

Nonrandom lattice fluid group contribution parameter for vapor-liquid equilibrium of esters and their mixtures

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Abstract—A group contribution version of the nonrandom lattice fluid equation of state (NLF-GC EOS) has been used to predict the vapor-liquid phase equilibria (VLE) of esters and their mixtures. The investigated esters were divided into groups according to the contribution scheme. Two different types of parameters were regressed from experimental datasets. Size parameters were fitted to pure component properties, and the group-group energy interaction parameters were simultaneously fitted to several binary mixture data sets. For systems containing propylene oxide, missing binary VLE data was predicted by using the COSMO-RS method. Parameters obtained by using the COSMO-RS method were later used to successfully predict experimentally measured binary propylene oxide+esters systems. The overall good prediction capability of the NLF-GC EOS could be proven for the investigated systems.

Key words: COSMO-RS, Esters, Group Contribution, Nonrandom Lattice Fluid Equation of State

INTRODUCTION

Group contribution-based models have been widely used in science and industrial applications due to their flexibility and predictability. The most commonly used contribution models, such as UNIFAC [1], are based on the excess Gibbs energy. On the other side, EOS-based approaches are still considered in the developing stage, especially in respect of the available parameter sets. Group contribution equations of state (GC-EOS) provide information about residual properties such as density and enthalpy, and are applicable to higher pressure regions where the Gibbs function based models are generally not adequate [2].

The nonrandom lattice fluid equation (NLF-EOS) based on Guggenheim's combinatorial theory [3] has been developed by Yoo, Lee and coworkers [4,5]. In the NLF-EOS framework the implicit non-random contribution was made explicit by an expansion method, and the association contribution derived from Veytsmann statistics [6] was extended to include dimer formation [7,8]. The resulting hydrogen bonding nonrandom lattice fluid equation of state (NLF-HB EOS) has been proven to accurately describe various mixture properties [9], including mixtures of associating components [10], making it a suitable foundation for the group contribution approach.

The basic scheme of the group contribution method involves the assembly of molecular parameters from group parameters. Intermolecular interaction energies are expressed as the average of inter-group energy parameters. The molecular size and surface area are the sum of corresponding group properties. The current group contribution version was introduced by Yoo and coworkers [11,12] and later generalized involving the group bulkiness factor [13,14]. The

association contribution used in NLF-HB EOS is formulated in a suitable way for group contribution approaches. Park et al. [15] suggested mean values to overcome the incompatibility of the surface area parameters. These considerations forming the foundation for the GC-EOS approach are utilized in this paper.

GROUP CONTRIBUTION EQUATION OF STATE

Derivations and various aspects of NLF-HB EOS are given in previous studies [4,5,8,9,16]. The equation of state is given as

$$\frac{PV_H}{RT} = \frac{z}{2} \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] - \ln(1 - \rho) + \rho \frac{l_M}{r_M} - v_{HB} \rho - \frac{z\beta}{2} \varepsilon_M \theta^2. \quad (1)$$

The physical contribution is characterized by the molecular segment number r_i and surface area parameter q_i is related to the segment number by

$$zq_i = r_i(z-2) + 2 \quad (2)$$

where, z stands for the coordination number. In addition, the unit lattice cell volume V_H must be provided. The molecular physical interaction parameters need to be obtained from corresponding group parameters,

$$r_i = \sum v_i^q r_q^G \quad (3)$$

and

$$\varepsilon_{ij} = \sum \sum \theta_i^q \theta_j^r \varepsilon_q^G \quad (4)$$

where, v_i^q is the number of type q groups in the component i and

$$\theta_i^q = v_i^q q_q^G / \sum_m v_i^m q_m^G \quad (5)$$

The group surface area parameter is related to the group segment number by

$$zq_q^G = r_q^G(z-2) + 2(1 - l_q^G) \quad (6)$$

where l_q^G is the group connectivity parameter that represents the

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number of contacts to adjacent groups. Thus l_q^G is equal 0.5 for a single connected group, 1 for a doubly connected group, etc.

