	0.540	*n*-butane: $2CH_3$, $2CH_2$
	1C	CH	middle group in hydrocarbon chain	0.4469	0.228	iso-butane: $3CH_3$, 1CH
2	C=C		olefin group, α-olefin only	1.3454	1.176	α-butene: 1C=C, $1CH_2$, $1CH_3$
3	ACH		aromatic carbon group	0.5313	0.400	Benzene: 6ACH
4	$ACCH_2$		aromatic carbon-alkane group			
	Subgroups:					
	4A	$ACCH_2$	general case	1.0396	0.660	Ethylbenzene: 5ACH, $1ACCH_2$, $1CH_3$
	4B	$ACCH_3$	toluene group	1.2663	0.968	Toluene: 5ACH, $1ACCH_3$
5	COH alcohol group, includes nearest CH_2					
	Subgroups:					
	5A	COH	general case	1.2044	1.124	Ethanol: $1CH_3$, 1COH
	5B	MCOH	methanol	1.4311	1.432	Methanol: 1MCOH
	5C	CHOH	secondary alcohol	0.9769	0.812	Isopropanol: $2CH_3$, 1CHOH
6	H_2O	water		0.9200	1.400	Water: $1H_2O$
7	ACOH	aromatic carbon-alcohol group		0.8952	0.680	Phenol: 5ACH, 1ACOH
8	CO	carbonyl group		0.7713	0.640	Acetone: $2CH_3$, 1CO
9	CHO	aldehyde group		0.9980	0.948	Propionaldehyde: $1CH_3$, $1CH_2$, 1CHO
10	COO	ester group		1.0020	0.880	Methyl acetate: $2CH_3$, 1COO
11	O	ether group		0.2439	0.240	Diethyl ether: $2CH_3$, $2CH_2$, 1 O
12	CNH_2	Primary amine group, includes nearest CH_2				
	Subgroups:					
	12A	CNH_2	general case	1.3692	1.236	n-propylamine: $1CH_3$, $1CH_2$, $1CNH_2$
	12B	$MCNH_2$	methylamine	1.5959	1.544	Methylamine: $1MCNH_3$
13	NH	secondary amine group		0.5326	0.396	Diethylamine: $2CH_3$, $2CH_2$, 1NH
14	$ACNH_2$	aromatic carbon-amine group		1.0600	0.816	Aniline: 5ACH, $1ACNH_2$
15	CCN	Nitrile group, includes nearest CH_2				
	Subgroups:					
	15A	MCCN	acetonitrile	1.8701	1.724	Acetonitrile: 1MCCN
	15B	CCN	general case	1.6434	1.416	Propionitrile: 1CCN, $1CH_3$
16	Cl	chloride group				
	Subgroups:					
	16A	Cl-1	Cl on end carbon	0.7660	0.720	1,2 dichloroethane: $2CH_2$, 2Cl-1
	16B	Cl-2	Cl on middle carbon	0.8069	0.728	1,2,3 trichloropropane: $2CH_2$, 1CH, 2Cl-1, 1Cl-2
17	$CHCl_2$	Dichloride group, end group only		2.0672	1.684	1,1 dichloroethane: $1CH_3$, $1CHCl_2$
18	ACCl	aromatic carbon-chloride group		1.1562	0.844	Chlorobenzene: 5ACH, 1ACCl

$$\Theta_m = \frac{Q_m X_m}{\Sigma_n Q_n X_n} \qquad (8)$$

where X_m is the mole fraction of group m in the mixture. The group interaction parameter Ψ_{mn} is given by

$$\Psi_{mn} = \exp - \left[\frac{U_{mn} - U_{nn}}{RT} \right] = \exp - (a_{mn}/T) \qquad (9)$$

where U_{mn} is a measure of the energy of interaction between groups m and n. The group-interaction parameters

a_{mn} (two parameters per binary mixture of groups) are the parameters which must be evaluated from experimental phase equilibrium data. Note that a_{mn} has units of degrees Kelvin and that $a_{mn} \neq a_{nm}$. Parameters a_{mn} and a_{nm} were obtained from a data base using a wide range of experimental results.

The combinatorial contribution to the activity coefficient [Equation (2)] depends only on the sizes and shapes of the molecules present. For large chain molecules, $q_i/r_i \rightarrow 1$, and in that limit, Equation (2) reduces to the Flory-Huggins equation used in the ASOG method.

The residual contribution to the activity coefficient [Equations (6) and (7)] depends on group areas and group interactions. When all group areas are equal, Equations (6) and (7) are similar to those used in the ASOG method.

The functional groups considered in this work are those given in Table 1. Whereas each group listed has its own values of R and Q, the subgroups within the same main group (for example, subgroups 1A, 1B, and 1C) are assumed to have identical group energy-interaction parameters. Example 1 in the Appendix illustrates the nomenclature and use of Table 1.

Only straight-chain alkanes were used in the data base to determine interactions with a CH_2 group. The CH group (1C) was introduced to enable the inclusion of β, γ, etc., substituted hydrocarbons such as, for example, 1, 2, 3-trichloropropane ($2CH_2$, 1CH, 2Cl-1, 1Cl-2). It is possible that the CH group may be used to predict activity coefficients for isomers such as iso-butane ($3CH_3$, 1CH), although that possibility has not been investigated in this work.

To determine interactions with a C=C group, data for α-olefins were used. The C=C group could be subdivided in a manner similar to that used for the CH_2 group, but at present this has not been done. However, as shown later, the activity coefficients of dienes are predicted well by using C=C group parameters based on monoolefin data.

For the $ACCH_2$ group, both ϕ—CH_3(toluene) and ϕ—CH_2R (for example, ethylbenzene) were included in the data base to increase the flexibility of the correlation.

Only primary alcohols (COH group, 5A) excluding methanol were included in the data base. Table 1 includes two similar groups, MCOH (5B, methanol) and CHOH (5C, secondary alcohols). Groups H_2O and ACOH are not assumed to have interaction parameters equal to those for the COH group. Note that both the ACOH and the COH group include the nearest carbon atom.

For primary amines, methylamine ($1MCNH_2$) was not included in the data base. Group CNH_2 includes the nearest carbon atom.

Both acetonitrile (1MCCN) and propionitrile ($1CH_3$, 1CCN) were included in the data base; groups MCCN and CCN are assumed to have identical interaction parameters.

Chlorine has different size and volume parameters depending upon its position in the hydrocarbon. Therefore, we distinguish between a Cl-1 group and a Cl-2 group. Group 16 only includes cases where there is one chlorine per carbon atom. 1,1-chlorides are covered by the $CHCl_2$ group, which has interaction parameters different from those for the Cl-1 and Cl-2 groups.

GROUP INTERACTION PARAMETERS

To make the UNIFAC method useful for process design, a large number of group-interaction parameters must be available. The broader the data base with respect to temperature and molecular species, the more reliable the

Table 2. Schematic Representation of Experimental Data Used in the Data Base

	C=C	ACH	$ACCH_2$	COH	H_2O	ACOH	CO	CHO	COO	O	CNH_2	NH	$ACNH_2$	CCN	Cl	$CHCl_2$	ACCl
CH_2	C	A	A	A	A	A	A	B	C	B	A	B	B	B	A	C	A
	C=C	B	B	C	B	x	B	x	x	x	C	C	x	B	C	C	x
		ACH	C	A	A	C	A	x	A	A	C	B	B	A	B	x	A
			$ACCH_2$	A	A	C	A	x	C	C	x	x	A	C	A	x	x
				COH	A	x	A	A	A	x	C	C	x	B	A	x	A
					H_2O	A	x	B	x	x	C	B	A	A	A	B	B
						ACOH	x	A	A	x	x	x	x	x	x	C	x
							CO	A	x	B	x	x	x	A	C	C	C
								CHO	x	x	x	x	x	x	x	x	C
									COO	B	x	x	x	x	x	x	C
										O	CNH_2	x	x	x	C	C	C
												NH	$ACNH_2$	CCN	Cl	$CHCl_2$	x

Approximate temperature range, °K
A: 275-375
B: 275-325
C: 325-375
x: Parameters not available

group-interaction parameters and the better the prediction of activity coefficients. A large data reduction problem is thus indicated. Binary vapor-liquid and liquid-liquid equilibrium data from more than 200 different literature references were used as the base data in this work. Wherever a choice was available, only those data were used which appeared to be most reliable. In most cases, however, less than adequate data are available, and for numerous group interactions no or very little data could be found. The extent of our data base is shown schematically in Table 2. While it was our goal to calculate group-interaction parameters for all possible binary combinations of groups shown in Table 1 and to obtain these parameters for the temperature range 275° to 400°K, at present it is not possible to reach this goal in its entirety because of a serious lack of reliable experimental data.

