Separation & Purification Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

Prediction of Separation Factors Using Group Contribution Methods a Review

Peter Rasmussen[a]; Aage Fredenslund[a]
[a] Instituttet for Kemiteknik, Technical University of Denmark, Lyngby, Denmark

To cite this Article Rasmussen, Peter and Fredenslund, Aage(1978) 'Prediction of Separation Factors Using Group Contribution Methods a Review', Separation & Purification Reviews, 7: 2, 147 — 182
To link to this Article: DOI: 10.1080/03602547808066062
URL: http://dx.doi.org/10.1080/03602547808066062

SEPARATION AND PURIFICATION METHODS, 7(2), 147-182 (1978)

PREDICTION OF SEPARATION FACTORS USING GROUP CONTRIBUTION METHODS A REVIEW

Peter Rasmussen and Aage Fredenslund
Instituttet for Kemiteknik, Technical University of Denmark, Bygning 229, DK-2800 Lyngby, Denmark

Introduction

For separation process design calculations such as distillation, absorption and extraction it is unconditionally necessary to have quantitative information on the mixtures in consideration, i.e. knowledge about phase equilibrium compositions, heats of mixing etc.

Since the number of different mixtures in chemical technology is extremely large, one cannot find all the desired information from experimentally determined observations. It is, therefore, necessary by means of thermodynamic equations and suitable models for the mixtures to predict the required information from the available experimental data. Very often we have no experimental data for our mixtures at all, and we have to rely on some generalized method for prediction of the required information.

Group contribution methods are examples of such methods; they have for many years with great success been used to predict properties for pure substances, f.ex.

heat capacities and critical constants. During the last 15 years, group contribution methods have also been developed for the prediction of thermodynamic properties of liquid mixtures. In these methods, the liquids are treated as mixtures of the functional groups (CH_3-, $-CH_2$-, -OH etc.) which when added make up the molecular species present. In chemical technology, the number of different groups is much smaller than the number of different molecules. Therefore, if we assume that a physical property of the liquid is the sum of the contributions of the molecules' groups, we can predict the properties of a very large number of mixtures in terms of a relatively small number of parameters characterizing the individual groups.

Deal and Derr[1] presented in 1968 an excellent review on group contribution methods for liquid mixtures. Some of the methods have since been further developed, and new ones have been added. It is the purpose of this article to review some of the work published after 1968 on group contribution methods for mixtures. The main emphasis is on methods for the prediction of activity coefficients in liquid mixtures.

For nonelectrolyte liquid mixtures it is today possible to make such predictions with reasonable accuracy and by means of rather simple calculation procedures. This allows us to predict separation factors used in equilibrium calculations. This article reviews the development and the use of these methods.

Phase Equilibrium

For the design of separation processes we have to find an answer to a problem of the following kind: A mixture with M components is distributed between a vapor and a liquid phase. The two phases have reached an equi-

librium state, and we know the temperature (T) and the mole fractions in the liquid phase ($x_1, x_2 \ldots x_M$). The question then is to find the mole fractions in the vapor phase ($y_1, y_2 \ldots y_M$) and the pressure (P).

To solve such a problem, we use the phase equilibrium condition:

$$f_i^v = f_i^\ell \qquad i = 1,2 \ldots M \qquad 1$$

where f_i is the fugacity of component i in the vapor (v) or liquid (ℓ) phase.

The fugacities are normally rewritten in terms of the vapor phase fugacity coefficient φ_i, the liquid phase activity coefficient γ_i and the liquid phase reference fugacity f_i^o.

$$\varphi_i y_i P = \gamma_i x_i f_i^o \qquad 2$$

The reference fugacity f_i^o of pure-component i at temperature T and pressure P may be written as

$$f_i^o = \varphi_i^S P_i^S \exp \int_{P_i^S}^{P} \frac{V_i}{RT} dP \qquad 3$$

$$= \varphi_i^S \cdot P_i^S \cdot POY_i$$

where φ_i^S is the vapor phase fugacity coefficient at the saturation pressure P_i^S and V_i is the molar liquid volume.

The separation factor (K_i), i.e. the ratio between the vapor and liquid phase mole fractions, may thus be calculated from equation 4

$$K_i = \frac{y_i}{x_i} = \gamma_i \cdot \frac{\varphi_i^S}{\varphi_i} \cdot \frac{P_i^S}{P} \cdot POY_i \qquad 4$$

At pressures up to a few bars, the fugacity coefficients φ_i^S and φ_i are readily calculated using f.ex. the

virial equation of state. This is explained in most textbooks, and f.ex. in Fredenslund et al.[2] one may find a detailed description of computer programs for such calculations. At these low pressures the ratio φ_i^S/φ_i is often nearly unity except for mixtures containing strongly associating components such as organic acids.

The Poynting correction factor POY_i is also nearly unity and it is easy to calculate POY_i within good accuracy by means of experimental or estimated values of V_i.

The vapor pressure P_i^S may f.ex. be calculated from the Antoine equation. This leaves us with the problem of finding a relation for calculating the activity coefficient γ_i.

The Wilson, NRTL, and UNIQUAC equations represent such relations which are widely used and for which many parameters have been published (see f.ex. Gmehling and Onken[3]).

It will, however, never be possible to furnish parameters for all possible binary combinations and hence it is necessary to rely on approximative methods, like group contribution methods, for the estimation of activity coefficients for mixtures for which no data are available.

Fundamental Equations

Wilson and Deal[4] presented in 1962 the assumptions and equations which have since become the basis for most group contribution methods used for the estimation of activity coefficients.

Assumption 1. The liquid solution can be treated as a solution of groups which make up the components of the mixture. The "groups" are chosen to be convenient structural units such as $-CH_3$, $-CH_2O-$ and $-CH_2NO_2$.

Assumption 2. The excess Gibbs energy of a solution is assumed to be the sum of two contributions - one associated with the differences in molecular size and shape and the other with energetic interactions between the groups. As a consequence of this assumption, the logarithm to the activity coefficient γ_i may be written as:

$$\ell n\ \gamma_i = \ell n\ \gamma_i^C + \ell n\ \gamma_i^R \qquad 5$$

where γ_i^C is the combinatorial or size or entropy part and γ_i^R is the residual or interaction or enthalpy part.