Thus the formulation gives us group parameters r_q^G , ϵ_{qr}^G , for fitted group variables and l_q^G for group connectivity constants, which has to be selected according to the molecular structure. As presented in previous studies, the lattice coordination number z was set to 10 and the lattice cell volume V_H was set to 9.75 cm³/mol. In this study the size and energy group parameters were considered to be temperature dependent in the following form:

$$p = p^1 + p^2(T - T_0) + p^3(T \ln T_0 / T + T - T_0) \quad (7)$$

where, $T_0 = 298.15$ K. The size group parameters can be fitted from pure component data, while the energy group parameters require vapor-liquid equilibrium (VLE) datasets. Since the energy parameters contain all the interaction information between the different groups, it is required to fit the group parameters by using broad sets of VLE within a database at the same time to include as much interaction information as possible. Since appropriated VLE datasets are not available for all intra-group parameters, the missing data gaps were filled by using the COSMO-RS [17,18] method implemented in the program COSMOtherm [19].

COSMO-RS

The conductor-like screening model for real solvents (COSMO-RS) theory is based on the quantum mechanical description of interacting molecular surface charges [20,21]. COSMO-RS combines an electrostatic theory of locally interacting molecular surface descriptors which are available from quantum mechanical calculations with statistical thermodynamics methodology. The interaction of the surface descriptors finally results in a consistent formulation for the chemical potential. First, all involved components are described by the surface density charges which would evolve when the component would be placed in an ideal conductor. Each component can be described by the probability distribution $p(\sigma)$ of the surface charge densities. Mixtures can be described as follows:

$$p(\sigma) = \sum_i x_i p_i(\sigma) \quad (9)$$

where, x_i stand for the mole fraction of the component i . The chemical potential has been derived by Klamt [21] through the summation of N different ensembles of charged surface segments:

$$\mu(\sigma) = -RT \left[\int d\sigma' p(\sigma') \exp \left(\frac{\mu(\sigma') - a_{eff} e(\sigma, \sigma')}{RT} \right) \right] \quad (10)$$

The expression $\mu(\sigma)$ appears on both sides of the equation so that it has to be solved iteratively. Thus, with the implementation of COSMO-RS, it is possible to calculate a mixture's equilibrium properties, such as vapor pressure, solubility, activity coefficients and phase diagrams [22].

RESULTS AND DISCUSSION

The group size parameters for the selected molecules were regressed from pure component properties. Pure vapor pressures and liquid densities were obtained from the Korean thermo physical properties Data Bank (KDB) [23] and the Dortmund Data Bank (DDB) [24]. Three different groups of esters were considered: the CH₃-COO group found in alkyl acetates, the CH₂-COO group found in methyl esters, alkyl propanoates and alkyl butanoates, and the HCOO group

Table 1. New groups and pure component properties calculation result

Groups	T_{Low}	T_{Up}	No. of components	AAD ^a
CO ₂	230.0	290.0	1	0.998165
CH ₂ -COO	290.0	500.0	3	0.843882
CH ₃ -COO	280.0	400.0	4	0.899282
HCOO	200.0	400.0	3	0.547769
CH ₂ -O-CH	290.0	330.0	1	0.999587

$$^a \text{AAD} = \frac{100}{N_{Data}} \sum_i \left| \frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}} \right| + \frac{100}{N_{Data}} \sum_i \left| \frac{\rho_i^{exp} - \rho_i^{cal}}{\rho_i^{exp}} \right|$$

Table 2. Types of mixtures considered in this study and energy parameter fitting result

Type of mixture	Groups	T_{min} (K)	T_{max} (K)	No. of systems	AAD ^a
R-Acetate+R-Acetate	CH ₃ +CH ₃ -COO	273.15	343.15	13	3.5118
R-Acetate+Alkane	CH ₂ +CH ₃ -COO	273.15	343.15	2	3.5118
R-Acetate+Epoxide	CH ₃ -COO+CH ₂ -O-CH	308.15	348.15	3	0.8097
R-Acetate+Alkene	CH ₃ -COO+ACH	283.15	363.15	11	1.4056
R-Acetate+CO ₂	CH ₃ -COO+CO ₂	298.15	323.15	8	8.3011
R-Acetate+Benzene	CH ₃ +COO+CH ₂ -(Cyclic)	293.15	328.15	5	2.5883
R-Formate+CO ₂	HCOO+CH ₃	303.15	323.15	6	5.8031
	HCOO+CH ₂	303.15	323.15	6	5.8031
	HCOO+CO ₂	303.15	323.15	6	5.8031
R-Formate+Toluene	HCOO+ACH	318.15	324.15	3	1.3528
	HCOO+AC-CH ₃	318.15	324.15	3	1.3528
R - Butyrate+Alkane	CH ₂ -COO+CH ₂	347.85	373.15	2	2.3417
	CH ₂ -COO+CH ₃	347.85	373.15	2	2.3417
R - Propionate+CO ₂	CH ₂ -COO+CO ₂	303.15	323.15	3	2.1762