Table 2 contains useful preliminary information for the user of the UNIFAC method. For a given phase equilibrium problem, a rapid glance at Table 2 indicates whether or not the necessary group-interaction parameters are available in the desired temperature range. To illustrate, suppose we want to predict the activity coefficients for the octane-α-octene-benzene-water system at 350°K. In that event, we need group-interaction parameters for (CH_2, C=C), (CH_2, ACH), (C=C, ACH), (H_2O, CH_2), (H_2O, C=C), and (H_2O, ACH). All of the required parameters are available, although the parameters for the (H_2O, C=C) group interaction are estimated from data in the 275° to 325°K temperature range, somewhat lower than desired. If the mixture, in addition to the above named components, also contains acetaldehyde, predictions cannot be made, since parameters for (CHO, ACH) are not available.

To obtain group-interaction parameters, it was necessary first to calculate activity coefficients from the data base. Only low-pressure, phase equilibrium data were used. Vapor-phase nonidealities were not taken into account except in those cases where the original authors had done so.

Binary phase equilibrium data used in the data base are listed in the Supplement which also gives activity coefficients and group assignments for each molecular species.

Group-interaction parameters a_{mn} were calculated wherever possible by using a nonlinear, least-squares, data reduction scheme. In reducing the data, the order of calculating the parameters is important. For example, if the (COH, CO) group-interaction parameters are to be estimated from alcohol-ketone vapor-liquid equilibrium

TABLE 3. GROUP INTERACTION PARAMETERS, a_{mn}, °K

	CH_2	C=C	ACH	$ACCH_2$	COH	H_2O	ACOH	CO	CHO	
CH_2	0	−200.0	32.08	26.78	931.2	1,452	1,860	1,565	685.9	1
C=C	2,520	0	651.6	1,490	943.3	578.3	x	1,400	x	2
ACH	15.26	−144.3	0	167.0	705.9	860.7	1,310	651.1	x	3
$ACCH_2$	−15.84	−309.2	−146.8	0	856.2	3,000	740.0	3,000	x	4
COH	169.7	254.2	83.50	92.61	0	−320.8	x	462.3	480.0	5
H_2O	657.7	485.4	361.5	385.0	287.5	0	462.6	470.8	234.5	6
ACOH	3,000	x	3,000	3,000	x	−558.2	0	x	x	7
CO	3,000	3,000	101.8	75.00	−106.5	−532.6	x	0	−49.24	8
CHO	343.2	x	x	x	3,000	−226.4	x	39.47	0	9
COO	348.0	x	325.5	3,000	167.5	x	−254.1	333.6	x	10
O	2,160	x	−75.50	3,000	−13.44	x	x	−39.81	x	11
CNH_2	−16.74	90.37	−38.64	x	−109.8	−527.7	x	x	x	12
NH	3,000	8.922	37.94	x	−700.0	−882.7	x	x	x	13
$ACNH_2$	3,000	x	3,000	3,000	x	236.6	x	x	x	14
CCN	27.31	43.03	−66.44	−150.0	337.9	227.0	x	447.7	x	15
Cl	−119.6	242.1	−90.43	52.69	357.0	618.2	x	62.00	x	16
$CHCl_2$	31.06	−72.88	x	x	x	467.0	x	37.63	x	17
ACCl	121.1	x	1,000	x	586.3	1,472	x	x	x	18
	1	2	3	4	5	6	7	8	9	

	COO	O	CNH_2	NH	$ACNH_2$	CCN	Cl	$CHCl_2$	ACCl	
CH_2	687.5	472.6	422.1	800.0	1,330	601.6	523.2	60.45	194.2	1
C=C	x	x	349.9	515.2	x	691.3	253.8	259.5	x	2
ACH	159.1	37.24	179.7	487.2	680.0	290.1	124.0	x	−99.9	3
$ACCH_2$	110.0	680.0	x	x	640.0	3,000	33.84	x	x	4
COH	174.3	−204.6	−166.8	3,000	x	79.85	194.6	x	69.97	5
H_2O	x	x	385.3	743.8	−314.6	118.5	158.4	247.2	190.6	6
ACOH	−470.2	x	x	x	x	x	x	x	x	7
CO	−180.1	475.5	x	x	x	−307.4	628.0	874.5	x	8
CHO	x	x	x	x	x	x	x	x	x	9
COO	0	−26.15	x	x	x	x	x	x	x	10
O	−290.0	0	x	x	x	x	x	x	x	11
CNH_2	x	x	0	x	x	x	x	x	−10.0	12
NH	x	x	x	0	x	x	x	x	−60.0	13
$ACNH_2$	x	x	x	x	0	x	x	x	3,000	14
CCN	x	x	x	x	x	0	−100.0	x	25.0	15
Cl	x	x	x	x	x	100.0	0	−308.5	x	16
$CHCl_2$	x	x	x	x	x	x	790.0	0	x	17
ACCl	x	x	3,000	3,000	110.0	3,000	x	x	0	18
	10	11	12	13	14	15	16	17	18	

data, it is necessary first to determine the (CH_2, CO) parameters from alkane-ketone data and the (CH_2, COH) parameters from alkane-alcohol data.

Group-interaction parameters are given in Table 3. In most cases the parameters were estimated as indicated above without difficulty. However, in some cases one of the two parameters describing the interaction of a pair of groups tends to become very large. For reasons of computer programming, an upper limit of 3 000°K was placed on the parameters, and subject to this constraint the optimal value of the corresponding other parameter was found. Note that where $a_{mn} = 3\,000$, $\Psi_{mn} \cong e^{-10}$, that is, very close to zero. In most of these cases the UNIFAC method represents the experimental data well.

In other, fortunately few, cases it was found that the UNIFAC method could not represent the activity coefficient data successfully. For this reason parameters for the (H_2O, COO) and (H_2O, O) group interactions are not as yet included in Table 3.

With the parameters in Table 3, it is now possible to predict activity coefficients for a large variety of binary and multicomponent systems. A detailed illustration is given in Example 2 of the Appendix.

RESULTS

The ultimate test of the UNIFAC method lies in its ability to predict activity coefficients for systems which were not included in the data base, that is, the set of data used to determine the parameters in Table 3. Therefore, we distinguish between calculated results for systems contained in the data base and predicted results for systems not contained in the data base.

Table 4 compares predicted and experimental activity coefficients at infinite dilution. Only the last ten entries correspond to systems that were included in the data base; also the open points of Figures 1 and 12 correspond to such systems. All the other results in this section are extrapolations of the data base with respect to molecular species or temperature.

The numerical operations carried out in the computer program for the prediction of activity coefficients consist of straightforward additions and multiplications. No iterations are required, and the computer time for calculating one typical activity coefficient is of the order of milliseconds on a CDC-6400 computer.