Assumption 3. The contribution from group interactions, the residual part, is assumed to be the sum of the individual contributions of each solute group in the solution less the sum of the individual contributions in the pure-component environment. We write

$$\ell n\ \gamma_i^R = \sum_{\text{all groups}}^{k} \nu_k^{(i)} \left[\ell n\ \Gamma_k - \ell n\ \Gamma_k^{(i)}\right] \qquad 6$$

$k = 1,2 \ldots N$, where N is the number of different groups in the mixture.

Γ_k is the residual activity coefficient of group k in a solution;

$\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i; and $\nu_k^{(i)}$ is the number of "interaction" groups of kind k in molecule i. In Equation 6 the term $\ell n \Gamma_k^{(i)}$ must attain the normalization that activity coefficient γ_i becomes unity as $x_i \rightarrow 1$. The standard state for the group residual activity coefficient need not be defined due to cancellation of terms.

Assumption 4. The individual group contributions in any environment containing groups of kinds 1,2 .. N are as-

sumed to be only a function of group concentrations and temperature:

$$\left.\begin{matrix}\Gamma_k \\ \Gamma_k^{(i)}\end{matrix}\right\} = F(X_1, X_2 \ldots X_N ; T) \qquad 7$$

The same function is used to represent Γ_k and $\Gamma_k^{(i)}$. The group fraction X is defined by:

$$X_k = \frac{\sum_i \nu_k^{(i)} x_i}{\sum_i \sum_j \nu_j^{(i)} x_i} \qquad 8$$

i = 1,2 .. M (number of components)

j = 1,2 .. N (number of groups)

According to this assumption, for example the residual activity coefficients for all ketone-alkane mixtures may be calculated from the same function F. That is, the same parameters are used to represent vapor-liquid equilibria in acetone-hexane mixtures and decane-5-nonanone mixtures.

The difference between the various group contribution methods is essentially due to differences in the definition of functional groups and in the equations used for calculating:

- The combinatorial or size activity coefficient, γ_i^C
- The group activity coefficient, Γ_k

Combinatorial or Size Activity Coefficient

Wilson and Deal[4] used a Flory-Huggins relation for calculating the size term

$$\ln \gamma_i^C = \ln r_i + 1 - r_i \qquad 9$$

$$r_i = n_i / \sum_j^{} n_j x_j \qquad j = 1,2 \ldots M \qquad 9a$$

n_i = number of atoms (other than hydrogen) in molecular component i

x_i = molecular mole fraction of component i

In 1969 the method was further developed by Derr and Deal[5] into the socalled ASOG-method (Analytical Solution Of Groups). Here r_i is defined as the ratio of solute groups to the total number of groups in the average liquid molecule:

$$r_i = S_i / \sum_j^{} S_j x_j \qquad j = 1,2 \ldots M \qquad 9b$$

here S are the number of "size" groups in each of the molecular species in the solution.

Normally, the size groups are taken as the chemical groups which might be expected on a chemical basis to interact. Acetone would thus be considered as two methyl and one carbonylic groups. However group identities and counts may be assigned in any desired manner. Any such assignments must, of course, be consistently used since the calculated values of γ_i^C and hence also the values of γ_i^R are dependent on the choice of groups. In applying the ASOG method one must recall that thermodynamic consistency requires that although the choice of groups and group counts may be made in any manner desired, the same assignments must be used in prediction of activity coefficients as were used in data reduction.

Scheller[6] presented in 1965 essentially the same procedure as proposed by Wilson and Deal[4]. A Flory-Huggins relation is again used for calculating γ_i^C but r_i is calculated by means of the molar volume V_i of pure component i in stead of the number of atoms in compo-

nent i. Thus it is not assumed that all atoms regardless of type have the same volume.

$$r_i = V_i / \sum_j^{} x_j V_j \qquad j = 1,2 \ldots M \qquad 9c$$

In 1969 Ratcliff and Chao[7] generalized an equation developed by Brønsted and Koefoed[8] for mixtures of n-paraffins; they used

$$\ln \gamma_i^C = B \left(n_i - \sum_j^{} x_j n_j\right)^2 \qquad 10$$

where n_i is the number of atoms other than hydrogen in molecular component i. The coefficient B is a function of temperature only, and a figure with B as a function of the temperature is presented by Ratcliff and Chao[7].

Although Ratcliff and coworkers[9,10] later use equation 10, they were apparently not totally satisfied with it. In 1975 Ronc and Ratcliff[11] give a most thorough discussion of the size contribution.

They observe that γ_i^C from the Brønsted-Koefoed relation is nearly unity and that the value might just as well be set equal to one.

For different binary alkane(1)-alcohol(2) mixtures they calculate the group residual activity coefficients Γ_{CH_2}.

According to equation 7, the group activity coefficients Γ_{CH_2} are only functions of group concentrations and temperature. It turned out, however, that the calculated values of Γ_{CH_2} were also functions of the specific alkane-alcohol system used.

The Γ_{CH_2}-values were thus only identical for mixtures with the same relative size ratio:

$$\rho = S_1/S_2 \qquad 11$$

Ronc and Ratcliff[11] could therefore conclude that the Brønsted-Koefoed relation did not present the total size contribution.

They assumed that γ_i^C was equal to unity for mixtures with $\rho = 1.0$ f.ex. hexane/1-pentanol, pentane/1-butanol. For such mixtures

$$\ln \Gamma_{CH_2} = \frac{1}{\nu_{CH_2}^{(1)}} \ln \gamma_1 \qquad 12$$

and the values of Γ_{CH_2} calculated from 12 may be considered to be the "true" values of Γ_{CH_2}. Using these true values of Γ_{CH_2} it is possible to calculate γ_1^C for mixtures with $\rho \neq 1$. Based on such calculations of γ_1^C it is proposed that γ_1^C is calculated from the following correlation

$$\ln \gamma_i^C = \alpha \ln \gamma_i^{FH} \qquad 13$$

where $\ln \gamma_i^{FH}$ is the Flory-Huggins activity coefficient calculated from equations 9 and 9a; α is a function of the size ratio ρ. This new size contribution is defined only for binary alkane-alcohol systems.

$$\alpha = 2.9239 - 5.4777\rho + 12.8016\rho^2 \qquad 14$$

An important conclusion of this careful study of the size contribution is that no effect of temperature could be observed.

