

From UNIQUAC to Modified UNIFAC Dortmund: A Discussion

Edison Muzenda

Abstract—This paper reviews and discusses the universal quasi-chemical theory and group contribution methods focusing on their application in phase equilibrium modeling and computation. The historical perspective, algorithm, strength, weaknesses and limitations are presented. The paper concludes with comparison of the performance of the various UNIFAC models.

Keywords—Gibbs energy, Group contribution, phase equilibrium, quasi-chemical, UNIFAC.

I. UNIVERSAL QUASI-CHEMICAL (UNIQUAC) EQUATION

THE UNIQUAC equation was developed by Abrams and Prausnitz in 1975, and is based primarily on Guggenheim's quasi-chemical lattice model developed in 1952 [1]. Guggenheim postulated that a liquid can be represented by a three-dimensional lattice with lattice sites spaced equidistant from each other. A volume, known as a cell, exists in the immediate vicinity of each lattice site. Each molecule in the liquid is divided into attached segments, and each segment occupies one cell. The total number of cells is then considered to be equal to the total number of segments [1]. In its original form, Guggenheim's lattice model was restricted to describing only small molecules which were essentially the same size. Abrams and Prausnitz however managed successfully to extend Guggenheim's lattice theory to mixtures containing molecules of different size and shape by incorporating and adapting Wilson's local-composition model into Guggenheim's lattice model [1].

A. Mixing Theory

The effects of volume on mixtures of nonelectrolyte liquids at constant temperature and constant pressure (remote from critical conditions) are minimal. However, Scatchard (1937) demonstrated that even minor volume changes can significantly affect the entropy- and enthalpy of mixing. Fortunately these effects are largely nullified in the excess Gibbs energy. Therefore, for mixtures of non-electrolyte liquids at low or modest pressures, Hildebrand and Scott (1950) proposed that the excess Gibbs energy of mixing (at constant temperature and pressure) is approximately equal to

the excess Helmholtz energy of mixing (at constant temperature and volume) [1]. This hypothesis leads to the generalised excess Gibbs energy UNIQUAC expression as defined in (1).

$$\left(\frac{a^E}{RT}\right)_{T,V} \approx \left(\frac{g^E}{RT}\right)_{T,P} = \left(\frac{g^E}{RT}\right)_C + \left(\frac{g^E}{RT}\right)_R \quad (1)$$

The UNIQUAC equation is described in terms of the combinatorial and residual terms. The combinatorial term is used to describe the dominant entropic contribution. It uses only pure-component data and is determined only by the size, shape and composition of the molecules in the mixture [2]. For binary mixtures the excess Gibbs energy expression of the combinatorial term is

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

The residual term is used to describe the intermolecular forces responsible for the enthalpy of mixing. Thus the two adjustable binary interaction parameters appear only in the residual term [2]. For binary mixtures the residual term is described in terms of excess Gibbs energy as in (3).

$$\left(\frac{g^E}{RT}\right)_R = -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12}) \quad (3)$$

The average segment fraction (Φ_i) is only used in the calculation of the combinatorial term. For a binary mixture, it is defined mathematically as

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad (4)$$

and

$$\Phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \quad (5)$$

The average area fraction is used in both the combinatorial and residual terms. When using the empirical adjustment of the (q'_i) parameters, as defined by Anderson [3], the average area fraction should be similarly depicted as (θ'_i). For a binary mixture, the average area fraction is defined as in (6)

E. Muzenda is with the Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Doornfontein, Johannesburg 2028; phone: 0027-11-5596817; Fax: 0027-11-5596430; e-mail: emuzenda@uj.ac.za).

$$\theta_1 \equiv \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \quad \text{or} \quad \theta_1 \equiv \frac{x_1 q'_1}{x_1 q'_1 + x_2 q'_2} \quad (6)$$

and

$$\theta_2 \equiv \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \quad \text{or} \quad \theta_2 \equiv \frac{x_2 q'_2}{x_1 q'_1 + x_2 q'_2}$$

B. Pure-component Structural Parameters

In terms of lattice theory, each molecule of component (*i*) consists of a set of bonded segments occupying a set volume (parameter r_i). In terms of component (*i*), parameter (r_i) is the van der Waals molecular volume relative to that of a standard segment [1] and is expressed as

$$r_i = V_{wi} / V_{ws} \quad (7)$$

In (7), (V_{wi}) is the van der Waals volume of molecule (*i*) as published by Bondi in 1968, and (V_{ws}) is the van der Waals volume of a standard segment. The volume for a standard sphere in terms of its radius (R_{ws}) is as in (8)

$$V_{ws} = 4/3\pi R_{ws}^3 \quad (8)$$

The UNIQUAC arbitrarily defines a standard segment as a sphere which satisfies (9) for a linear polymethylene molecule of infinite length

$$\left(\frac{z}{2}\right)(r - q) = r - 1 \quad (9)$$

Numerical results are insensitive to the value of the lattice co-ordination number (z) provided a reasonable number between 6 and 12 is selected. The lattice co-ordination number is thus arbitrarily set equal to 10. Segments differ in terms of their external contact area (parameter q_i) for example the CH₃ molecules of pentane have a larger exposed external area than the CH₂ molecules, but the central carbon of neopentane has no external contact area at all. Parameter (q_i) is referred to as the van der Waals molecular area relative to that of a standard segment [1] and is defined as