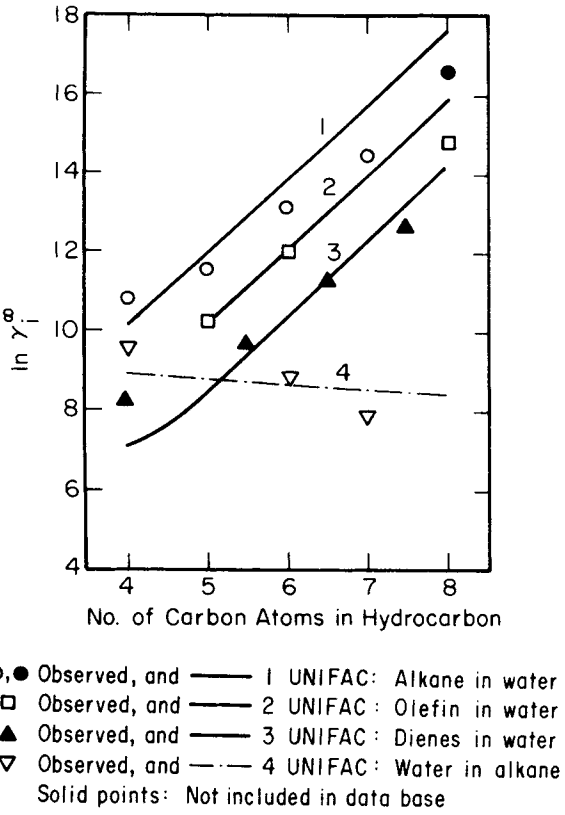

Fig. 1. Activity coefficients at infinite dilution in binary hydrocarbon-water systems at room temperature. (Black, et al., 1948, and McAuliffe, 1966).

TABLE 4. OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS AT INFINITE DILUTION

System	T, °K	γ_1^∞ (obs)	γ_1^∞ (calc)	
n-pentane(1)-acetonitrile(2)	298	20	18	Gerster et al. (1960)
Water(1)-hexadiene(2)	293	226	105	Black et al. (1948)
Hexadiene(1)-water(2)	298	26,900	30,600	McAuliffe (1966)
Aniline(1)-water(2)	373	80	115	Cukor and Prausnitz (1969)
1,2 dichloroethane(1)-*n*-propanol(2)	370	12.9	6.7	Sagnes and Sanchez (1971)
n-propanol(1)-1,2 dichloroethane(2)	357	23	14	
Methylamine(1)-nonane(2)	273	4.8	5.5	Wolff et al. (1964)
Nonane(1)-methylamine(2)	273	10.7	13.2	
Ethylamine(1)-butane(2)	293	3.2	3.4	
Butane(1)-ethylamine(2)	293	3.1	2.7	
Methylamine(1)-*n*-hexane(2)	273	5.4	7.0	
n-hexane(1)-methylamine(2)	273	8.3	8.6	
n-octane(1)-polyethylene, $\overline{M}_N = 1{,}600$(2)	400	0.32	0.22	Newman and Prausnitz (1973)
Diethylamine(1)-chlorobenzene(2)	313	1.17	1.17	Included in data base. For references see supplement.
Chlorobenzene(1)-diethylamine(2)	313	1.41	1.43	
Ethanol(1)-diethyl ether(2)	273	2.82	3.21	
Diethyl ether(1)-ethanol(2)	273	3.84	3.50	
Benzene(1)-water(2)	298	488	458	
Water(1)-benzene(2)	298	430	359	
Phenol(1)-butyl acetate(2)	318	0.12	0.13	
Butyl acetate(1)-phenol(2)	318	0.18	0.19	
n-propanol(1)-*n*-propylamine(2)	320	0.37	0.35	
n-butylamine(1)-*n*-butanol(2)	392	0.50	0.48	

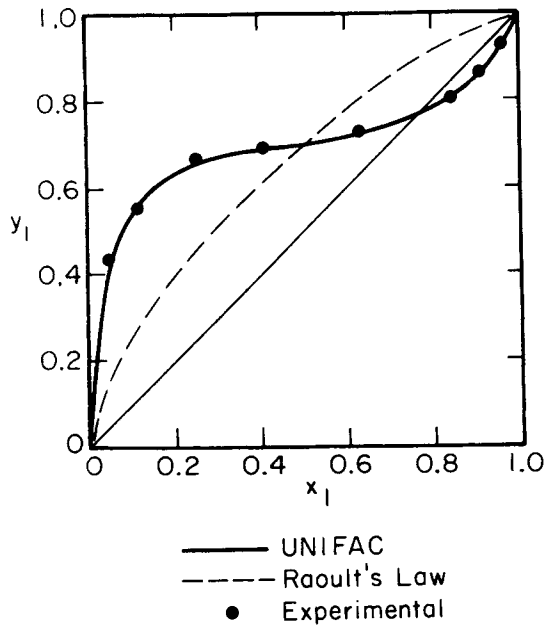

Fig. 2. Vapor-liquid equilibria for the ethanol (1)-toluene (2) system at 328°K. (Kretschmer and Wiebe, 1949).

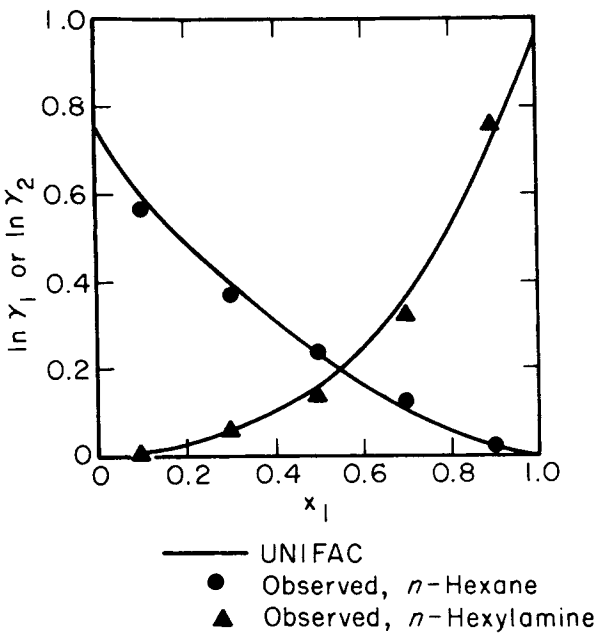

Fig. 4. Activity coefficients for the n-hexane (1)-n-hexylamine (2) system at 333°K (Humphrey and Van Winkle, 1967).

The discussion of predictions is divided into three parts: activity coefficients at infinite dilution, binary systems, and ternary systems.

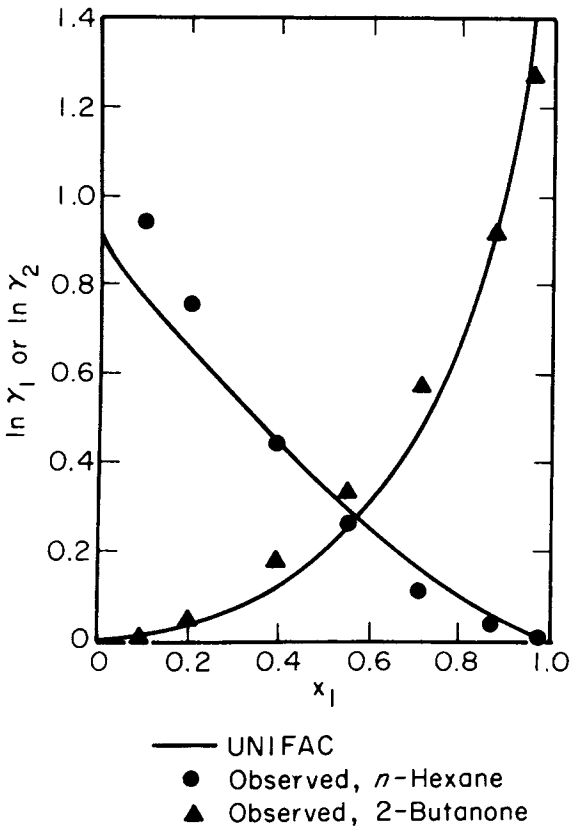

Fig. 3. Activity coefficients for the n-hexane (1)-2-butanone (2) system at 333°K (Hanson and Van Winkle, 1967).