Fredenslund, Jones and Prausnitz[12] proposed in 1975 the UNIFAC group-contribution method based on the UNIQUAC model[13] for liquid mixtures.

In the UNIFAC method, the combinatorial term of the activity coefficient takes into account not only the differences in molecular sizes as given by the group volumes but also the differences in molecular forms as presented by group surface areas.

The somewhat arbitrary selection of a relation for calculating γ_i^C is now removed. In the UNIFAC method, the combinatorial contribution is uniquely related to the expression for the residual term of the activity coefficient, γ_i^R.

The combinatorial activity coefficient is calculated from

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + \ell_i - \frac{\Phi_i}{x_i} \sum_j x_j \ell_j$$

$$\ell_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \; ; \quad z = 10 \qquad 15$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \; ; \qquad \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

Molecular surface area fraction — Molecular volume fraction

$j = 1,2 \ldots M$ (number of components)

The van der Waals volume: $r_i = \sum_k^k \nu_k^{(i)} R_k$

and van der Waals surface area: $q_i = \sum_k^k \nu_k^{(i)} Q_k$ 16

$k = 1,2 \ldots N$ (number of groups in molecule i)

are found by summation of the corresponding group properties.

Note that γ_i^C does not depend on temperature. The combinatorial contribution is often small. It is, however, far from negligible when the molecules differ much in size and shape.

The definition of groups and the values for R_k and Q_k are given by Fredenslund et al.[2,14].

Table I shows some calculated combinatorial activity coefficients for an equimolar mixture of acetone (1) and methanol (2).

The use of equation 9b corresponds to the ASOG method while equations 9c and 13/14 represent slightly modified ASOG methods.

Group Activity Coefficients

In order to understand the practical use of the group activity coefficients Γ_k, we first show how Γ_k values can be found from experimental activity coefficients.

For a binary alkane(1)-alcohol(2) mixture we may calculate Γ_{CH_2} from equations 5 and 6 and from a relation for γ_i^C. For a mixture of decane(1) and 1-propanol(2) we may thus write:

$$\ln \Gamma_{CH_2} = 0.1 \ln \gamma_1^R \qquad 17$$

In pure decane, the value of $\Gamma_{CH_2}^{(1)}$ equals one, the group fraction for CH_2 is $X_{CH_2} = 1.0$ (assuming no difference between groups CH_3 and CH_2). In pure 1-propanol, X_{CH_2} is 0.75, assuming that 1-propanol consists of 3 CH_2 groups and 1 OH group. Equation 17 will thus give Γ_{CH_2}-values for solutions built from OH and CH_2 groups in the CH_2 group fraction range 0.75-1.00.

Based on the residual activity coefficient for 1-propanol(2) we can now calculate $\Gamma_{OH}/\Gamma_{OH}^{(2)}$.

$$\ln \gamma_2^R = 3 \cdot (\ln \Gamma_{CH_2} - \ln \Gamma_{CH_2}^{(2)}) + \ln \Gamma_{OH}/\Gamma_{OH}^{(2)} \qquad 18$$

Since we do not know $\Gamma_{OH}^{(2)}$ (the group activity coefficient of OH in pure 1-propanol), it is not possible from data for this particular mixture to estimate Γ_{OH}, and we are not able to move below a methylene group fraction of 0.75.

TABLE I

Combinatorial Activity Coefficients

Acetone (1) - Methanol (2)

$x_1 = x_2 = 0.5$

Method	γ_1^C	γ_2^C
r_i calculated as $n_i/\sum_j n_j x_j$ eq. 9a	0.9554 (n_1=4)	0.9304 (n_2=2)
$S_i/\sum_j S_j x_j$ eq. 9b	0.9825 (S_1=3)	0.9771 (S_2=2)
	0.9098 (S_1=3)	0.8244 (S_2=1)
$V_i/\sum_j x_j V_j$ eq. 9c ($T = 25\ ^oC$)	0.9654 (V_1=73.33)	0.9490 (V_2=40.41)
Brønsted-Koefoed eq. 10 ($B=-0.00113$, $T = 25\ ^oC$)	0.9989 (n_1=4)	0.9989 (n_2=2)
Ronc-Ratcliff eq. 13 and 14	0.9160 (S_1=3)	0.8915 (S_2=2)
UNIFAC eq. 15 and 16	0.9737 ($r_1 = 2.5735$, $q_1 = 2.336$)	0.9634 ($r_2 = 1.4311$, $q_2 = 1.432$)

If we continue our calculations with data for water (1)-1-propanol(2) mixtures, it is possible to calculate Γ_{OH} from:

$$\ell n\ \gamma_1^R = 1.4\ \ell n\ \Gamma_{OH} \qquad 19$$

In equation 19 it is assumed that the number of OH interaction groups in pure water is 1.4 (see below). Based on the activity coefficients for 1-propanol we have:

$$\ell n\ \gamma_2^R = 3\ \ell n\ \Gamma_{CH_2}/\Gamma_{CH_2}^{(2)} + \ell n\ \Gamma_{OH} - \ell n\ \Gamma_{OH}^{(2)} \qquad 20$$

In equation 20 we know Γ_{OH} and $\Gamma_{OH}^{(2)}$ from eq. 19 and $\Gamma_{CH_2}^{(2)}$ from eq. 17, and hence it is possible to calculate Γ_{CH_2} for values of X_{CH_2} from 0.0 up to 0.75. From equation 19 we have Γ_{OH} in the same concentration range. Combining these results with the previous calculated values of $\Gamma_{OH}/\Gamma_{OH}^{(2)}$ from eq. 18 the values of Γ_{CH_2} and Γ_{OH} can be found for the whole CH_2 group fraction range 0.0-1.0.

Figure 1 shows Γ_{CH_2} and Γ_{OH} as a function of X_{CH_2} based on data presented by Ratcliff and Chao[7] and applying eq. 9b for the calculation of the combinatorial activity coefficient.

Figure 1 allows us to predict the activity coefficients for all possible mixtures containing water and/or any alkanes and/or any alcohols.