$$q_i = A_{wi} / A_{ws} \quad (10)$$

In (10), (A_{wi}) is the van der Waals surface area of molecule (*i*) as published by Bondi in 1968, and (A_{ws}) is the van der Waals surface area of a standard segment, described in (9). The area of a standard sphere in terms of its radius (R_{ws}) is provided as

$$A_{ws} = 4\pi R_{ws}^2 \quad (11)$$

Bondi stipulated that van der Waals volume and area of an *n*-mer of polymethylene are *n* times the volume and area of a methylene group:

$$V_{wi} = n(10.23) \text{ cm}^3 / \text{mole} \quad (12)$$

$$A_{wi} = n(1.35) \times 10^9 \text{ cm}^2 / \text{mole} \quad (13)$$

Substituting (7), (8) and (10), (11) and (12), (13) into (9) with (R_{ws}) being fixed at 10.95×10^{15} cm/mole as *n* tends to infinity, yields the following expressions for the parameters (r_i) and (q_i):

$$r_i = V_{wi} / 15.17 \quad (14)$$

$$q_i = A_{wi} / (2.5 \times 10^9) \quad (15)$$

C. Binary Adjustable Parameters (τ_{ij})

The binary adjustable parameters (τ_{ij}) contain the characteristic interaction energy parameters (u_{ij}) which represent average intermolecular energies, since in a given molecule the segments are not necessarily chemically identical [1]. These in turn relate to the UNIQUAC binary interaction parameters (a_{ij}) as shown in (16).

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) \equiv \exp\left(-\frac{a_{12}}{T}\right) \quad (16)$$

and

$$\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) \equiv \exp\left(-\frac{a_{21}}{T}\right) \quad (17)$$

The parameters (a_{ij}) are determined from binary experimental data [3], sourced mainly from VLE data (P, y, x) at constant temperature, VLE data (T, y, x) at constant pressure and total pressure data (P, x or y) at constant temperature. The UNIQUAC can be used to calculate activity coefficients for a binary mixture according to (18) and (19).

$$\ln \gamma_1 = x_1 \ln \frac{\Phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1} + \Phi_2 \left(l_1 - \frac{r_1}{r_2} l_2 \right) - q_1 \ln(\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) \quad (18)$$

and

$$\ln \gamma_2 = x_2 \ln \frac{\Phi_2}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\Phi_2} + \Phi_1 \left(l_2 - \frac{r_2}{r_1} l_1 \right) - q_2 \ln(\theta_2 + \theta_1 \tau_{12}) + \theta_1 q_2 \left(\frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} - \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} \right) \quad (19)$$

The pure-component parameters (l_1) and (l_2) are determined as in (20) and (21)

$$l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1) \quad (20)$$

$$l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1) \quad (21)$$

Strengths

The UNIQUAC model gives reliable estimates of both vapour-liquid and liquid-liquid equilibria for binary and multi-component mixtures containing a variety of non-electrolyte polar or non-polar mixtures [2].

The UNIQUAC model uses only two adjustable parameters per binary. This makes the equation simpler to use for multi-component mixtures [2].

The UNIQUAC model can yield adequate results even when available experimental data is limited.

Weaknesses

Molecular-dynamic calculations have shown that UNIQUAC often over-rectifies the deviations for random mixing because the magnitudes of the arguments of the Boltzmann factors are too large. Thus UNIQUAC is often not as accurate as NRTL for LLE calculations, and Wilson for VLE calculations.

II. GROUP CONTRIBUTION METHODS

Reliable phase equilibrium data is essential for optimum separation process synthesis, design and operation. When experimental binary data is available, phase equilibrium behavior is easily modeled with the help of cubic EoS (using fugacity coefficient data) and local composition g^E -models (using activity coefficient data). When little or no experimental data are available, group contribution methods can be employed to predict the phase equilibrium under specified conditions of temperature and composition [4].

A. Historical Perspective

The concept of solution-of-groups is accredited to Langmuir (1925) who postulated that the force field around a group or radical which can interact with other molecules is characteristic of that group or radical, and is largely independent of the nature of the rest of the molecule of which it forms part. He considered the various interfacial (van der Waals) energies that could occur between pairs of dissimilar groups in contact within molecules in a liquid or liquid mixture, and ignored local molecular orientation and segregation contributions to excess entropy. Each of the interfacial energies were summed based on the respective kinds of intra-molecular surface fractions, as well as the overall surface fraction of solute and solvent in a binary mixture. Expressions for the partial pressures of the components in binary mixtures were then derived based on the above summations, which were similar to van Laar equations expressed in terms of surfaces [5]. Thus, if the physical interactions between such groups could be quantitatively characterised, then intermolecular interactions could possibly be estimated [6]. By incorporating the above into a suitable thermodynamic model, Langmuir believed that thermodynamic properties could be estimated. Langmuir's hypothesis was only realised with the development of the Analytical Solution of Groups (ASOG) model in the late 1950s and 1960s, and the Universal Quasi-chemical Functional Activity Coefficient (UNIFAC) model in 1975.