ACTIVITY COEFFICIENTS AT INFINITE DILUTION

Table 4 shows activity coefficients at infinite dilution. The infinitely dilute region provides an especially severe test of the UNIFAC method, since the corresponding calculated activity coefficients are very sensitive to the interaction parameters. By taking into account that the activity coefficients in this region are subject to relatively large experimental error, the predicted and experimental activity coefficients at infinite dilution agree satisfactorily. The activity coefficients listed in Table 4 span five orders of magnitude. The pentane-acetonitrile, butane-ethylamine, and 1,2-dichloroethane-propanol systems were not included in the data base at all, and neither were systems containing dienes or methylamine.

Figure 1 shows infinite-dilution activity coefficients for alkane-water, olefin-water, and diene-water systems as functions of the number of carbon atoms. These results are typical for systems with very large activity coefficients [$\exp(14) \cong 10^6$]. The UNIFAC method gives correct trends with respect to number of carbon atoms and number of double bonds. The prediction of the activity coefficients for dienes is encouraging.

Among the mixtures covered in this work, negative deviations from Raoult's law are observed for the systems phenol-ester, benzene-ether, amine-alcohol, and ketone-chloroalkane. The last four entries of Table 4 indicate that the UNIFAC method also represents well systems with negative deviations. Predictions for systems of this type outside the data base could not be tested owing to scarcity of experimental data.

BINARY SYSTEMS

Predictions for various binary systems are shown in Figures 2 to 11 and Table 5. Figure 2 for the ethanol-toluene system indicates very poor results based on Raoult's law; the UNIFAC method, however, predicts vapor compositions well. Ethanol-toluene data were included in the data base, but not at 328°K.

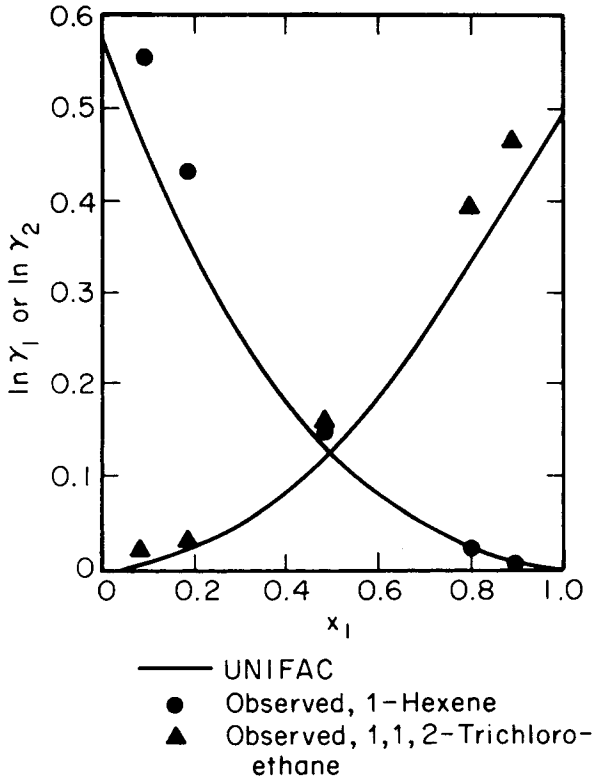

Fig. 5. Activity coefficients for the 1-hexene (1)-1,1,2-trichloroethane (2) system at 333°K. (Hanson and Van Winkle, 1967).

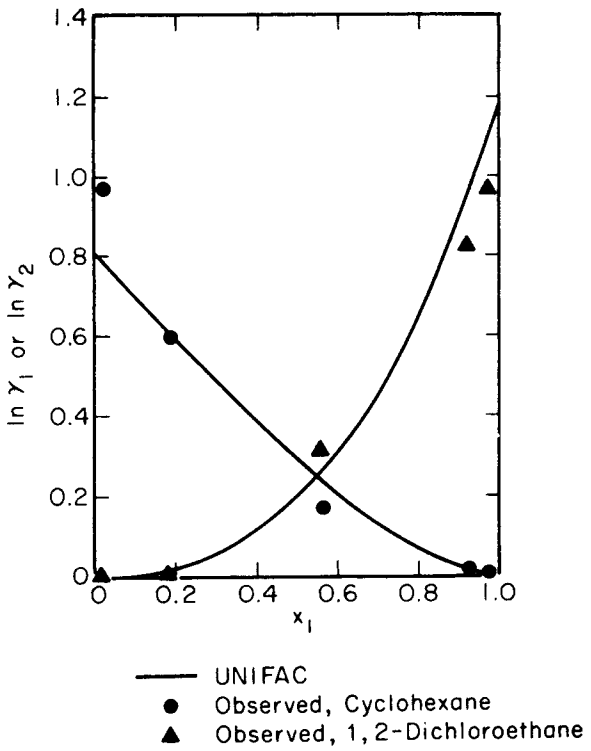

Fig. 6. Activity coefficients for the cyclohexane (1)-1,2-dichloroethane (2) system at 1 atm. (Mesnage and Marson, 1971).

Figures 3, 4, and 5 show activity coefficients for systems that are related to, but not identical with, those included in the data base. The system heptane-2-butanone was included in the data base, but the system hexane-2-butanone was not. No amines larger than butylamine appear in the data base. The α-hexene-1,1,2-trichloroethane system was not included in the data base. Calculated and experimental activity coefficients are in good agreement for these and similar systems.

Cyclic alkanes were not included in the data base. Figures 6 and 7 show good predictions for the systems cyclohexane-1,2-dichloroethane and cyclohexane-methyl acetate; these favorable results suggest that the UNIFAC method is applicable to systems containing cyclohexane ($6CH_2$ groups) and, perhaps, other cyclic alkanes.

Only primary alcohols excluding methanol were used in data reduction. Attempts were made to include methanol in the predictions counting methanol as one MCOH group with R and Q given in Table 1 and by assuming that the group-interaction parameters for MCOH are equal to those for COH. For methanol, this method was unsuccessful. However, as already indicated, a similar procedure was successful for methylamine. For methanol, it appears that either R_{MCOH} and Q_{MCOH} should be changed or else that methanol, like water, must be treated as a separate group with its own group-interaction parameters.

Predictions were also made for systems containing secondary alcohols. Parameters R_{CHOH} and Q_{CHOH} from Table 1 were used, and the group-interaction parameters for CHOH were assumed equal to those for COH. Figures 8 and 9 show calculated and observed activity coefficients for the systems 1-propanol-water and 2-propanol-water. The calculated and observed activity coefficients are in excellent agreement for the first system and in fair agreement for the second system. Table 5 shows results of

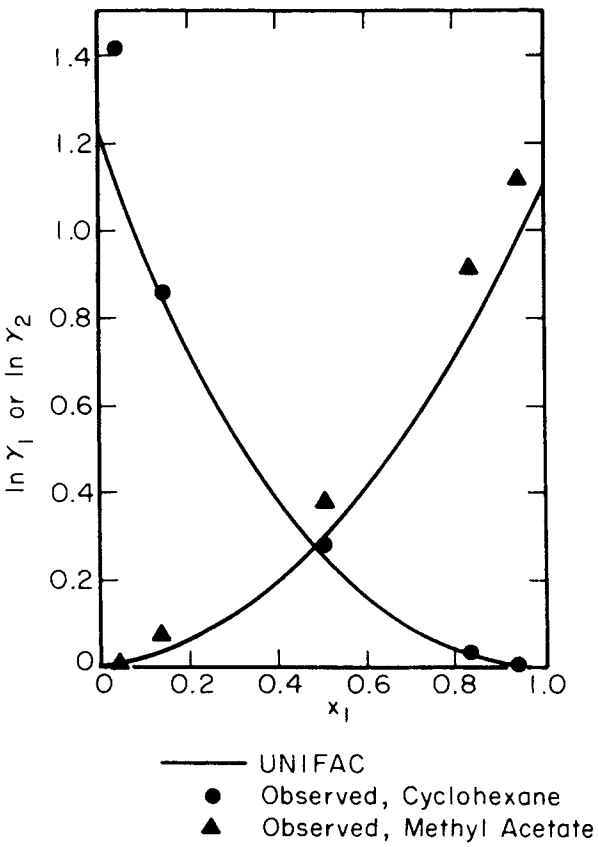

Fig. 7. Activity coefficients for the cyclohexane (1)-methyl acetate system at 1 atm. (Nagata, 1962).

