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# Extension of the group-contribution lattice-fluid equation of state

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## Abstract

This work focuses on the extension of the numbers of group parameters and application of the group-contribution lattice-fluid equation of state (GCLF EOS). The new group parameters of the GCLF EOS were evaluated by means of the volume translated Peng–Robinson equation of state (VTPR EOS) and the UNIFAC model. Values for 20 main groups and 33 subgroups are added into the current parameter matrix. The procedure used in this work can also be used to evaluate group parameters for the groups not present in the current matrix. Some examples are given to show the reliability of the new group parameters. Two new applications of the GCLF EOS are present: the effect of polymeric additive to solvents in extractive distillation and prediction of the crystallinity of polymers in the presence of gas.

*Keywords:* Group-contribution lattice-fluid equation of state (GCLF EOS); Group parameters; UNIFAC model; Extractive distillation; Crystallinity

## 1. Introduction

A typical problem in polymer processing involves the determination of thermodynamic properties of mixtures of polymers, solvents, plasticizers, antiplasticizers and diluents. Models for describing phase equilibria of polymer–solvent systems can be classified into two general categories: activity coefficient models (e.g. UNIFAC-FV, entropic-FV, GK-FV and UNIFAC-ZM models) [1] and equations of state (e.g. Sanchez–Lacombe, Panayiotou–Vera, group-contribution lattice-fluid equations of state) [2–4]. Equations of state are preferred over activity coefficient models for the calculation of polymer–solvent phase equilibria because equations of state can disclose the dependence of phase volume on pressure, which is especially important in estimating the swelling degree of polymers in polymer processing.

Among the equations of state for polymer–solvent systems, the group-contribution lattice-fluid equation of state (GCLF EOS) has unique features [5,6,38]. The only input required for this model is the molecular structures of polymer and solvent in terms of their functional groups. At extreme conditions (very high pressure and very low temperature), it is very difficult to carry out experiment and thus a predictive model is indispensable. Unfortunately, the number of group parameters available for the GCLF EOS is somewhat limited, and involve only 24 main groups and 47 subgroups by far. There are many gaps in the group interaction parameter table [7].

In this work the missing group interaction parameters of the GCLF EOS are evaluated based on the principle that all the group parameters can be obtained using only pure component and binary equilibrium properties of low molecular weight components, and PVT data of polymers are not needed. In other words, the group interaction energy ($e_{0,k}$, $e_{1,k}$, $e_{2,k}$) and reference volume parameters ($R_{0,k}$, $R_{1,k}$, $R_{2,k}$) may be derived by means of an equations of state (EOS), e.g. Peng–Robinson (PR) EOS or its modification [8]; the group binary interaction parameters, $\alpha_{mn}$, may be derived using activity coefficient models, e.g. the UNIFAC model [9–18]. The accuracy and reliability of the PR EOS or its modifications for predicting $P$–$V$–$T$ behavior of low molecular weight pure compounds and the UNIFAC model for predicting activity coefficient of low molecular weight binary system have already been accepted. The UNIFAC model is one of the most important academic contributions of Prof. Jürgen Gmehling and first developed by Fredenslund et al. [39]. Prof. Jürgen Gmehling's work has affected our research in the field of polymer thermodynamics and special distillation processes until now.

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Of course, one possibility to obtain the necessary information is to carry out experimental measurements for the pure component and the mixture of interest. But measurements are often very time-consuming and expensive. For example, for 10 new-added groups (assuming that they belong to different main groups), there are 105 group parameters to be correlated. If an average number of 10 data points is required to determine one group parameter, in total there are 1050 data points to be measured. However, the existing parameter matrix of the UNIFAC model is developed to include 64 main groups and over 100 subgroups. That is to say, to fill the gap of missing group parameters, the amount of experimental work is apparently too large since the data cannot be found in the literatures. This work provides a way to extend the group parameter matrix of the GCLF EOS which can be used when the experiments are time-consuming and expensive under extreme conditions.

The use of the GCLF EOS to predict the influence of polymeric additives to solvents for extractive distillation [19,20] is tested. In recent years, the use of polymers as additives in solvents for extractive distillation has received increasing attention [21–23], but no thermodynamic model has been used to evaluate the influence of the polymers on the separation factor.

In polymer processing, the crystallinity of a polymer in the presence of gas is difficult to measure and has never been reported in the literatures. However, the crystallinity of a polymer is an important physical quantity, which would help us to explore the interaction between semicrystalline polymer and gas and to explain the change of solubility and swelling degree at different temperatures and pressures. In this work, a method is described to predict the crystallinity of a polymer by the GCLF EOS.

