



# New modified UNIFAC parameters using critically evaluated phase equilibrium data<sup>☆</sup>



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## ABSTRACT

New modified UNIFAC property prediction model parameters are reported for 89 main groups and 984 group–group interactions using critically evaluated phase equilibrium data including vapor–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE), solid–liquid equilibrium (SLE), excess enthalpy (HE), infinite dilution activity coefficient (AINF) and excess heat capacity (CPE) data. The new algorithmic framework for quality assessment of phase equilibrium data is applied for qualifying the consistency of data and screening out possible erroneous data. Substantial improvement over previous versions of UNIFAC is observed due to inclusion of experimental data from recent publications and proper weighting based on a quality assessment procedure. The systems requiring further verification of phase equilibrium data were identified where insufficient number of experimental data points is available or where existing data are conflicting.

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## 1. Introduction

Various versions of UNIFAC models [1–10] are commonly used for process design when experimental determination of phase equilibrium data is difficult or time consuming. In our previous publication [11], a new procedure for evaluation of UNIFAC interaction parameters was proposed and complete set of group–group interaction parameters was provided for 52 main groups. Group–group interaction parameters were reported for NIST-UNIFAC and NIST-KT-UNIFAC models. Recently, an algorithmic framework for quality assessment of phase equilibrium data [12,13] which covers VLE, LLE, SLE, ACT and HE data has been developed and implemented in the NIST ThermoData Engine [14–23] designed to be a software realization of the concept of dynamic data evaluation for thermophysical and thermochemical properties [24,25]. Implementation of this algorithmic framework can be used to assess phase equilibrium data and screen out

possible erroneous data sets. Furthermore, this procedure can be applied for the development of UNIFAC model parameter matrices.

Because of the requirements of having additional parameters associated with the temperature-dependent terms, the modified UNIFAC model proposed by Gmehling and co-workers [2–6] covers wide range of phase equilibrium data including HE and SLE. Some of the parameters of this model are published in the literature whereas many others are available to the UNIFAC Consortium [26] members only. As the amount of published phase equilibrium data grows continuously, there is a need for periodic updates of the parameter matrix which reflects most recent information for phase equilibrium. In this work, we present the results of our assessment of the interaction parameters for modified UNIFAC (NIST-modified UNIFAC model) using data set prescreening and weighting procedures based on the software implementation of the algorithmic framework for quality assessment of phase equilibria data we reported previously [12,13].

## 2. Description of NIST-modified UNIFAC model and parameter fitting procedure

### 2.1. NIST-modified UNIFAC models

The expressions for activity coefficient and other properties using various versions of UNIFAC models are presented in the

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previous publications [1–10], and details will not be discussed here. The modified UNIFAC model proposed by Gmehling and co-workers [2–6] has a slightly different formulation for average volume parameters. The values used are

$$\phi_i = \frac{r_i}{\sum_{j=1}^{NC} x_j r_j} : \text{used in all UNIFAC versions} \quad (1)$$

$$\phi'_i = \frac{r_i^{3/4}}{\sum_{j=1}^{NC} x_j r_j^{3/4}} : \text{used in modified UNIFAC together with } \phi_i \quad (2)$$

where  $r_i$  is volume of  $i$ -th structural subgroup and  $x_i$  is mole fraction among all subgroups composing the mixture.

Interaction parameters in original UNIFAC [1] were assumed as independent in temperature.

$$\Delta u_{mk} = a_{mk,1} \quad (3)$$

where  $a_{mk,1}$  is the temperature independent coefficient of parameter for  $m$ - $k$  group interaction.

For the improvement in the temperature dependencies in VLE and estimation of excess enthalpies, temperature ( $T$ ) - dependent formulations can be used. The first order form with regard to temperature was used in KT-UNIFAC [8] and the second order form was used in modified UNIFAC [2].

$$\Delta u_{mk} = a_{mk,1} + a_{mk,2}(T - T_0) \quad (4)$$

For KT-UNIFAC,  $T_0$  is a constant, and for NIST-KT-UNIFAC [11]  $T_0 = 0$ . For modified UNIFAC,

$$\Delta u_{mk} = a_{mk,1} + a_{mk,2}T + a_{mk,3}T^2. \quad (5)$$

Exactly the same formulations previously described for modified UNIFAC were used for the development of the NIST-modified UNIFAC matrix.