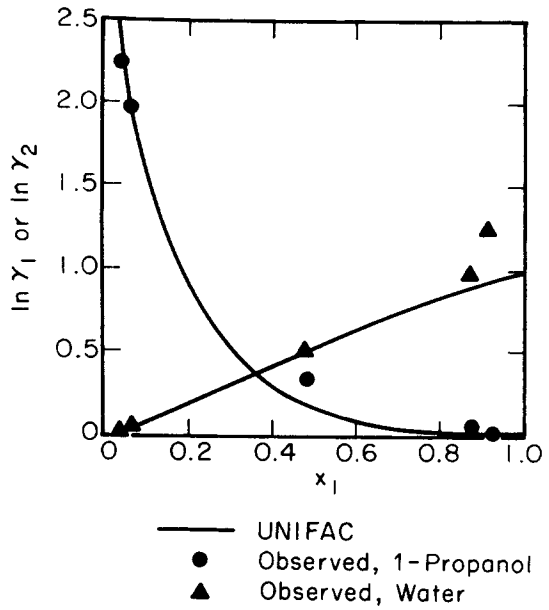

Fig. 8. Activity coefficients for the 1-propanol (1)-water (2) system at 333°K. (Murti and Van Winkle, 1958).

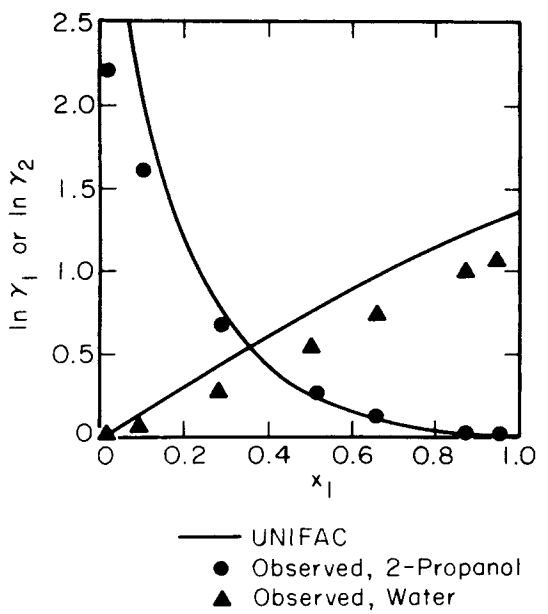

Fig. 9. Activity coefficients for the 2-propanol (1)-water (2) system at 1 atm. (Wilson and Simons, 1952).

similar calculations for alcohol-heptane systems. Predictions for the system 1-octanol-heptane are encouraging. No alcohol larger than propanol entered into the data base for the determination of the (COH, CH_2) group interaction parameters. Table 5 shows that whereas activity coefficients for secondary alcohol-heptane systems are lower than those for primary alcohol-heptane systems, the magnitude of the decrease is exaggerated in the calculated activity coefficients. Although the predictions for the secondary alcohols are not highly erroneous, we believe that systems containing alcohols should be reexamined to ensure the successful inclusion of methanol and secondary alcohols in the UNIFAC method and to improve predictions for systems containing primary alcohols in the very dilute region.

Experimental data are scarce for systems containing many different functional groups. One of the main advantages of the UNIFAC method is its ability to predict activity coefficients for systems of this type from experimental information on normal systems, that is, those with only a few different functional groups. Results for the system ethylbenzene ($1CH_3$, $1ACCH_2$, 5ACH) cellosolve ($1CH_3$, $2CH_2$, 1COH, 10) shown in Figure 10 illustrate this ability. Twenty group-interaction parameters were used in the calculation of these activity coefficients. Systems containing cellosolve ($CH_3CH_2OCH_2CH_2OH$) were not included in the data base.

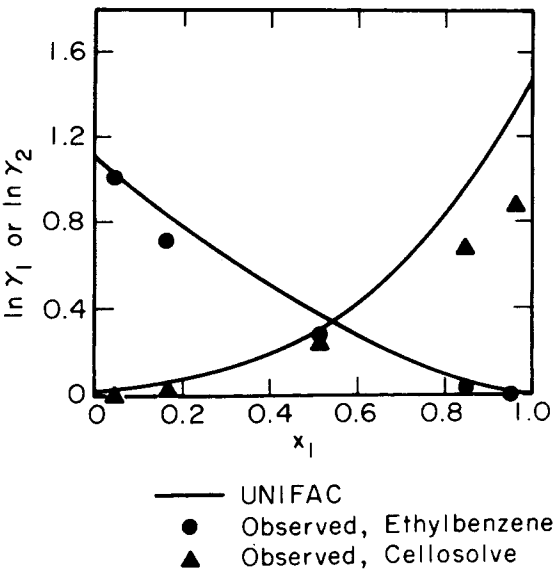

Fig. 10. Activity coefficients for the ethylbenzene (1)-Cellosolve (2) system at 1 atm. (Murti and Van Winkle, 1957).

Table 5. Observed and Calculated Activity Coefficients for Alcohol(1)-*n*-Heptane(2) Systems

Alcohol	T, °K	Observed γ_1 at $x_1 = 0.1$	Observed γ_2 at $x_2 = 0.1$	Calculated γ_1 at $x_1 = 0.1$	Calculated γ_2 at $x_2 = 0.1$	Reference
1-propanol	303	6.02	4.98	6.01	4.74	Van Ness et al. (1967)
1-propanol	333	5.38	4.58	5.29	4.42	
2-propanol	303	5.75	4.98	3.10	2.68	
2-propanol	333	5.06	4.43	2.80	2.53	
1-octanol	313	3.90	2.45	3.06	2.08	Geiseler et al. (1971)
2-octanol	313	3.59	2.27	2.03	1.61	
3-octanol	313	3.31	2.23	2.03	1.61	

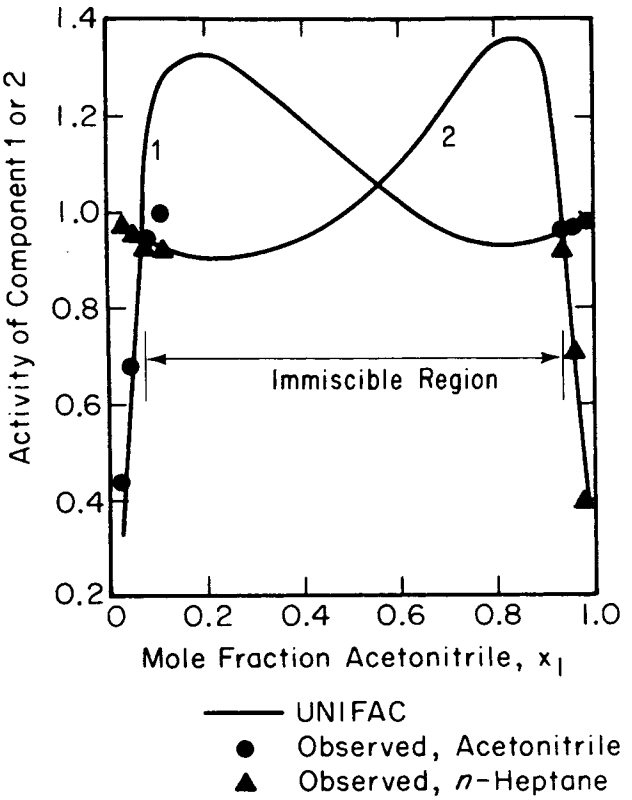

Fig. 11. Activities for the system acetonitrile (1)-*n*-heptane (2) at 318°K. (Palmer and Smith, 1972).