In 1962 Wilson and Deal[4] used a such graphical composition relation derived directly from an appropriate set of experimental data. Others have presented the group activity coefficients in a similar way: Scheller[6], Ratcliff and Chao[7] for alkane-alcohol-water mixtures,

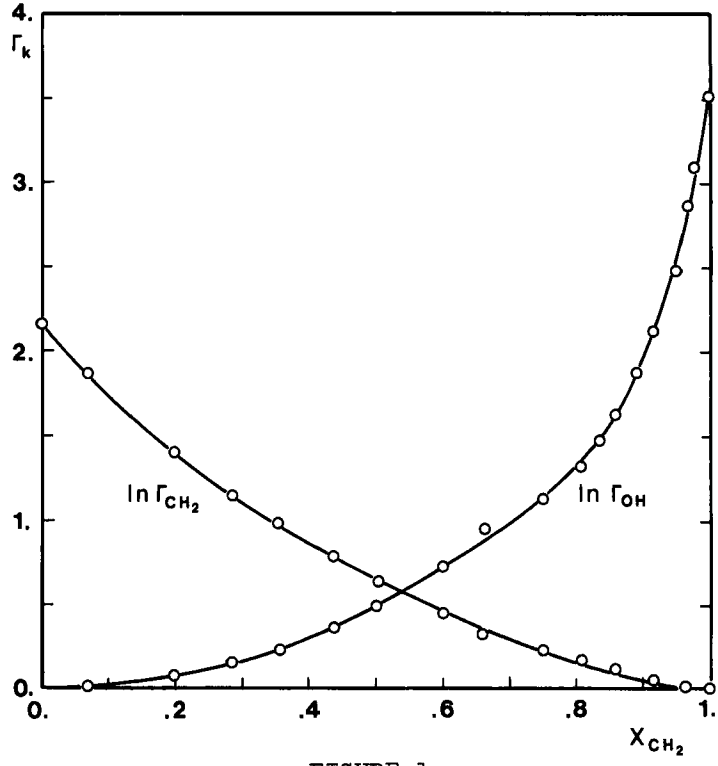

FIGURE 1

Group activity coefficients for solutions built from OH and CH_2 groups at 90 °C.

Maripuri and Ratcliff[15] for alcohol-aromatic hydrocarbon mixtures.

It has later turned out to be much more convenient having an analytical expression for the group activity coefficients. Maripuri and Ratcliff[9] thus fit the group activity coefficients for methylene and carbonyl groups in alkane-ketone mixtures by power series in the carbonyl group fractions.

The method is, however, still dependent on full-range binary data in order to define the dependence of the

group activity coefficients on group fractions, and it is in practice restricted to systems having a maximum of two groups.

The ASOG Method

In 1969 Derr and Deal[5] proposed the Analytical Solution Of Groups (ASOG) method. This method presented a most significant step in the evolution of group contribution methods for correlating and predicting activity coefficients.

Derr and Deal[5] use the Wilson equation for the calculation of the group activity coefficients. For a group k in a mixture containing groups 1, 2, ... N, the following expression is used:

$$\ell n\, \Gamma_k = 1 - \ell n \sum_n^n X_n a_{kn} - \sum_n^n \frac{X_n a_{nk}}{\sum_m^m X_m a_{nm}} \qquad 21$$

$$n,m = 1,\ 2 \ldots N$$

where a are binary group parameters analogous to conventional molecular binary parameters, the X_n are group fractions of interaction groups n as defined by eq. 8. The sums are to be taken over all groups in the mixture including k.

In order to apply the ASOG method it is necessary

1) to establish the "size" and the "interaction" groups to be dealt with. The size groups are used as previously explained (equations 9 and 9b) to calculate the combinatorial activity coefficient. Normally the size and the interaction groups are identical, but in some cases they are chosen differently. The reason is that negative parameters a_{nm} may result in negative values for the argument

of the logarithmic term in eq. 21. Only positive parameters can therefore give meaningful results. By changing the interaction group definition and/or count it is possible to ascertain positive values of the parameters.

Table II shows some group assignments for various compounds as presented by Derr and Deal[5].

2) to establish group interaction parameters a_{nm}. Such parameters may be estimated by fitting equation 21 to experimental values of Γ_k obtained as previously explained. Since it is assumed that eq. 21 gives a good representation of Γ_k for all group fractions X_k, one may select only a few experimental results as the basis for the parameter determination.

Derr and Deal[5] recommend using limiting activity coefficients only. They[5] give interaction parameters for alcohol-hydrocarbon-water systems at 60 °C, methanol-glycerol systems at 25 °C, ketone-alcohol-water systems at 60 °C, ether-alcohol-water systems at 60 °C, aqueous nitrile systems at 75 °C, ester-alcohol systems at 50 °C, aromatic hydrocarbon-alcohol systems at 80 °C, chloride systems, some fluoro-compound containing mixtures, and aromatic hydrocarbon-ketone mixtures. The parameters vary with temperature but no mathematical relation is presented.

Derr and Deal[16] extended in 1973 the ASOG method to cover solvent-alkyd resin solutions. The solvents included paraffin, aromatic, chloride, ketone, ester, and alcohol types. The resins used had varying methylene/aromatic ratios. Tables with group definitions and counts and with interaction parameters are given. These parameters are different from the ones presented previously[5].

TABLE II

Group Assignments in the ASOG method

Compound i	Size Groups S_i	Interaction groups								
		CH_2	CH=	ACH	OH	GOH	CO	-O-	CN	COO
Pentane	5	5								
Heptane	7	7								
Benzene	6			6						
Toluene	7	1		6						
Methanol	2	1			1					
Ethanol	3	2			1					
1-Butanol	5	4			1					
Glycerol	6					6				
Water	1				1.4					
Acetone	3	2					1			
2-Butanone	4	3					1			
Diethyl ether	5	4						1		
1,4-Dioxane	6	4						2		
Acetonitrile	3	1							1	
Acrylonitrile	4	1	1						1	
Propyl formate	6	3								3
Ethyl propanoate	8	5								3
Methyl acetate	5	2								3

Palmer[17] presented in 1975 a most detailed and easy-to-read description of the ASOG method with a worked out example of how to use the method. New groups and interaction parameters are included for carboxylic acids and anhydrides.