The primary function of solution-of-groups models is to predict phase equilibria of systems for which no experimental data exists, using existing phase equilibrium data [1]. For many mixtures of technical interest, binary data is often incomplete or totally absent, hence the need for predictive systems. To account for systems with missing binary data Scatchard (1931), and Hildebrand and Wood in 1933, independently developed the first powerful and widely

applicable predictive model based on regular solution theory [7], using pure-component data. However, the greatest weakness of regular solution theory was that it could not be applied to polar systems and this was addressed with the introduction of the ASOG model in 1969.

B. Solution of Groups Concept

Whilst thousands of chemical compounds exist, the number of functional groups which constitute these compounds is much smaller. It is therefore convenient to correlate the properties of the large number of chemical compounds in terms of a much smaller group of parameters. It is assumed that a molecule is characterized by contributions of individual chemical groups making up the composition of the molecule concerned, and that the molecule's physical properties are the sum of contributions made by the molecule's functional groups [8]. Basically, certain functional groups (such as ketones) influence their molecules in certain ways, which will differ from the way other molecular groups (such as alcohols) interact with their molecules. Similarly, the contribution of the carbonyl group in a ketone (such as acetone) will differ to that of a carbonyl group in an organic acid (such as acetic acid). However, the contribution of the carbonyl group within differing ketones (such as acetone and 2-butanone) will be similar [8].

Group contribution methods (GCMs) are thus based on the principal hypothesis that they are additive, and that the contribution made by one group is assumed to be independent of that made by another group (known as the proximity effect) [8], [9]. This assumption is only considered valid when the influence of any one group in a molecule is unaffected by the properties of other groups within that molecule.

The assumption of group independence is not thermodynamically correct – for example, there will be differences between the properties of the ketone group in 1-hexanone to that of 3-hexanone [2]. Furthermore, any group within a molecule is not totally independent of other groups within the same molecule [6]. Because group contribution methods do not account for the above, these models are in essence approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule [8].

The accuracy of group contribution methods correlation would improve by increasing distinction within groups, such as distinguishing between a straight-chain carbonyl and that found in a cyclic hydrocarbon. Thus in the limit, as more and more distinctions are made, the ultimate group (the molecule itself) is recovered. Whilst this would improve agreement of group contribution methods with experimental results, the advantage is lost. In practice a suitable GCM is a compromise, where the number of distinct groups remains small but not so small as to neglect significant effects of molecular structure on physical properties [8].

Strengths

The number of functional groups is much smaller (less than 100) than the number of possible multi-component liquid compounds of interest (possibly in the millions) [4], [8].

Weaknesses

Prausnitz [2] emphasised that group contribution methods (GCMs) only yield approximate VLE data, a viewpoint supported by Fredenslund *et al* [8]. As such, Prausnitz cautioned that the predicted VLE data should only be used for preliminary design, and when available, reliable experimental data should be used for detailed design.

C. Analytical Solution of Groups (ASOG)

Initial development

ASOG had its roots established in 1959, when Derr and co-workers [10], [11] used group contributions to correlate heats of mixing. Thereafter in 1962 Wilson and Deal [12] expanded the solution-of-groups concept to include determination of activity coefficients. The above work culminated in 1969 with the presentation of the Analytical-Solution-of-Groups (ASOG) by Derr and Deal. The model was further developed by Ronc and Ratcliff in 1971 and 1975 [13].

Later development

The ASOG model was redefined in 1979 by Kojima and Tochigi, who simultaneously modified group interaction parameters (GIPs) for 31 groups in an attempt to account for the effect of temperature changes. By 1990, with the assistance of Tochigi *et al*, the number of GIPs had increased to 341 group pairs comprising 43 groups. Work was also done on GIPs for group pairs comprising hydrofluoroethers in 2002 and 2007, and on tetrahydropyran in 2008 [14]. In 2011 work was done to revise and extend GIPs relating to NMP in particular [14]. The ASOG derivations discussed below are based on the model as defined by Kojima and Tochigi [15].

ASOG model algorithm – Wilson's Four Rules for solution-of-groups

The basic structure of the ASOG model is founded on the four rules as laid out by Wilson and Deal [12]. Rules 1, 2 and 3 were based on the hypothesis that the excess entropy of mixing which resulted from size effects could not be associated with the residual energy resulting from group interactions. Wilson's Fourth Rule enabled experimental data from one system to be applied to a second system involving the same groups. Wilson's First Rule specifies that the logarithm of the molecular activity coefficient is assumed to be the sum of two contributions. The first term (the combinatorial term) describes the entropic contributions resulting from differences in molecular sizes of the solute and its solvent environment. The second term (the residual term) describes the enthalpic contributions resulting from intermolecular interactions, as well as any entropic contributions unaccounted for in the combinatorial term [12]. Wilson's First Rule led to the mathematical expression described in (22).