Highly accurate activity coefficient data are needed for quantitative calculations in liquid-liquid equilibria. For such equilibria, the UNIFAC method can provide only approximate results. However, Figure 11 for the system acetonitrile-heptane suggests that it is possible to use the UNIFAC method to predict phase splitting in highly non-ideal liquid mixtures.

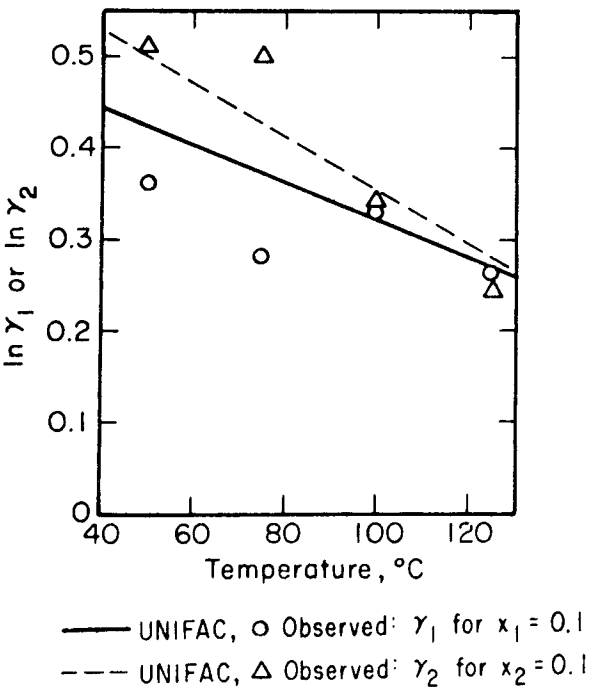

Fig. 12. Activity coefficients for the chlorobenzene (1) decane (2) system as a function of temperature. (Edwards and Ibanez, 1968).

Table 6. Observed and Calculated Activity Coefficients for Three-Component Systems

The acetonitrile(1)-benzene(2)-*n*-heptane(3) system at 318°K (Palmer and Smith, 1972)

x_1	x_2	γ_1 (obs)	γ_1 (calc)	γ_2(obs)	γ_2 (calc)	γ_3(obs)	γ_3 (calc)
0.0620	0.5379	5.09	5.70	1.11	1.08	1.27	1.20
0.3527	0.3942	2.00	2.13	1.08	1.09	2.16	2.20
0.8869	0.0991	1.03	1.02	2.15	2.23	16.93	19.13
0.0297	0.8648	3.34	3.74	1.02	1.01	1.49	1.62
0.5719	0.4120	1.23	1.21	1.37	1.44	6.17	7.12

The Ethanol(1)-benzene(2)-water(3) system at 1 atm. (Norman, 1945)

x_1	x_2	γ_1 (obs)	γ_1 (calc)	γ (obs)	γ_2 (calc)	γ (obs)	γ_3 (calc)
0.4564	0.0416	1.21	1.06	11.70	13.60	1.52	1.49
0.2720	0.0270	1.60	1.30	25.89	39.61	1.14	1.44
0.8780	0.0180	1.00	1.00	4.51	4.93	2.55	1.85
0.3970	0.5415	1.43	1.42	1.57	1.57	7.07	6.69

The acetone(1)-acetonitrile(2)-water(3) system at 1 atm. (Pratt, 1947)

x_1	x_2	γ_1 (obs)	γ_1 (calc)	γ_2(obs)	γ_2 (calc)	γ_3(obs)	γ_3 (calc)
0.0810	0.6420	1.02	0.79	1.15	1.16	2.79	2.72
0.0043	0.0507	7.83	10.98	7.11	7.39	0.99	1.01
0.0043	0 8834	0.95	0.92	1.01	1.05	4.16	5.18
0.1440	0.0455	2.96	2.63	3.68	2.77	1.17	1.18
0.2680	0.5010	1.07	0.91	1.14	1.14	3.26	2.58

Because of the semitheoretical nature of UNIQUAC and the large temperature span of the data base, the UNIFAC method usually predicts the correct temperature dependence of the activity coefficients. Figure 12 shows an example.

TERNARY SYSTEMS

The UNIFAC method given by Equations (1), (2), (6), (7), (8), and (9) is directly applicable to multicomponent systems; Table 6 gives activity coefficients calculated from these equations for three ternary systems. No ternary systems were included in the data base. There is excellent agreement between calculated and observed activity coefficients for these systems.

APPLICATIONS: PRESENT AND FUTURE

In the preceding sections we have indicated that UNIFAC may be used to predict multicomponent vapor-liquid equilibria when no mixture data at all are available. However, the prediction of multicomponent activity coefficients using UNIFAC may also be carried out in a slightly different manner. A given multicomponent system contains a number of constituent binary systems. In many cases, experimental activity coefficients may be available for some, but not all, of these binaries. In that event, UNIFAC may be used to predict the activity coefficients for each of the components in the unknown binaries. These predicted activity coefficients can then be used to generate binary parameters in any model for the excess Gibbs energy. As described in many texts and articles, multicomponent vapor-liquid equilibria can readily be estimated when all constituent binaries are characterized.

Further, UNIFAC may be useful for extrapolating existing (possibly proprietary) data with respect to molecular structure; thus, if experimental data are at hand for systems chemically similar to those of interest, UNIFAC can establish trends indicating how activity coefficients change with molecular size or with modifications in the nature or assembly of a molecule's functional groups.

Finally, UNIFAC may be useful for estimating activity coefficients of highly sensitive or transitory (activated complex) molecules whose properties are experimentally unattainable.

Future applications are limited only by scarcity of reliable data. As more data become available, it will become possible and worthwhile to consider refinements in UNIFAC. Although the group-interaction parameters now available are useful for a large variety of practical phase equilibrium problems, Table 3 does not exhaust the groups that eventually should be included. Not included at present are fluorides, carboxylic acids, tertiary amines, sulfur-organic compounds, carbon tetrachloride, chloroform, methanol, and many others. Inclusion of these in the UNIFAC method is straightforward, provided reliable experimental data are available. (However, for mixtures containing carboxylic acids it will be essential to include vapor phase corrections in data reduction.)

Isomeric effects have so far been studied to only a limited extent. However, inclusion of components such as iso-butane in UNIFAC appears to be straightforward.

The UNIFAC model assumes that accessibility for interaction of a functional group is determined by its area parameter Q which is independent of the size, number, and nature of other functional groups in the same molecule. This assumption may require modification for polymers, where some of the groups are partially shielded by other groups of the chain. Further, it appears likely that free-volume contributions may be required to represent activity coefficients in polymer solutions. Nevertheless, limited experience with polymers indicates that it may be possible to include these in UNIFAC, especially since Derr and Deal (1973) have reported modest success in applying their ASOG method to polymer-solvent systems.

CONCLUSION

A generalized group-contribution model for the prediction of activity coefficients of nonelectrolytes has been developed. Existing phase equilibrium data were used to generate a large number of group-interaction parameters. These are useful for prediction of activity coefficients in binary and multicomponent systems where little or no experimental information exists. The method gives good predictions for a large variety of systems and should, therefore, provide a useful tool for solving practical phase equilibrium problems as encountered in chemical process design.