Cukor[18] distinguished between interactions involving methyl (CH_3) and methylene (CH_2) groups, and he redefines the alcohol and ether groups to ensure a good fit to experimental data. A table of group interaction parameters at 25 °C is presented for the following groups H_2O, CH_2, CH_3, COH (alcohol), CO, COO, OCH_3 (ether), CN and ACH. Note that Cukor has a special H_2O-group.

The aim of Cukor's work was to predict activity coefficients of volatile solutes typically encountered in water pollution abatement and in vacuum drying of food products. Such systems may contain polyfunctional molecules (f.ex. fructose) and Cukor states that group interaction parameters reduced from data for simple polar molecules are not capable of reflecting polyfunctional molecules. This experience is common for all group contribution methods.

Cukor assumes that the group interaction parameters vary with temperature according to the following relation:

$$a_{nm} = \frac{S_m}{S_n} \exp(-(\lambda_{nm} - \lambda_{nn})/RT) \qquad \underline{22}$$

The S's are the size group counts, R is the gas constant and T is the absolute temperature. The λ's represent interaction energies between groups n and m. The parameters $\lambda_{nm}-\lambda_{nn}$ are assumed independent of temperature.

Tochigi and Kojima[19] determine group interaction parameters from infinite dilution activity coefficients at temperatures between 40 and 100 °C. Parameters from mix-

tures containing CH_2, OH and CO groups are presented as functions of temperature:

$$\ell n\ a_{nm} = A_{nm} + B_{nm}/T \qquad 23$$

Here A_{nm} and B_{nm} are constants for the pair of groups n and m.

Tochigi and Kojima treat the CH interaction group (as is found in 2-propanol and 2,3-dimethyl butane) as 0.8 CH_2 groups.

Tochigi et al.[20] extend the ASOG method to vapor-liquid equilibria in which chemical reactions may occur. Group interaction parameters are determined on the basis of measured infinite dilution activity coefficients for five binary systems made up of CH_2, OH, COO and COOH groups.

Scheller et al.[21] combine a rapid method for determining activity coefficients by gas-liquid chromatography with group contribution parameter estimation. The method is restricted to systems made up from groups of not more than two kinds and cannot be applied to ternary and higher systems of groups. The same restrictions hold for the application of the group contribution method described by Tikhonova, et al.[22].

Methods Similar to the ASOG Method

Ronc and Ratcliff[10] use equation 10 for calculation of the combinatorial activity coefficient and eq. 21 for the group activity coefficients. Group interaction parameters for methylene/hydroxyl mixtures are presented as temperature functions similar to eq. 22.

Ronc and Ratcliff[11] use equations 13/14 for the combinatorial activity coefficients. To calculate the group activity coefficients, they use the Wilson equation 21 multiplied by a constant C. The reason for this correction factor is that the Wilson equation cannot generate

activity coefficients above a certain limit and the "true" values of Γ_{CH_2} determined by equation 12 are above this limit. For alcohol/alkane/water mixtures the value of C is 1.6. Group parameters for methylene/hydroxyl mixtures are presented.

Group Counts for Water in the ASOG and Similar Methods

The water molecule is assumed to consist only of the hydroxyl group, thereby avoiding a special "water" group. Since the water molecule forms hydrogen bonds with either of its hydrogen atoms it seems reasonable that the interaction group count may be larger than unity.

Derr and Deal[5] choose 1.4 for the H_2O group, and Ronc and Ratcliff[10,11] use a number of, respectively, 1.2 and 1.55, based on empirical observations for the relation between interactions in mixtures containing alcohol and water.

Scheller[6] has shown a plot of the molar volumes of n-alcohols versus the reciprocal OH-group fraction of the alcohols. An extrapolation to the molar volume of water gives a number of 1.6 OH groups in water. The value 1.6 is also used by Tochigi et al.[19,20].

The UNIFAC Method

The UNIFAC method was proposed by Fredenslund, Jones and Prausnitz[12] in 1975. The combinatorial activity coefficient is calculated from equations 15/16 and the group activity coefficient for group k by:

$$\ln \Gamma_k = Q_k[1-\ln(\overset{m}{\Sigma}\theta_m\Psi_{mk}) - \overset{m}{\Sigma}(\theta_m\Psi_{km}/\overset{n}{\Sigma}\theta_n\Psi_{nm})] \qquad 24$$

m and n = 1,2 ... N (all groups)

Equation 24 also holds for $\Gamma_k^{(i)}$, the group activity coefficient for group k in pure compound i. The equation

is similar to the one used in the UNIQUAC model for calculating the residual activity coefficient γ_i^R

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad ; \qquad X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j} \qquad 25$$

Group surface area fraction — Group fraction

$j = 1,2 \ldots M$ (all compounds); $n = 1,2 \ldots N$

In equation 24 the parameter Ψ_{nm} is given by

$$\Psi_{nm} = \exp(-a_{nm}/T) \qquad 26$$

where a_{nm} is the group interaction parameter between groups n and m. Note that the value of a_{mn} is different from the value of a_{nm}, and that we need two parameters per pair of groups.

In order to apply the UNIFAC method it is necessary:

1) to know the definition of groups and the corresponding values of group volumes, R_k, and areas, Q_k. Such values are given for many different groups by Fredenslund et al.[12] Fredenslund et al.[2,14] have later revised and extended the range of applicability of the UNIFAC method and they present R_k and Q_k values for 56 different groups.

2) to know the values of the group interaction parameters. These parameters must be evaluated from phase equilibrium data and Fredenslund et al.[2,14] have determined parameters for so many different groups that the basis of the UNIFAC method now covers 70% of all published vapor-liquid equilibrium data.

There is some difference in the approach used by the authors of ASOG and UNIFAC publications. The ASOG parameters have mostly been determined from experimentally measured infinite dilution activity coefficients and hence from a minimum of data points. The experimental information must, therefore, be highly accurate. A given pair of UNIFAC parameters is obtained from a collection of all available, consistent, relevant experimental data. For example, the parameters $a_{CH_2/COOH}$ and a_{COOH/CH_2} are based on information on several systems with alkanes (including isomers) and organic acids; data at various compositions and temperatures are used.

The UNIFAC parameters are essentially independent of temperature for the temperature range applicable for the method, typically 30-125 °C. A thorough discussion on this problem is given by Fredenslund et al.[2].