$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^G \quad (22)$$

Wilson's Second Rule [12] stipulates that the combinatorial term is arbitrarily estimated by using the athermal Flory-Huggins equation which is expressed in terms of the numbers of constituent atoms in a molecule (i) other than hydrogen. This results in the combinatorial contribution expressed in (23), with the summation being made over all the components (j) in the solution.

$$\ln \gamma_i^{FH} = 1 + \ln \left(\frac{\nu_i^{FH}}{\sum_{j=1}^{NC} x_j \nu_j^{FH}} \right) - \frac{\nu_i^{FH}}{\sum_{j=1}^{NC} x_j \nu_j^{FH}} \quad (23)$$

Wilson's Third Rule assumes that the contribution resulting from molecular group interactions is the summation of the individual contributions of each solute group (k) in the solution environment, less the summation of the individual contributions in the conventional standard state (i.e. pure solute) environment [12]. The individual group activity coefficients are arbitrarily defined as a mixture of pure groups. Thus

$$\ln \gamma_i^G = \sum_{k=1}^{NG} \nu_{k,i} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (24)$$

The group interaction contributions are based on the assumption that the total free energy arising from group interactions depends only on the group environment. This assumption can be made because inter-atomic interactions are highly localized, with significant interactions occurring only between the nearest atomic neighbors, which are mostly non-bonded groups. The contributions therefore are not affected by how or whether the groups are connected together.

Wilson's Fourth Rule states that the individual group contributions (Γ_k) in any environment containing a specified number of groups are assumed to be only a function of group concentrations, in this case, group fractions (X_n). Thus for individual mixture group contributions (Γ_k) and pure-component group contributions ($\Gamma_k^{(i)}$)

$$\ln \Gamma_k = 1 - \ln \left(\sum_{n=1}^{NG} X_n a_{kn} \right) - \sum_{n=1}^{NG} \left\{ \frac{X_n a_{nk}}{\sum_m^{NG} X_m a_{nm}} \right\} \quad (25)$$

The group interaction parameter (a_{kn}), characteristic of groups (k) and (n), is defined as

$$a_{kn} = \exp \left(\frac{m_{kn} + n_{kn}}{T} \right) \quad (26)$$

In (26), (m_{kn}) and (n_{kn}) are the group pair parameters, characteristic of groups (k) and (n) which are independent of temperature [16] and that $a_{kn} \neq a_{nk}$. The group fractions are defined mathematically as

$$X_k = \frac{\sum_{i=1}^{NC} x_i \nu_{n,i}}{\sum_{i=1}^{NC} x_i \sum_{k=1}^{NG} \nu_{k,i}} \quad (27)$$

D. Universal Quasi-chemical Functional Activity Coefficient (UNIFAC)

Historical perspective

Work commenced on the development of the original UNIFAC model in 1973 by Gmehling, under the directive of Onken, at the University of Dortmund. Gmehling thereafter collaborated with Fredenslund from the University of Lyngby, Denmark, where a decision was made to pursue further development of UNIFAC instead of ASOG. The original UNIFAC model was initially published by Fredenslund, Jones and Prausnitz in 1975 [8], followed by the publication of a book on UNIFAC in 1977 by Fredenslund, Gmehling and Rasmussen [17]. The publication included the exact calculation procedure, a large number of group interaction parameters, numerous applications of UNIFAC, and extensive software source code in 1977 [7]. Thereafter the UNIFAC parameters were revised, extended and published in a series of five papers between 1977 and 1991 [18]. The most extensive of these were the papers presented by Gmehling *et al* in 1982, Macedo *et al* in 1983 and Tiegs *et al* in 1987 [19].

Overview

UNIFAC (the acronym for UNIQUAC Functional-group Activity Coefficients) is used in predicting thermodynamic properties (especially activity coefficients) in non-electrolyte liquid mixtures [8]. The model combines the solution-of-groups concept of Wilson [12] in 1962 with the UNIQUAC model. The UNIQUAC model, which in turn is based on an extension of Guggenheim's quasi-chemical theory of liquid mixtures [1], has been slightly adapted for use with group contributions. In essence the UNIFAC model involves [8]:

- suitable reduction of experimentally obtained activity coefficient data in order to obtain parameters which characterize the interactions between pairs of structural groups, and
- the use of these parameters in predicting activity coefficients for other systems for which no experimentally obtained data is available, but which contain the same functional groups.

The group-interaction parameters thus obtained can predict activity coefficients in a large number of binary and multicomponent mixtures with reasonably good accuracy. The UNIFAC model contains two adjustable parameters per pair of functional groups.

The Original UNIFAC model unfortunately had its weaknesses. In order to mitigate the effects of these weaknesses, various modifications to the original UNIFAC model were proposed. The most notable of these changes is the Modified UNIFAC Dortmund (Abbreviated Do.) model

published by Weidlich and Gmehling [20] in 1987, and the Modified UNIFAC Lyngby model presented by Larsen, Rasmussen and Fredenslund in 1987 [21].

III. THE UNIFAC GROUP CONTRIBUTION MODEL

A. The Original UNIFAC

Original UNIFAC Algorithm

As with the ASOG and UNIQUAC models, all UNIFAC models consists of a combinatorial contribution (which describes the excess Gibbs energy arising due to differences in molecular size and shape) and a residual term (which describes the excess Gibbs energy differences due to molecular interactions [6]. Thus, defined mathematically [8]

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (28)$$

The combinatorial term is identical to that of the UNIQUAC and is derived from statistical mathematical arguments. The interpretation selected for use in both UNIQUAC and Original UNIFAC is the Staverman-Guggenheim potential [17]. The Staverman-Guggenheim potential consists of the original Flory-Huggins combinatorial as refined by Huggins in 1942 (29) [21] along with a Staverman-Guggenheim correction term proposed by Staverman in 1950.