$$^a \text{AAD} = \frac{100}{N_{Data}} \sum_i \left| \frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}} \right|$$

included in alkyl formates. To obtain representative group parameters, the fitting process included fitting properties of several components simultaneously. In this study, the parameters for carbon dioxide previously published [25] have been revised for more accurate representation of VLE data sets. Table 1 shows the new groups added to the parameter matrix with the corresponding temperature range. Other group parameters were taken from previous publications [15, 25, 26] when needed. The group size parameter $\text{CH}_2\text{-O-CH}$ for propylene oxide was fitted by using pure component properties available in the KDB.

The inter-group energy parameter calculation was done by grouping appropriated VLE data and regressing parameters one by one. The grouping and the number of systems involved are listed in Table

Table 3. Group size parameters and connectivity parameters

Groups	r_a	r_b	r_c	l_q
CH_2	1.5525E+0	-7.0335E-5	6.0318E-4	1.0
CH_3	2.6293E+0	-3.5423E-4	3.0078E-3	0.5
$\text{CH}_2\text{-(Cyclic)}$	1.6515E+0	3.4004E-6	1.2138E-3	1.0
ACH	1.4008E+0	1.7078E-4	9.7940E-4	1.0
AC- CH_3	2.9927E+0	-8.5680E-4	-5.9319E-4	1.0
$\text{CH}_2\text{-O-CH}$	3.9168E+0	2.2433E-3	5.9196E-3	0.5
$\text{CH}_2\text{-COO}$	3.8087E+0	1.7972E-4	3.3615E-3	1.0
$\text{CH}_3\text{-COO}$	4.8990E+0	3.9683E-3	3.0880E-2	0.5
HCOO	3.3186E+0	2.1998E-3	8.3595E-3	0.5
CO_2	3.6814E+0	-1.9537E-2	-1.9537E-2	0.0

Table 4. Group-group interaction parameters.

Groups	e_a	e_b	e_c
$\text{CH}_2+\text{CH}_2\text{-CO}$	1.2615E+2	1.5299E-2	-3.1909E-1
$\text{CH}_3+\text{CH}_2\text{-CO}$	1.4789E+2	-1.0384E+0	-7.4662E+0
$\text{CH}_2\text{-CO}+\text{CH}_2\text{-CO}$	1.6250E+2	2.8783E+0	2.2663E+1
CH_2+CO_2	9.8896E+1	-1.1664E-1	3.6097E-1
CH_3+CO_2	6.3693E+1	5.3938E-2	-2.2078E+0
CO_2+CO_2	8.7811E+1	2.6138E-1	-3.5391E+0
$\text{CH}_2\text{-COO}+\text{CH}_2\text{-COO}$	1.8174E+2	-3.8296E+0	-1.9831E+1
$\text{CH}_2\text{-COO}+\text{CO}_2$	1.3045E+2	1.4058E+0	-4.8921E-1
$\text{CH}_3\text{-COO}+\text{CH}_3\text{-COO}$	1.2390E+2	2.1163E-1	-1.3604E+0
$\text{CH}_3\text{-COO}+\text{CH}_2\text{-O-CH}$	1.2134E+2	3.4711E-1	8.0966E-1
$\text{CH}_3\text{-COO}+\text{CO}_2$	1.3571E+2	-6.3886E-1	-2.4935E+1
$\text{CH}_2\text{-(Cyclic)}+\text{CH}_3\text{-COO}$	1.1006E+2	-6.9645E-1	-1.1794E+1
$\text{CH}_2+\text{CH}_2\text{-COO}$	1.2095E+2	-1.3305E+0	-6.6250E+0
$\text{CH}_3+\text{CH}_2\text{-COO}$	5.5229E+1	3.9466E+0	1.9875E+1
$\text{CH}_2+\text{CH}_3\text{-COO}$	1.0965E+2	-3.2287E-2	-3.7867E-1
$\text{CH}_3+\text{CH}_3\text{-COO}$	1.2580E+2	-3.6968E-1	3.3814E-1
CH_2+HCOO	1.1635E+2	-3.9659E-2	-3.0280E-1
CH_3+HCOO	1.5284E+2	3.2959E-1	1.1668E+1
$\text{HCOO}+\text{HCOO}$	1.1148E+2	-7.8662E-1	-1.9222E+1
$\text{HCOO}+\text{CO}_2$	1.5667E+2	6.7012E-1	3.3350E+0
ACH + $\text{CH}_2\text{-COO}$	1.4730E+2	-1.4244E+1	-7.5377E+1
ACH + $\text{CH}_3\text{-COO}$	1.2823E+2	-9.6628E-2	-8.7453E-1
ACH + HCOO	1.3173E+2	1.2668E+0	2.4420E+1
AC- CH_3 + HCOO	1.2440E+2	-2.2920E+0	-4.2989E+1