Here[2] one may also find a detailed description of how to use the method, and many comparisons between calculated and experimental activity coefficients for binary and ternary mixtures are given. The method can be used for nonelectrolyte solutions made up of two, three or more different groups. Isomers such as branched hydrocarbons, secondary alcohols, and others may be included with good results (see also Rasmussen[23], page 476).

Gmehling and Onken[24,25] also desribe the UNIFAC method and present some results.

The UNIFAC method as presented by Fredenslund et al.[2] does not apply to polymers. As a rough guide, it should rarely be applied to mixtures containing components with more than ten functional groups. Oishi and Prausnitz[26] have most recently extended the UNIFAC method to polymer solutions. In the UNIFAC method as applied by Fredenslund et al.[2], the changes in free-volume caused by mixing

are negligible. In polymer-solvent solutions, however, these effects are far from negligible. Oishi and Prausnitz rewrite eq. 5 by adding a free-volume term.

$$\ell n\ \gamma_i = \ell n\ \gamma_i^C + \ell n\ \gamma_i^R + FV \qquad 27$$

The combinatorial and residual parts are calculated as previously described. The FV term is estimated based on a relation proposed by Flory[27]. The results presented by Oishi and Prausnitz indicate that the solvent-activities in solvent-polymer systems calculated from UNIFAC alone are too low. The free-volume correction improve the predictions so that the agreement with experiment is within ± 10%. It should be noted that the free-volume term does not require extra adjustable parameters.

Comparison Between ASOG and UNIFAC

The UNIFAC method was not published before 1975[12]. Only a few authors have therefore made comparisons between the UNIFAC and ASOG methods.

Roekens and Verhoeye[28] compare experimental values of azeotropic temperatures and compositions for various alkane/alcohol mixtures with values computed by means of 4 different methods. One of these is the UNIFAC method and the remaining three are ASOG variants: 1) eq. 9/9b and eq. 21, 2) eq. 10 and eq. 21, 3) eq. 13/14 and eq. 21 multiplied by a factor of 1.6 (see the section: Methods Similar to the ASOG Method).

All four methods yield excellent predictions. UNIFAC and ASOG variant 1) are the best.

Messow et al.[29] compare experimental and computed values of the excess Gibbs energy for binary mixtures. They use equimolar mixtures of a solvent (cyclohexane, benzene, toluene, acetone or 2-butanone) and an alkane. For each solvent different alkanes with a carbon atom

number between 5 and 20 are used. Even though the interaction parameters used for the UNIFAC method and for the ASOG methods are determined from experimental data with lower alkanes (alkanes with a number of carbon atoms less than ten), the agreement between experimental and calculated values is good for all the mixtures. Messow et al. conclude that it is not possible to distinguish between the UNIFAC and the ASOG methods with respect to accuracy.

As a general remark we may add that a real comparison between ASOG and UNIFAC is rather difficult. As stated by Messow et al. it is not possible to see much difference in the accuracy of the predictions. Both methods give as a crude average the activity coefficients with an accuracy of $\pm$ 10%. Yet we think that at present the UNIFAC method does have some advantages compared with ASOG methods. (For obvious reasons, our point of view may be slightly biased but it is supported by others, see f.ex. Palmer[23], p. 451.)

1) The UNIFAC method has a broad range of applicability because a large number of interaction parameters has been published.

   The most severe limitation to the applicability of the ASOG method is that only a limited number of group interaction parameters are published in the open literature. Most of the published work has centered on a limited number of groups, and the groups have been the same in most of the publications.

   Some industrial companies do have extensive lists of ASOG parameters applicable to mixtures which are of importance to the company. The possession of such a list is indicated by van Aken et al.[30].

2) The group interaction parameters are much less dependent on temperature for UNIFAC than for ASOG.

3) The UNIFAC method is based on the UNIQUAC model, and hence the relations for the calculation of the combinatorial and residual terms are theoretically based. Much of the arbitrariness in the choice of equations for the two terms in ASOG is thus removed and the user will have no difficulties in defining the structural groups building up a given mixture.

4) The differences in molecular structures are taken closely into account by the use not only of the group volumes but also the group areas.

Liquid-Liquid Equilibria

For the design and operation of liquid-liquid extraction and azeotropic distillation apparatus it is essential to know the compositions of the two liquid phases in equilibrium.

The condition for equilibrium between two liquid phases I and II containing different components is:

$$x_i \, {}^{I}\gamma_i \, {}^{I} = x_i \, {}^{II}\gamma_i \, {}^{II} \qquad i = 1,2 \ldots M \qquad 28$$

Several attempts have been made to use the ASOG and UNIFAC methods to predict the liquid-liquid equilibrium compositions. In general, the interaction parameters estimated from vapor-liquid equilibrium data are not the best for predicting liquid-liquid equilibria and vice versa.

The use of the UNIFAC method for liquid-liquid calculations is described by Fredenslund et al.[2]. Prediction of liquid-liquid equilibrium compositions has been

carried out for several ternary systems exhibiting phase-splitting. In general the UNIFAC method yields a phase-split in cases where such occurs, but the predicted liquid compositions are usually not quantitatively acceptable for the design of extraction cascades. It has to be noted that only vapor-liquid equilibrium based parameters have been used in these calculations.

ASOG methods are also described for liquid-liquid calculations [31,32].

Tochigi and Kojima[31] discuss the prediction of liquid-liquid equilibria for 9 ternary systems made up of CH_2 ($\equiv CH_3$), OH and CO groups at 25 °C and 37.8 °C. The parameters were estimated from vapor-liquid equilibrium data.

Sugi and Katayama[32] measure liquid-liquid equilibrium data for three different aqueous alcohol solutions. Based on the data for the mutual solubility of the water-1-butanol system at 25 °C they determine the group-interaction parameters $a_{CH_2/OH}$ and a_{OH/CH_2}. These parameters are then used for the prediction of liquid-liquid equilibria for all the other measured systems.

The agreement between experimental and calculated equilibrium compositions is not too convincing in either of the two articles.

There is a strong need for more work on methods for the correlation and prediction of liquid-liquid equilibria. Such work is at the moment going on at our department and at other universities, and we can only hope for good and rapid progress in these activities.