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i} \quad (29)$$

Staverman [22] extended the Flory-Huggins combinatorial to compensate for molecules containing rings and crosslinks. Furthermore, Staverman [22] revised Guggenheim's (q) parameter to account for molecular ring formation as well as back bending of flexible and branched molecules. The addition of the Staverman-Guggenheim correction term results in the following combinatorial term as in (30):

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i} - \frac{z}{2} q_i \left(\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \right) \quad (30)$$

The form of the Staverman-Guggenheim equation used by Fredenslund *et al* [8] is shown in (31).

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (31)$$

In (31) the pure-component lattice parameter (l_i) is defined as in (32) [8].

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (32)$$

Later representations of the Original UNIFAC combinatorial utilize the expression in **Error! Reference source not found.** [20],[21],[23]. In these representations, the lattice parameter shown in **Error! Reference source not found.** is absorbed during simplification of the combinatorial term in **Error! Reference source not found.**. It should be noted that whilst the combinatorial contribution is usually smaller than the residual contribution, its contribution becomes

notable when the molecules differ appreciably in size and shape [17].

Definition of parameter (θ_i)

Parameter (θ_i) is the area fraction of component (i) and is expressed as in (33) [8]

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (33)$$

The pure-component area parameter (q_i) is calculated as the sum of the group area parameters (Q_k) which are obtained from published tables, i.e. [8].

$$q_i = \sum_k v_k^{(i)} Q_k \quad (34)$$

In (34), ($v_k^{(i)}$) is the number of groups of kind (k) in a molecule of component (i) and is thus always an integer [1]. The group area parameter is obtained from the van der Waals group surface areas (A_{wk}) as defined by Bondi in 1968, thus [8]

$$Q_k = A_{wk} / (2.5 \times 10^9) \quad (35)$$

Definition of parameter (Φ_i)

Parameter (Φ_i) is the segment (i.e. volume) fraction of component (i) and is defined as [8]

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (36)$$

The pure-component volume parameter (r_i) is calculated as the sum of the group volume parameters (R_k) which are obtained from published tables, i.e. [8]

$$r_i = \sum_k v_k^{(i)} R_k \quad (37)$$

The group volume parameter is obtained from the van der Waals group volume (V_{wk}) as defined by Bondi in 1968 as in (38) [8].

$$R_k = V_{wk} / 15.17 \quad (38)$$

The group residual activity coefficients are computed similarly to the residual part of the UNIQUAC equation [18] but adapted to conform to the solution-of-groups concept as in (39) [8].

$$\ln \gamma_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (39)$$

In (39), parameter (Γ_k) is the residual activity coefficient of the group (k), whereas parameter ($\Gamma_k^{(i)}$) represents the residual activity coefficient of group (k) in a reference solution which contains only molecules of type (i). The group residual activity coefficients (Γ_k) and ($\Gamma_k^{(i)}$) are calculated using (40) [8]:

$$\ln \Gamma_k = Q_k \left[1 - \ln \sum_m \Theta_m \Psi_{mk} - \sum_m \left(\frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right) \right] \quad (40)$$

The group area fraction (Θ_m) is defined as [8]

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (41)$$

The mole fraction of group (m) in the mixture (X_m), is calculated as in (42) [17]:

$$X_m = \frac{\sum_j v_m^{(j)} X_j}{\sum_j \sum_n v_n^{(j)} X_j} \quad (42)$$

The group interaction parameter (Ψ_{mk}) is given by (43) [8]:

$$\Psi_{mk} = \exp \left[- \frac{U_{mn} - U_{nn}}{RT} \right] = \exp \left(- \frac{a_{mn}}{T} \right) \quad (43)$$

Limitations

Fredenslund *et al* [17] reported the following limitations to the application of the UNIFAC:

- The accuracy of UNIFAC is only guaranteed within a temperature range of 300 – 425 Kelvins (27°C – 152°C).
- UNIFAC can only model systems at low to moderate pressures (up to a few atmospheres).
- UNIFAC may be applied to nonelectrolyte systems containing binary and multicomponent mixtures at conditions where the UNIQUAC model applies. Thus UNIFAC is only applicable for systems remote from critical conditions.
- All components must be condensable.
- Original UNIFAC is not suited to systems containing polymers as the absence of the free-volume (FV) term in the combinatorial term has a marked impact on the accuracy of results.
- The model should be used with extreme caution when modelling systems containing more than ten functional groups.

Strengths

The UNIFAC method is applicable to a wide range of non-electrolyte mixtures exhibiting either positive or negative deviations from Raoult's law.

UNIFAC may be used to predict activity coefficients for components in unknown binary systems which form part of a given multicomponent system. The predicted activity coefficients can then be used to generate binary parameters in any excess Gibbs energy model [8].

Weaknesses

Poor results are predicted for enthalpies of mixing, hence the temperature dependence of the Gibbs excess energy is not estimated to the required degree of accuracy [20].

Poor results are obtained for infinite dilution activity coefficients, excess enthalpies (h^E) and systems with compounds very different in size. This is because the VLE data base used for fitting group interaction parameters was of limited concentration range (5 - 95 %) and is therefore not from the dilute region [4].