SUPPLEMENT

A Supplement to this paper is available from the authors.

The Supplement contains

(1) A listing of the binary phase equilibrium data used in the data base.

(2) A description and printout of a "UNIFAC Prediction Computer Program" for the estimation of activity coefficients as a function of composition and temperature.

ACKNOWLEDGMENT

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NOTATION

a = see Equation (9)
l = see Equation (3)
q = pure component area parameter
Q = group area parameter
r = pure component volume parameter
R = gas constant (without subscript)
R_k = group volume parameter (with subscript)
T = temperature
u_{ji} = UNIQUAC binary interaction parameter
U_{nm} = UNIFAC binary interaction parameter
x = liquid phase mole fraction
X = liquid phase group fraction
y = vapor phase mole fraction
z = lattice coordination number, a constant here set equal to ten

Greek Letters

γ_i = activity coefficient of component i
Γ_k = activity coefficient of group k
$\Gamma_k^{(i)}$ = activity coefficient of group k in pure component i

Φ_i = segment fraction of component i
$\nu_k^{(i)}$ = number of groups of kind k in a molecule of component i
θ_i = area fraction of component i
Θ_k = area fraction of group k
τ see Equation (3)
Ψ see Equation (9)

Superscripts

C = combinatorial
R = residual
$^\infty$ = infinite dilution

Subscripts

i, j, k = component i, j, and k
k, m, n = group k, m, and n

LITERATURE CITED

Abrams, D. S., and J. M. Prausnitz, "Statistical Thermodynamics of Liquid Mixtures. A New Expression for the Excess Gibbs Energy of Partly and Completely Miscible Systems," *AIChE J.*, **21**, 116 (1975).

Black, C., G. G. Joris, and H. S. Taylor, "The Solubility of Water in Hydrocarbons," *J. Chem. Phys.*, **16**, 537 (1948).

Bondi, A., *Physical Properties of Molecular Crystans, Liquids and Glasses*, Wiley, New York (1968).

Cukor, P. M., and J. M. Prausnitz, "Calculation of Binary and Multicomponent Vapor-Liquid Equilibria with Models based on the Local Composition Concept," *I. Chem. E. Symp. Ser. no. 32* (Instn. Chem. Engrs., London) 3:88 (1969).

Derr, E. L., and C. H. Deal, "Analytical Solutions of Groups: Correlation of Activity Coefficients Through Structural Group Parameters," *I. Chem. E. Symp. Ser. No. 32* (Instn. Chem. Engrs., London) 3:40 (1969).

———, "Predicted Compositions during Mixed Solvent Evaporation from Resin Solutions Using the Analytical Solution of Groups Method," *Advan. Chem. Ser.*, **124**, 11 (1973).

Derr, E. L., and M. Papadopoulos, "Group Interaction II. A Test of the Group Model on Binary Solutions of Hydrocarbons," *J. Am. Chem. Soc.*, **81**, 2285 (1959).

Edwards, J., and F. Ibanez, "Vapor Pressure and Activity Coefficients in the Mixture n-Decane-Chlorobenzene," *Z. Physik. Chem.*, Frankfurt, **58**, 45 (1968).

Geiseler, G., K. Quitzsch, H.-G. Vogel, D. Pitz, and H. Sachse, "Thermodynamische Untersuchungen an Mischsystemen aus Stellungsisomeren hydroxygruppenhaltigen n-Alkanderivaten und n-Heptan," *J. Phys. Chem.* (Leipzig), **56**, 288 (1971).

Gerster, J. A., J. A. Gorton, and R.-B. Eklund, "Selective Solvents for Separation of n-Pentane from l-Pentene by Extractive Distillation," *J. Chem. Eng. Data*, **5**, 43 (1960).

Hanson, D. O., and M. Van Winkle, "Alteration of the Relative Volatility of n-Hexane-l-Hexene by Oxygenated and Chlorinated Solvents," *J. Chem. Eng. Data*, **12**, 319 (1967).

Humphrey, J. L., and M. Van Winkle, "Vapor-Liquid Equilibria at 60°C for n-Hexane-Alkyl Amines and l-Hexene-Alkyl Amines," *ibid.*, **12**, 526.

Kretschmer, C. B., and R. Wiebe, "Liquid-Vapor Equilibrium of Ethanol-Toluene Solutions," *J. Am. Chem. Soc.*, **71**, 1793 (1949).

Langmuir, I., *The Distribution and Orientation of Molecules*, Third Colloid Symposium Monograph, The Chemical Catalog Company, Inc., New York, (1925).

Lo, T. C., H. H. Bieber, and A. E. Karr, "Vapor-Liquid Equilibrium of n-Pentane-Acetone," *J. Chem. Eng. Data*, **7**, 327 (1962).

McAuliffe, C., "Solubility in Water of Paraffin, Cycloparaffin, Olefin, Acetylene, Cycloolefin, and Aromatic Hydrocarbons," *J. Phys. Chem.*, **70**, 1267 (1966).

Mesnage, J., and A. A. Marsan, "Vapor-Liquid Equilibria at Atmospheric Pressure," *J. Chem. Eng. Data*, **16**, 434 (1971).

Murti, P. S., and M. Van Winkle, "Vapor-Liquid Equilibria and Heat of Mixing: n-Octane-Ethylbenzene-Cellosolve System," *AIChE J.*, **3**, 517 (1957).

Murti, P. S., and M. Van Winkle, "Vapor-Liquid Equilibria for Binary Systems of Methanol, Ethanol, 1-Propanol, and 2-Propanol with Ethyl Acetate and 1-Propanol-Water," *Chem. Eng. Data Ser.*, **3**, 72 (1958).

Nagata, I., "Vapor-Liquid Equilibria for the Ternary System Methyl Acetate-Benzene-Cyclohexane," *J. Chem. Eng. Data*, **7**, 461 (1962).

Newman, R. D., and J. M. Prausnitz, "Thermodynamics of Concentrated Polymer Solutions Comtaining Polyethylene, Polyisobutylene, and Copolymers of Ethylene with Vinyl Acetate and Propylene," *AIChE J.*, **19**, 704 (1973); **20**, 206 (1974).

Norman, W. S., "The Dehydration of Ethanol by Azeotropic Distillation," *Trans. Inst. Chem. Engrs.*, **23**, 66 (1945).

Palmer, D. A., and B. D. Smith, "Thermodynamic Excess Property Measurements for Acetonitrile-Benzene-n-Heptane Systems at 45°C," *J. Chem. Eng. Data*, **17**, 71 (1972).

Pratt, H. R. C., "Continuous Purification and Azeotropic Dehydration of Acetonitrile Produced by the Catalytic Acetic Acid-Ammonia Reaction," *Trans. Inst. Chem. Engrs.*, **25**, 43 (1947).

Redlich, O., E. L. Derr, and G. Pierotti, "Group Interaction I. A Model for Interaction in Solution," *J. Am. Chem. Soc.*, **81**, 2283 (1959).

Ronc, M., and G. A. Ratcliff, "Prediction of Excess Free Energies of Liquid Mixtures by an Analytic Group Solution Model," *Can. J. Chem. Eng.*, **49**, 875 (1971).

Sagnes, M., and V. Sanchez, "Équilibre liquid-vapeur isobare de trois systèmes ternaires," *Gen. Chim.*, **104**, 1649 (1971).

Van Ness, H. C., C. A. Soczek, G. L. Peloquin, and R. L. Machado, "Thermodynamic Excess Properties of Three Alcohol-Hydrocarbon Systems," *J. Chem. Eng. Data*, **12**, 217 (1967).

Wilson, A., and E. L. Simons, "Vapor-Liquid Equilibria. 2-Propanol-Water System," *Ind. Eng. Chem.*, **44**, 2214 (1952).