Solid-Liquid Equilibria

Gmehling et al.[33] have most recently used the UNIFAC method to calculate the solubility of a solid 2 in a

liquid solvent 1. Such solubilities of solids in pure and mixed solvents are of interest in chemical process design, especially when process conditions must be specified to prevent precipitation of a solid.

As a basis for the calculations, Gmehling et al. use the following relation which is derived from standard thermodynamic considerations

$$\ell n\ \gamma_2 x_2 = \frac{\Delta H_f}{RT}\left(\frac{T}{T_m} - 1\right) \qquad 29$$

where γ_2 is the activity coefficient of the solidifying component in the solution, x_2 is the mole fraction, ΔH_f is the heat of fusion, T_m is the melting temperature of pure solid, and T is the temperature of the system.

Gmehling et al. apply the previously determined interaction parameters[2] based on vapor-liquid equilibrium data to calculate the activity coefficient γ_2. Solubilities of naphthalene, anthracene and phenanthrene in various solvents like alcohols, diethyl ether, acetone, chloroform, tetrachloromethane, hexane and acetic acid are calculated. There is a remarkable good agreement between experimental results and solubilities calculated using UNIFAC. UNIFAC does also in general predict eutectic temperatures and compositions, which are in good agreement with experiments.

Few experimental data have been reported on the solubilities of nonelectrolyte solids in mixed solvents. Gmehling et al. have found some data for the solubility of naphthalene in alcohol-water mixtures and for the solubility of anthracene in mixtures of acetone and ethanol. The experimental and predicted solubilities agree well in most cases.

Other Group Contribution Methods

A recent group-contribution model for phase equilibria, Nitta et al.[34] and Nitta et al.[23], page 421, derives - as does UNIFAC - from the lattice model for the liquid state. An equation for the configurational partition function for the mixture of groups forms the basis for calculating all liquid phase thermodynamic properties such as activity coefficients, heats of mixing, and molar volumes. ASOG and UNIFAC can not be used to predict volumetric properties. However, the model by Nitta et al. suffers from the serious disadvantage that the method can not give the activity coefficients explicitly as functions of mole fractions and temperature. This means that additional trial-and-error calculations must be carried out in the determination of separation factors.

At present, Nitta et al. give group parameters for mixtures of alkanes, alcohols and ketones only. For these mixtures, the predicted activity coefficients appear to be of similar accuracy as those resulting from ASOG and UNIFAC.

Because of their roots in lattice theory, ASOG, UNIFAC, and the model by Nitta et al. can only be used to predict liquid phase properties. A group-contribution model which can predict simultaneously the thermodynamic properties of liquid and vapor phases would be a decided improvement. This would enable the prediction of high-pressure phase equilibria, Henry constants, and other such properties. An approach suggested by Wilson[23], page 429 and Cunningham[35] may ultimately lead to a model of this type.

Wilson derives an equation of state from relations for the activity coefficients in the liquid state. Based on a group contribution method for calculation of the

activity coefficients it is thus possible to derive an analogous equation of state. The equation is called the PFGC (parameters from group contributions) equation of state.

The PFGC equation was used to simultaneously calculate vapor- and liquid-phase non-idealities: vapor pressures, densities, K-values and infinite dilution activity coefficients. The equation appears suitable for both polar and non-polar compounds.

More work is needed to see if a general equation of state applicable both in the vapor and liquid phase eventually may be derived based on the ideas behind the PFGC equation.

In the solution-of-groups approximation, there is no difference between a mixture of two or more components and a pure substance as long as the groups and the group fractions in the liquids are identical. This means that f.ex. the UNIFAC method can be used not only for mixtures but also for pure compounds. Hence it should be possible at least in principle to estimate group interaction parameters from pure component properties f.ex. vapor pressures.

Fredenslund and Rasmussen[36] have extended the UNIFAC method into correlations which are capable of predicting simultaneously pure-component vapor pressures and standard Gibbs energies of formation and mixture vapor-liquid equilibrium compositions. The results support the approach, but it is not yet possible to use the method for accurate estimation of interaction parameters from pure component properties.

Wilson[37] has used an equation of state approach to relate the vapor pressure of pure compounds from the

properties of the constituent groups. The method assumes that interacting groups are small enough that they can be considered as interacting spheres, and that the properties of materials can be correlated in terms of entropy (non-interacting hard spheres, joining interchangeable lattice groups, polar effects) and energy (ideal and non-ideal interacting between groups) contributions. Good representation of vapor pressures was obtained.

Conclusion

Our review shows that it is possible to predict with reasonable accuracy vapor-liquid equilibria for systems for which we have no experimental information.

The different methods are all based on the group-contribution concept, i.e. the liquid mixtures are considered as solutions of structural groups and not of the actual molecules. This is necessarily an approximation because any group within a molecule is not completely independent of the other groups within that molecule. But it is precisely this independence which is the basis for every group-contribution method. Despite this approximative character, the group-contribution methods have evolved into effective and reliable tools to be used by the design engineer.

ASOG and UNIFAC are the methods which are furthest developed. It is not possible to make a conclusive comparison between these two methods, but the potential user will find it more easy to implement the UNIFAC method than the ASOG methods. The reason for this is that all the necessary information and parameters for the use of UNIFAC have been published in a ready-to-use form[2,14].

Most of the published work has centered on vapor-liquid equilibria, and hence the interaction parameters are mostly based on experimental data for vapor-liquid equilibria. It may be dangerous to extend the application of the methods to other areas without changing the parameters. In the review we have shortly discussed the problems with the prediction of liquid-liquid equilibria. The same problems are encountered in the recent attempts to correlate and predict heats of mixing by means of the ASOG and UNIFAC methods. The list of references does include some publications from this area: UNIFAC[2,38]; ASOG[39,40,41,42].

As a final conclusion, we may add that even though we have good procedures for predicting vapor-liquid equilibria at low to moderate pressures for many mixtures of industrial interest, it would still be extremely helpful if more different groups were included.