Poor results are obtained for systems with compounds which are very different in size. This is because the model was derived for compounds similar in size [4].

It is generally acknowledged that UNIFAC is the most successful of the g^E -models [24]. However, the UNIFAC model from two major types of weaknesses. The first are those weaknesses that prevail for all types of g^E -models such as the inability of these models to describe critical conditions, and that other thermodynamic properties such as density and enthalpy cannot be described from the same model. The second class of weaknesses are those inherited from the Original UNIFAC model.

In order to mitigate or rectify the inconsistencies relating to the second class of weaknesses, and hence improve on the accuracy of the original UNIFAC model, different modifications to UNIFAC were proposed by various authors. Changes to both combinatorial and residual terms, as well as the introduction of temperature-dependant group interaction parameters are some of the modifications introduced. The various modifications are discussed in the following sections.

B. Effective UNIFAC

Nagata and Koyabu [25] in 1981 published the 'Effective UNIFAC' model, the first major proposed modification to the Original UNIFAC model. They based their modifications to the original UNIFAC on an extension of the 'effective UNIQUAC' model published by Nagata and Katoh earlier in 1981, which was shown to possess some improvements on the original UNIQUAC equation in calculating VLE, LLE and SLE data. Nagata and Koyabu chose to leave the combinatorial term unchanged, and decided instead to focus on modifications to the residual term. Firstly, a Flory-Huggins type term was introduced at the end of the residual activity coefficient term ($\ln \gamma_i^R$), resulting in (44):

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] - \left(\ln \frac{\Theta_i}{x_i} + 1 - \frac{\Theta_i}{x_i} \right) \quad (44)$$

Furthermore, the group surface area fraction (θ_m) used in the original expression for the group residual activity coefficient ($\ln \Gamma_k$) was replaced by the group molar fraction (X_m) to yield (45).

$$\ln \Gamma_k = Q_k \left[1 - \ln \sum_m X_m \Psi_{mk} - \sum_m \left(\frac{X_m \Psi_{km}}{\sum_n X_n \Psi_{nm}} \right) \right] \quad (45)$$

In (45), (X_m) is calculated using the Original UNIFAC equation for the group molar fraction and the group interaction parameter expression was modified as in (46).

$$\Psi_{mn} = \left(\frac{Q_m}{Q_n} \right) \left[\exp \left(- \frac{a_{mn}}{T} \right) \right] \quad (46)$$

Weaknesses

The Effective UNIFAC yielded similar results to Original UNIFAC in most cases [25]. Thus no marked improvement in infinite dilution activity coefficients prediction was achieved. Voutsas and Tassios [26] concur that Effective UNIFAC

showed limited improvements in describing residual Gibbs energy over other modified UNIFAC publications.

Thus, further development of Effective UNIFAC as an alternative to the Original UNIFAC was subsequently abandoned.

C. Modified UNIFAC (Lyngby)

The work of Kikic *et al* in 1980 [27] and Alessi *et al* in 1982 [23] form part of the foundational changes implemented in the Modified UNIFAC (Lyngby) model, which was published by Larsen, Rasmussen and Fredenslund in 1987 [21]. In contrast to Nagata and Koyabu, work done on the Modified UNIFAC (Lyngby) model focused on improvements to the combinatorial expression of Original UNIFAC.

The publication of Kikic *et al* (1980)

The work of Kikic *et al* focused on the publication in 1975 by Donohue and Prausnitz, which investigated possible modifications to the group volume fraction parameter (Φ_i). Donohue and Prausnitz proposed the following three alternate expressions [27]

a) Replacing the expression for (Φ_i) – equation (36) – with the expression for the group surface area fraction (θ_i) – equation **Error! Reference source not found.**

b) Replacing the van der Waals molecular volume parameter (r_i) contained in the original expression for (Φ_i) – i.e. equation **Error! Reference source not found.** – with a molar volume (V_i). This would result in the following changes to (36):

$$\psi_i = \frac{V_i x_i}{\sum_j V_j x_j} \quad (47)$$

c) Retaining parameter (r_i), but with the inclusion of an exponent of $2/3$ to (r_i) – this was based on comparisons of experimental results of a large number of aliphatic hydrocarbons. This would result in the following expression:

$$\psi_i = \frac{r_i^{2/3} x_i}{\sum_j r_j^{2/3} x_j} \quad (48)$$

In (47), (ψ) represents the revised group volume fraction parameter. After investigating the three proposals, it was concluded that the use of options (b) and (c) resulted in much improved predictions, and it was proposed that one of these two expressions be used for future modifications to UNIFAC.

The publication of Alessi *et al* (1982)

Alessi *et al* [23] investigated the use of GLC data to obtain activity coefficients, which could then be used to estimate reliable UNIFAC parameters. They also investigated the possibility of a modified UNIFAC combinatorial term using the expression derived in equation (48). They concluded that the modification to Original UNIFAC proposed was enough to produce reliable activity coefficients.