2. A total of 73 VLE systems were selected from the database, considering the consistency of data sets and used for the parameter fitting. The obtained group size and energy parameters are listed in Table 3 and Table 4, respectively. The connectivity parameters are presented in Table 3.

Fig. 1 shows the prediction result for the methyl acetate+propyl acetate system, which shows an acceptable agreement with the experimental data. The results for the methyl acetate+benzene for different temperatures are shown in Fig. 2.

For the calculations of the $\text{CH}_2+\text{CH}_2\text{-CO}$ and $\text{CH}_3+\text{CH}_2\text{-CO}$ group interaction parameters, no experimental datasets are available. Thus, for this case binary VLE datasets with different temperatures for alkane+1,2 propylene oxide were calculated by using COSMOtherm. The group parameters were then fitted to this data, in order to obtain the specific group energy parameters. In the next step the obtained parameters were used to correlate the propylene oxide+

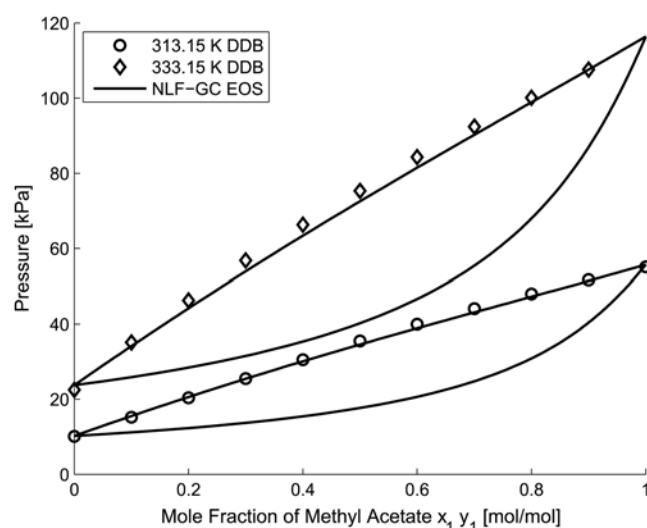


Fig. 1. Prediction result for the methyl acetate+propyl acetate system at different temperatures.

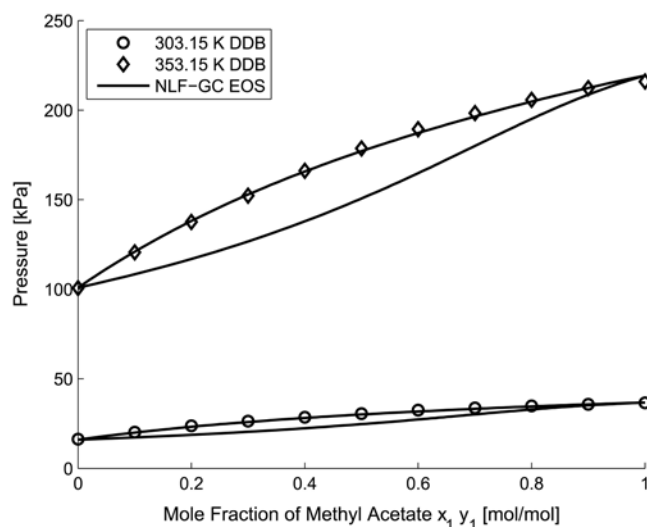


Fig. 2. Prediction results for the methyl acetate+benzene system at different temperatures.