List of Symbols

a_{nm}	interaction parameter between groups n and m
f_i	fugacity of component i
f_i^o	liquid phase reference fugacity
ΔH_f	heat of fusion
K_i	separation factor for component i ($\equiv y_i/x_i$)
M	number of components in a mixture
N	number of groups in a system
n_i	number of atoms (other than hydrogen) in component i

P	pressure
P_i^S	vapor pressure of pure component i
q_i	area parameter for pure component i
Q_k	area parameter for group k
r_i	size parameter for pure component i
R_k	volume parameter for group k
R	the gas constant
S_i	number of size groups in component i
T	temperature
T_m	melting point
V_i	molar liquid volume of component i
x_i	liquid phase mole fraction of component i
X_k	group fraction of group k
y_i	vapor phase mole fraction of component i
γ_i	activity coefficient of component i
γ_i^C	combinatorial part of the activity coefficient γ_i
γ_i^R	residual part of the activity coefficient γ_i
Γ_k	activity coefficient of group k
$\Gamma_k^{(i)}$	activity coefficient of group k in pure component i
θ_i	area fraction of component i

θ_k area fraction of group k

$\nu_k^{(i)}$ number of interaction groups of kind k in component i

ρ relative size ratio ($\equiv S_1/S_2$)

φ_i fugacity coefficient of component i

Φ_i volume fraction of component i

References

1. C.H. Deal and E.L. Derr, Ind. Eng. Chem., 60(4), 28 (1968).

2. Aa. Fredenslund, J. Gmehling and P. Rasmussen, "Vapor-Liquid Equilibria using UNIFAC", Elsevier, 1977.

3. J. Gmehling and U. Onken, "Vapor-Liquid Equilibrium Data Collection", Dechema Chemistry Data Series, Frankfurt 1977.

4. G.M. Wilson and C.H. Deal, I&EC Fundamentals 1(1), 20 (1962).

5. E.L. Derr and C.H. Deal, I. Chem. E. Symp. Ser., 32, 3:37 (1969).

6. W.A. Scheller, I&EC Fundamentals 4(4), 459 (1965).

7. G.A. Ratcliff and K.C. Chao, Can. J. Chem. Eng., 47, 148 (1969).

8. J.N. Brønsted and J. Koefoed, Det Kgl. Danske Videnskabernes Selskab, Mat.-Fys. Meddelelser, 22(17), 1 (1946).

9. V.C. Maripuri and G.A. Ratcliff, Can. J. Chem. Eng., 49, 375 (1971).

10. M. Ronc and G.A. Ratcliff, Can. J. Chem. Eng., 49, 825 (1971).

11. M. Ronc and G.A. Ratcliff, Can. J. Chem. Eng., 53, 329 (1975).

12. Aa. Fredenslund, R.L. Jones and J.M. Prausnitz, AIChE Journal, 21(6), 1086 (1975).

13. D.S. Abrams and J.M. Prausnitz, AIChE Journal, 21 (1), 116 (1975).

14. Aa. Fredenslund, J. Gmehling, M.L. Michelsen, P. Rasmussen and J.M. Prausnitz, I&EC Proc. Des. Dev., 16, 450 (1977).

15. V.C. Maripuri and G.A. Ratcliff, Can. J. Chem. Eng., 49, 506 (1971).

16. E.L. Derr and C.H. Deal, Adv. in Chemistry Series, 124, Am. Chem. Soc., 1973, p. 11.

17. D.A. Palmer, Chemical Engineering, June 9, 1975, p. 80.

18. P.M. Cukor, Ph.D. Dissertation, University of California, Berkeley, 1970.

19. K. Tochigi and K. Kojima, J. Chem. Eng. Japan, 9 (4), 267 (1976).

20. K. Tochigi, S. Minami and K. Kojima, J. Chem. Eng. Japan, 10(5), 349 (1977).

21. W.A. Scheller, J.L. Petricek and G.C. Young, I&EC Fundamentals, 11(1), 53 (1972).

22. N.K. Tikhonova, T.V. Rogovina, S.I. Goloborodkin and A.S. Mozzhukhin, Zh. Prikl. Khim., 49(2), 342 (1976).

23. T.S. Storwick and S.I. Sandler (Editors), "Phase Equilibria and Fluid Properties in the Chemical Industry", ACS Symposium Series 60, 1977.

24. J. Gmehling and U. Onken, Ber. Bunsenges., 81(10), 1023 (1977).

25. U. Onken and J. Gmehling, Chem. Ing. Techn., 49(5), 404 (1977).

26. T. Oishi and J.M. Prausnitz, Submitted to I&EC Proc. Des. Dev. (1978).

27. P.J. Flory, Disc. Far. Soc., 49, 7 (1970).

28. E.J.L. Roekens and L.A.J. Verhoeye, J. Appl. Chem. Biotechnol., 26, 595 (1976).

29. U. Messow, H. Becke, W.H. Hauthal and K. Quitzsch, Chem. Techn., 29(7), 396 (1977).

30. A.B. van Aken, J.N.J.J. Lammers and M.M. Simon, World Congress on Chemical Engineering, Amsterdam, Holland, June 1976.

31. K. Tochigi and K. Kojima, J. Chem. Eng. Japan, 10(1), 61 (1977).

32. H. Sugi and T. Katayama, J. Chem. Eng. Japan, 10(5), 400 (1977).

33. J. Gmehling, T.F. Anderson and J.M. Prausnitz, Submitted to I&EC Fundam. Quarterly (1978).

34. T. Nitta, E.A. Turek, R.A. Greenkorn and K.C. Chao, AIChE Journal, 23(2), 144 (1977).

35. J. Cunningham, Masters Thesis, Brigham Young University, Provo, Utah, 1974.

36. Aa. Fredenslund and P. Rasmussen, Submitted to AIChE Journal (1978).

37. G.M. Wilson, Paper no. 34d, AIChE 63rd Annual Meeting, Chicago, 1970.

38. I. Nagata and T. Ohta, Chem. Eng. Sci., 33, 177 (1978).

39. T.H. Nguyen and G.A. Ratcliff, Can. J. Chem. Eng., 49, 889 (1971).

40. T.H. Nguyen and G.A. Ratcliff, Can. J. Chem. Eng., 52, 641 (1974)

41. T.H. Nguyen and G.A. Ratcliff, J. Chem. Eng. Data, 20(3), 256 (1975).

42. T.H. Nguyen and G.A. Ratcliff, Can. J. Chem. Eng., 49, 120 (1971).