The Modified UNIFAC (Lyngby) Model

The publication of the Modified UNIFAC (Lyngby) Model

by Larsen, Rasmussen and Fredenslund in 1987 [21] incorporated the change proposed by Kikic *et al*, along with another major change to the combinatorial term. The Staverman-Guggenheim (S-G) correction to the Flory-Huggins combinatorial was dropped because the effects of the S-G corrections were often negligible and some excessively large S-G corrections resulted in negative excess entropy values, which were considered unrealistic. The Modified UNIFAC (Lyngby) revised combinatorial term is as in (49) [21].

$$\ln \gamma_i^C = \ln \frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i} \quad (49)$$

In (49), (ψ) represents the modified group volume fraction parameter proposed by Kikic *et al* [27] in 1980 as expressed in **Error! Reference source not found.** The residual term was left unchanged from the Original UNIFAC version. However temperature dependence was introduced to the interaction parameter (Ψ_{mn}) [28], [29].

$$\Psi_{mn} = \exp \left\{ - \left[\frac{a_{mn} + b_{mn}(T - T_0) + c_{mn} \left(T \ln \frac{T_0}{T} + T - T_0 \right)}{T} \right] \right\} \quad (50)$$

Strengths

The Modified UNIFAC (Lyngby) yields 'somewhat better' VLE data predictions than Original UNIFAC.

D. Modified UNIFAC Dortmund

Due to increased demand for a more accurate model than Original UNIFAC, the research groups of Prof. Fredenslund (University of Denmark, Lyngby) and Dr. Gmehling (University of Dortmund) agreed to collaborate on the dual development of a modified UNIFAC model [20], [21] in order to ensure success. Thus, work proceeded simultaneously on the development of Modified UNIFAC (Lyngby) and Modified UNIFAC (Dortmund) (Do) [30]. This resulted in the publication of the Modified UNIFAC (Do) model by Gmehling and co-workers in 1987, the same year that Modified UNIFAC (Lyngby) was also published. Modified UNIFAC (Do) model incorporated the following changes to Original UNIFAC [20]:

- As was the case for Modified UNIFAC (Lyngby), a modified combinatorial term was introduced whilst the residual term was left unchanged.
- As was the case for Modified UNIFAC (Lyngby), temperature-dependent group interaction parameters were introduced.
- Van der Waals volume and surface area parameters were introduced for cyclic alkanes, and alcohols were reclassified as primary, secondary and tertiary alcohols with their own van der Waals volume and surface area parameters.
- The fitting of Modified UNIFAC group interaction parameters was extended to include activity coefficients at infinite dilution, VLE and excess enthalpies in order to

improve the accuracy of these parameters.

As was the case for Modified UNIFAC (Lyngby), the combinatorial expression of Original UNIFAC was changed by modifying the group volume fraction parameter (Φ_i). However unlike Modified UNIFAC (Lyngby), the Staverman-Guggenheim correction term was retained in the combinatorial term as used by Alessi *et al* [23], where the modified parameter (Φ_i) was only incorporated into the Flory-Huggins part of the combinatorial expression resulting in (51).

$$\ln \gamma_i^C = \ln \Phi_i' + 1 - \Phi_i' - 5q_i \left(\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \right) \quad (51)$$

In (51), the van der Waals volume term (r_i) for the modified parameter (Φ_i') was expressed as an exponent of $\frac{3}{4}$ instead of the exponent of $\frac{2}{3}$ used by Kikic *et al* [27]. The exponent of $\frac{3}{4}$ was selected after preliminary investigations into simultaneously optimizing activity coefficients at infinite dilution for various alkane/alkane, alkane/alcohol, and alcohol/alcohol experimental data into the combinatorial term. The modified parameter (Φ_i') was therefore expressed as in (52) [20].

$$\Phi_i' = \frac{r_i^{3/4} x_i}{\sum_j r_j^{3/4} x_j} \quad (52)$$

The expressions for the original parameter (Φ_i), used in the S-G correction, and for parameter (θ_i) remained unchanged. The residual term remained unchanged. However the temperature dependence of the group interaction parameter (Ψ_{mn}) was modified as in (53) [20].

$$\Psi_{mn} = \exp \left[- \frac{a_{mn} + b_{mn}T + c_{mn}T^2}{T} \right] \quad (53)$$

Strengths

Modified UNIFAC (Do) yields more reliable results for infinite dilution activity coefficients than the Modified UNIFAC (Lyngby) model [31].

The modification of the combinatorial term has resulted in improved description of asymmetric mixtures in comparison to Original UNIFAC [30].

The inclusion of excess enthalpy data in the group interaction parameters fitting procedure has yielded improved predictions of these values [20].

The introduction of temperature-dependent group interaction parameters has improved results for the calculation of enthalpies of mixing [20].

Weaknesses

The introduction of primary, secondary and tertiary alcohol groups is insufficient to provide much improved prediction of enthalpies of mixing for alcohol/alcohol systems, although predicted results are better when compared to Original UNIFAC [20].

Like the Original UNIFAC, Modified UNIFAC (Do) is unable to calculate excess enthalpies for alkane/alkane

systems, since excess enthalpies rely on the residual term, which equates to zero since only one main group is present [20].