## 2. Extension of the group parameter matrix

### 2.1. Equation of state

The GCLF EOS is derived based on the Panayiotou–Vera EOS [24,25], and is of the form [4–7]:

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+q/r-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \tag{1}$$

where $\tilde{P}$, $\tilde{T}$ and $\tilde{v}$ are the reduced pressure, temperature and molar volume, respectively, and defined by:

$$\tilde{P} = \frac{P}{P^*},\quad \tilde{T} = \frac{T}{T^*},\quad \tilde{v} = \frac{v}{v^*},\quad \theta = \frac{q/r}{\tilde{v}+q/r-1} \tag{2}$$

$$P^* = \frac{z\varepsilon^*}{2v_\mathrm{h}},\quad T^* = \frac{z\varepsilon^*}{2R},\quad v^* = v_\mathrm{h}r \tag{3}$$

$$zq = (z-2)r + 2 \tag{4}$$

where $z = 10$, $R = 8.314\,\mathrm{J\,mol^{-1}\,{}^{-1}}$, $v_\mathrm{h} = 9.75 \times 10^{-3}\,\mathrm{m^3\,kmol^{-1}}$, $q$ is the interaction surface area parameter, $r$ the number of lattice sites occupied by a molecule, $z$ the coordination number, $R$ the universal gas constant, $v_\mathrm{h}$ the volume of a lattice site and $P^*$, $T^*$ and $v^*$ are referred to as scaling parameters.

This equation of state contains two adjustable parameter: the molecular interaction energy, $\varepsilon^*$, and the molecular reference volume, $v^*$. Once these two parameters are known, all of the remaining parameters in Eq. (1) can be determined from Eqs. (2)–(4) at a given temperature and pressure. Properties of a system can then be determined by solving Eq. (1) with respect to reduced volume.

For pure components, the molecular interaction energy between like molecules, $\varepsilon_i^*$, is obtained from the following mixing rule:

$$\varepsilon_i^* = \sum_k \sum_m \Theta_k^{(i)} \Theta_m^{(i)} (e_{kk} e_{mm})^{1/2} \tag{5}$$

where $e_{kk}$ is the group interaction energy between like groups $k$:

$$e_{kk} = e_{0,k} + e_{1,k}\left(\frac{T}{T_0}\right) + e_{2,k}\left(\frac{T}{T_0}\right)^2 \tag{6}$$

where $T$ (K) is the system temperature, and $T_0$ is the arbitrarily set to 273.15 K. The group surface area fractions, $\Theta_k^{(i)}$, are expressed by:

$$\Theta_k^{(i)} = \frac{n_k^{(i)} Q_k}{\sum_n n_n^{(i)} Q_n} \tag{7}$$

where $n_k^{(i)}$ is the number of group $k$ in component $i$, and $Q_k$ is the dimensionless surface area parameter of group $k$, as used in the UNIFAC method. The molecular reference volume, $v_i^*$, is calculated from the group reference volume parameter, $R_k$, using the following mixing rule:

$$v_i^* = \sum_k n_k^{(i)} R_k \tag{8}$$

where $R_k$ is given by:

$$R_k = \frac{1}{10^3}\left[R_{0,k} + R_{1,k}\left(\frac{T}{T_0}\right) + R_{2,k}\left(\frac{T}{T_0}\right)^2\right] \tag{9}$$

For a binary mixture, the basic form of Eq. (1) is unchanged and thus the solving procedure is similar as that of pure components. But the following mixing rules are introduced:

$$\varepsilon^* = \bar{\theta}_1\varepsilon_{11} + \bar{\theta}_2\varepsilon_{22} - \bar{\theta}_1\bar{\theta}_2\dot{\Gamma}_{12}\,\Delta\varepsilon,\quad \Delta\varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12} \tag{10}$$

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}(1-k_{12}) \tag{11}$$

$$\varepsilon_{ii} = \sum_k \sum_m \Theta_k^{(i)} \Theta_m^{(i)} (e_{kk} e_{mm})^{1/2} \tag{12}$$

$$k_{12} = \sum_m \sum_n \Theta_m^{(\mathrm{M})} \Theta_n^{(\mathrm{M})} \alpha_{mn} \tag{13}$$

$$v^* = \sum x_i v_i^* \tag{14}$$

$$\Theta_k^{(i)} = \frac{n_k^i Q_k}{\sum_p n_p^{(i)} Q_p},\qquad \Theta_k^{(\mathrm{M})} = \frac{\sum_i n_k^{(i)} Q_k}{\sum_p \sum_i n_p^{(i)} Q_p} \tag{15}$$