Wilson, G. M., and C. H. Deal, "Activity Coefficients and Molecular Structure," *Ind. Eng. Chem., Fundamentals*, **1**, 20 (1962).

Wolff, H., A. Hoepfner, and H.-M. Hoepfner, "Die Assoziation von Methyl-, Aethyl-, und n-Propylamin in gesaettigten aliphatischen Kohlenwasserstoffen," *Ber. Bunsenges. Physik. Chem.*, **68**, 410 (1964).

APPENDIX

Example 1

Consider an equimolar benzene (1)-*n*-propanol (2) binary mixture. Benzene has six ACH groups, group No. 3. Thus $\nu_3^{(1)} = 6$, $R_3 = 0.5313$, and $Q_3 = 0.400$. $r_1 = 6 \cdot 0.5313 = 3.1878$; $q_1 = 6 \cdot 0.400 = 2.400$. *n*-propanol has one CH_3 group (1A), 1 CH_2 group (1B), and 1 COH group (5A). Thus $\nu_{1A}^{(2)} = 1$, $\nu_{1B}^{(2)} = 1$, and $\nu_{5A}^{(2)} = 1$; $R_{1A} = 0.9011$, $R_{1B} = 0.6744$, $R_{5A} = 1.2044$, and $r_2 = 1 \cdot 0.9011 + 1 \cdot 0.6744 + 1 \cdot 1.2044 = 2.7799$. Similarly, $q_2 = 1 \cdot 0.848 + 1 \cdot 0.540 + 1 \cdot 1.124 = 2.512$. The needed group interaction parameters are obtained from Table 3:

$$a_{1,5} = 931.2,\ a_{5,1} = 169.7,\ a_{1,3} = 32.08,\ a_{3,1} = 15.26,$$

$$a_{3,5} = 705.9 \text{ and } a_{5,3} = 83.50°\text{K}.$$

$$x_1 = x_2 = \frac{1}{2}$$

$$X_{1A} = (1/2)/(6/2 + 1/2 + 1/2 + 1/2) = \frac{1}{9}$$

$$X_3 = (6/2)/(6/2 + 1/2 + 1/2 + 1/2) = \frac{2}{3}$$

Similarly, $X_{1B} = X_{5A} = \frac{1}{9}$

At constant temperature, the activity coefficient of group k (k = 1A, 1B, 3, or 5A) is a function of the group composition:

$$\Gamma_k = \Gamma(X_{1A}, X_{1B}, X_3, X_{5A})$$

For an equimolar mixture

$$\Gamma_k = \Gamma\left(\frac{1}{9}, \frac{1}{9}, \frac{2}{3}, \frac{1}{9}\right)$$

In pure benzene (1)

$$\Gamma_3^{(1)} = \Gamma(0, 0, \quad 1, \quad 0) = 1$$

In pure *n*-propanol (2)

$$\Gamma_k^{(2)} = \Gamma\left(\frac{1}{3}, \frac{1}{3}, 0, \frac{1}{3}\right) \neq 1 \quad (k = 1A, 1B, \text{ or } 5A)$$

Example 2

It is desired to obtain the activity coefficients for the acetone (1)-*n*-pentane (2) system at 307°K and $x_1 = 0.047$:

$$r_1 = 2 \cdot 0.9011 + 1 \cdot 0.7713 = 2.5735; \qquad q_1 = 2 \cdot 0.848 + 1 \cdot 0.640 = 2.336$$

$$r_2 = 2 \cdot 0.9011 + 3 \cdot 0.6744 = 3.8254; \qquad q_2 = 2 \cdot 0.848 + 3 \cdot 0.540 = 3.316$$

$$\Phi_1 = \frac{2.5735 \cdot 0.047}{2.5735 \cdot 0.047 + 3.8254 \cdot 0.953} = 0.0321; \qquad \Phi_2 = 0.9679$$

$$\theta_1 = \frac{2.336 \cdot 0.047}{2.336 \cdot 0.047 + 3.316 \cdot 0.953} = 0.0336; \qquad \theta_2 = 0.9664$$

$$l_1 = 5(2.5735 - 2.336) - 1.5735 = -0.3860$$

$$l_2 = 5(3.8254 - 3.316) - 2.8254 = -0.2784$$

$$\ln \gamma_1^C = \ln \frac{0.0321}{0.047} + 5 \cdot 2.336 \ln \frac{0.0336}{0.0321} - 0.3860 + \frac{0.0321}{0.047}(0.047 \cdot 0.3860 + 0.953 \cdot 0.2784) = -0.403$$

$CH_3 = 1A; \quad CH_2 = 1B; \quad CO = 8$

$a_{1,8} = 1\,565; \quad a_{8,1} = 3\,000$°K (see Table 3)

$\Psi_{1,8} = \exp\{-1\,565/307\} = 0.00611$

$\Psi_{8,1} = \exp\{-3\,000/307\} = 0.000057$

For pure acetone

$$\ln \Gamma_{1A}^{(1)} = \ln \Gamma_{1A}^{(1)}\left(X_{1A} = \frac{2}{3}, X_8 = \frac{1}{3}\right)$$

$$\theta_{1A}^{(1)} = \frac{\frac{2}{3} \cdot 0.848}{\frac{2}{3} \cdot 0.848 + \frac{1}{3} \cdot 0.640} = 0.726; \quad H_8^{(1)} = 0.274$$

$$\ln \Gamma_{1A}^{(1)} = 0.848\left[1 - \ln\{0.726 + 0.274 \cdot 0.000057\} - \left\{\frac{0.726}{0.726 + 0.274 \cdot 0.000057} + \frac{0.274 \cdot 0.00611}{0.726 \cdot 0.00611 + 0.274}\right\}\right] = 0.2664$$

$$\ln \Gamma_8^{(1)} = 0.640\left[1 - \ln\{0.726 \cdot 0.00611 + 0.274\} - \left\{\frac{0.726 \cdot 0.000057}{0.726 + 0.274 \cdot 0.000057} + \frac{0.274}{0.726 \cdot 0.00611 + 0.274}\right\}\right] = 0.8284$$

For $X_1 = 0.047$

$$X_{1A} = \frac{0.047 \cdot 2 + 0.953 \cdot 2}{0.047 \cdot 3 + 0.953 \cdot 5} = 0.4077 \cdot X_{1B} = 0.5828; \qquad X_8 = 0.0096$$

$$H_{1A} = 0.5187; \quad H_{1B} = 0.4721; \quad H_8 = 0.0092$$

$$\ln \Gamma_{1A} = 0.848\left[1 - \ln\{0.5187 + 0.4721 + 0.0092 \cdot 0.000057\} - \left\{\frac{0.5187 + 0.4721}{0.5187 + 0.4721 + 0.000057 \cdot 0.0092} + \frac{0.0092 \cdot 0.00611}{(0.5187 + 0.4721)0.00611 + 0.0092}\right\}\right] = 0.0047$$

$$\ln \Gamma_8 = 0.640\left[1 - \ln\{(0.5187 + 0.4721) \cdot 0.00611 + 0.0092\} - \left\{\frac{(0.5187 + 0.4721) \cdot 0.000057}{0.5187 + 0.4721 + 0.0092 \cdot 0.000057} + \frac{0.0092}{(0.5187 + 0.4721)0.00611 + 0.0092}\right\}\right] = 2.9310$$

$$\ln \gamma_1^R = 2 \cdot (0.0047 - 0.2664) + 1 \cdot (2.9310 - 0.8284) = 1.5792$$

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R = -0.403 + 1.5792 = 1.5389$$

Thus $\gamma_1 = 4.66$

By following exactly the same procedure for pentane (2), it is found that $\gamma_2 = 1.02$. The corresponding experimental values (Lo et al., 1962) are $\gamma_1 = 4.41$; $\gamma_2 = 1.11$.

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