Extensive comparative research conducted in 1990 of the various modified UNIFAC models confirmed that Modified UNIFAC (Do) model was superior to the Lyngby model [31]. It was therefore decided to continue development of the Dortmund model instead of the Lyngby model. Subsequent work of Voutsas and Tassios [28] confirms that Modified UNIFAC (Do) is superior to Modified UNIFAC (Lyngby) in most cases. Further work focused on the revision and extension of group interaction database for the model in order to increase the range of the model's applicability and these included:

- 1993 (group interaction parameters were fitted for 45 main groups by Gmehling, Li and Schiller) [31].
- 1998 (78 new or revised group interaction parameters were presented, with additional fitting to SLE data of eutectic systems and high temperature enthalpies of mixing in order to improve on their accuracy, by Gmehling *et al*) [30].
- 2001 (the new main group 'dialkylated amides' was added, and the interaction between formates and water was presented by Wittig *et al*) [32].
- 2002 (new groups for different amides, along with the addition or revision of 43 group interaction parameters, was presented by Gmehling *et al*) [33].
- 2005 (group interaction parameters were fitted for alkane/ester systems for both VTPR and Modified UNIFAC (Do) by Collinet and Gmehling) [34].
- 2006 (a new main group 'formamides', along with revisions to existing parameters, was presented by Jakob *et al*. Furthermore, some gaps for reactive mixtures in the existing parameter table were filled with data predicted using the COSMO-RS (O1) model) [35].

E. Other UNIFAC – Type Models

Other UNIFAC-type models derived from the various UNIFAC models are now briefly discussed.

a) UNIFAC-LLE [28]

This model, developed by Magnussen *et al* in 1981, is especially suited for computation of LLE data. It is based on Original UNIFAC, with the group interaction parameters having been fitted from LLE experimental data.

b) UNIFAC - γ^∞ [28]

This model, based on Original UNIFAC, was developed by Bastos *et al* in 1988 especially designed for computation of infinite dilution activity coefficients. This model utilises the S-G combinatorial term with the modified van der Waals volume term (r_i) for parameter (Φ_i) as suggested by Kikic *et al* [27], equation **Error! Reference source not found.** The temperature dependence of the interaction parameter (Ψ_{mn}) and the residual term remains unchanged from that of Original

UNIFAC [9].

c) Modified UNIFAC of Hooper *et al* [28]

This model, developed in 1988, was designed specifically for the correlation of LLE data for water/hydrocarbon mixtures. This model utilises the same modified van der Waals volume term (r_i) for parameter (Φ_i) and combinatorial expression derived for the Modified UNIFAC (Lyngby) model – equations **Error! Reference source not found.** and **Error! Reference source not found.** respectively. However the temperature dependence of the interaction parameter (Ψ_{mn}) is that of the Modified UNIFAC (Do) model (53).

d) Original UNIFAC of Hansen *et al* [28]

This model is identical to Original UNIFAC – however the temperature dependence of the interaction parameter (Ψ_{mn}) is modified as in (54).

$$\Psi_{mn} = \exp \left\{ - \left[\frac{a_{mn} + b_{mn}(T - T_0)}{T} \right] \right\} \quad (54)$$

The reference temperature is arbitrarily set to 298.15 K.

e) UNIFAC-FV and Entropic-FV [36]

Elbro *et al* reported that free volume effects must be accounted for in mixtures of polymers and solvents. The UNIFAC-FV and Entropic-FV models have been developed specifically to account for free volume effects of polymer solutions. The UNIFAC-FV model, developed by Oishi and Prausnitz in 1978, is based on Original UNIFAC with the free volume contribution term added onto the overall activity coefficient expression as in (55)

$$\ln \Omega_i = \ln \Omega_i^C + \ln \Omega_i^R + \ln \Omega_i^{FV} \quad (55)$$

In (55), (Ω_i) is the weight fraction activity coefficient (WFAC) of a solvent in a solution. The UNIFAC-FV model is unreliable in describing highly non-ideal systems in the dilute regions, which are characterised by large infinite dilution activity coefficients.

The Entropic-FV model, developed by Kontogeorgis *et al* in 1993, utilises the combined combinatorial and free-volume term published by Elbro *et al* in 1990, with the residual term of the Original UNIFAC model. The WFAC of a solvent in a solution for this model is described as in (56).

$$\ln \Omega_i = \ln \Omega_i^{Comb-FV} + \ln \Omega_i^R \quad (56)$$

The combinatorial-free volume term in this model is much simpler to use than the complicated UNIFAC-FV term. Furthermore, linear temperature-dependent GIPs are used in this method instead of the temperature-independent parameters used in UNIFAC-FV.

Lee and Danner [36] compared the above models with three other polymer models and found them to perform generally poorly in comparison with the other models. However, Entropic-FV seems to yield better results than UNIFAC-FV.

UNIFAC Models Performance [28], [29]

For prediction of infinite dilution activity coefficients of Alkane/Alkane mixtures, it was concluded that Modified UNIFAC (Lyngby) and (Do) and UNIFAC - γ^∞ performed satisfactorily, with UNIFAC - γ^∞ being generally superior. For

infinite dilution activity coefficients of non-aqueous polar mixtures, Modified UNIFAC (Do) is superior to all the other models, which often yielded large errors. None of the Modified UNIFAC models were able to satisfactorily predict infinite dilution activity coefficients of strongly non-ideal water-containing mixtures.

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