## 2.2. Assessment of phase equilibrium data

In our previous publications, we described a quality assessment algorithm for vapor–liquid equilibrium data (VLE) [12] and a hierarchical procedure for checking other types of phase equilibrium data (LLE, SLE, ACT and HE) [13]. It is of a particular importance, the use of the quality factors for VLE data sets to assess their weighting parameters “blending” them together for the construction of the UNIFAC matrix. Also, quality factors developed for solid–liquid equilibrium (SLE) data sets were used for weighting in the adequacy function described in the next section. For HE, ACT and LLE, the erroneous data sets were excluded from consideration using the procedure outlined previously [13].

## 2.3. Parameter fitting procedure

The adequacy (objective) function for the regression of UNIFAC parameters is given as follows;

$$A_{\text{total}} = w_{\text{VLE}}A_{\text{VLE}} + w_{\text{LLE}}A_{\text{LLE}} + w_{\text{SLE}}A_{\text{SLE}} + w_{\text{AC}}A_{\text{AC}} + w_{\text{HE}}A_{\text{HE}} + w_{\text{CPE}}A_{\text{CPE}} \quad (6)$$

where  $A_{\text{VLE}}$ ,  $A_{\text{LLE}}$ ,  $A_{\text{SLE}}$ ,  $A_{\text{AC}}$ ,  $A_{\text{HE}}$  and  $A_{\text{CPE}}$  are the adequacy functions for VLE, LLE, SLE, activity coefficients, excess enthalpy, and excess heat capacities, respectively, and  $w$  represents a weighting factor associated with each quantity.

Detailed discussion of the adequacy function and inclusion of uncertainty associated with the data sets are described in our previous publication [11]. For LLE, SLE and CPE which were not presented in [11], a similar approach was used. The weighting factors of each type of data can be adjusted to give better prediction capabilities of certain data types. In this work, highest priority was given to the VLE data and less weight was given to other types of phase equilibrium data.

Because of the principal limitations of the local composition model [27], the modified UNIFAC model cannot successfully predict VLE, SLE and LLE simultaneously except for a few cases. This specific version of parameters is intended to provide the best predictive capabilities for VLE, and we are planning to develop separate sets of parameter matrices optimized for SLE and LLE in future work.

Both the maximum-likelihood method proposed by Anderson et al. [28] and simplex method [29] were used for the fitting of group–group interactions parameters. Due to instability problems arising from derivative evaluation in the maximum-likelihood method, the robust simplex method was used in many cases.

Obviously, generation of all parameters simultaneously in one step is impractical because of the enormity of the optimization space involving hundreds of parameters. Therefore, the fitting algorithm represented a stepwise process. First, each group–group interaction parameter was determined based on the analysis of data for a given class of components (i.e.; alkane + benzene for  $\text{CH}_2 + \text{ACH}$  interaction, alkane + alcohol for  $\text{CH}_2 + \text{OH}$  interaction, etc. . . .). After completion of this first step, each interaction was re-examined and “tuned-up” a number of times within the whole set of phase equilibrium data related to this specific interaction to produce more accurate results.

## 3. Results and discussion

### 3.1. Status of NIST-modified UNIFAC parameter matrix

Experimental phase equilibria data collected within the NIST SOURCE Data Archival System [30] and processed through NIST ThermoData Engine [14] were used in the parameter optimization process. After initial data prescreening conducted in accordance to the procedures described in [13], 186,773 VLE data points, 15,662 LLE data points, 7943 SLE data points, 15,662 ACT data

**Table 1**  
Performance comparison of various UNIFAC models.<sup>a</sup>

Model	VLE		LLE	SLE	HE	ACT	CPE
	$\Delta p$ (%)	$\Delta y$ (%)					
Original UNIFAC [32]	7.21	2.06	532.95	43.48	240.07	185.88	292.32
Modified UNIFAC [2–6]	4.83	1.81	74.96	42.81	112.12	32.94	555.18
NIST-modified UNIFAC (present article)	3.80	1.76	71.40	32.22	143.16	24.98	230.51
No. of data points	46,258	26,409	6,010	2,712	36,601	5,619	1,446

<sup>a</sup> Model performance assessments are limited to components composed of common groups (main group 1–40) among three versions of UNIFAC. Systems with unavailable parameters are excluded from the analysis.

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