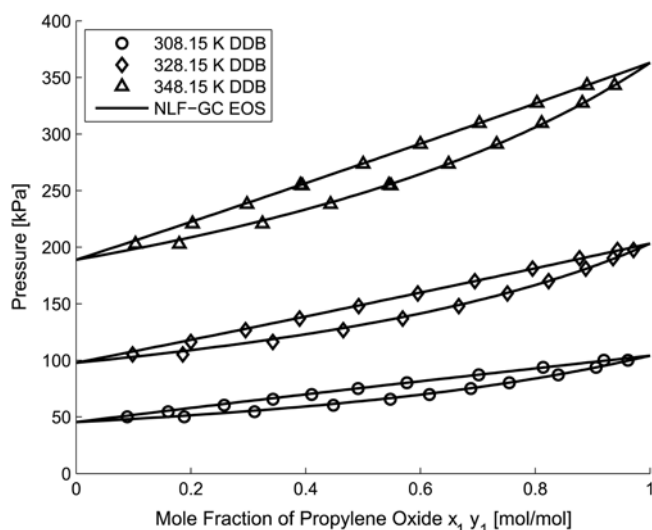


Fig. 3. Prediction results for the propylene oxide+methyl acetate system at different temperatures.

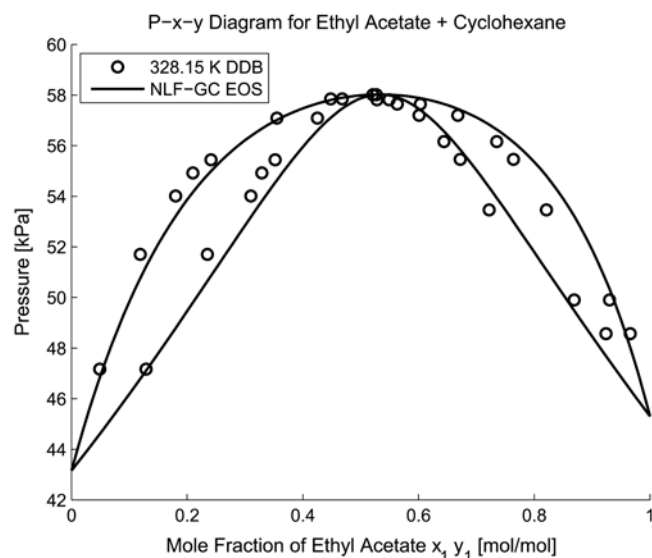


Fig. 4. Prediction results for the ethyl acetate+cyclohexane system.

methyl acetate system. The results show a good agreement with the experimental data as shown in Fig. 3.

In the case of the ethyl acetate+cyclohexane system (Fig. 4), the behavior of the system is highly nonideal and the range of bubble- and dew-point line is very narrow. Thus, the results are not as good as the other presented mixtures, but the group contribution method could well predict the azeotropic point of the mixture, without further need of additional interaction parameters.

The prediction of mixtures containing small molecules is usually a difficult task when using a group contribution EOS, because of the absence of appropriated group interaction energy parameters. In this study, the prediction results for systems containing carbon dioxide, a rather small molecule, are in good agreement with the experimental data, as can be seen in Fig. 5.

CONCLUSION

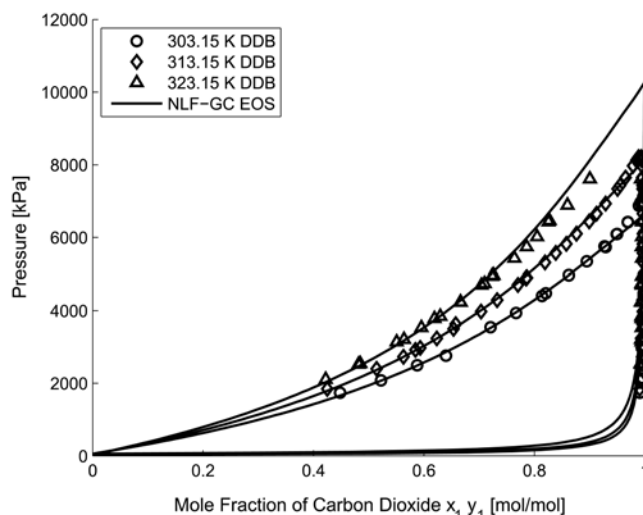


Fig. 5. Prediction results for the carbon dioxide+ethyl propionate system at different temperatures.

In this study the capability of the NLF-GC for the correlation of systems containing esters and was shown. With careful fitting of interaction parameters, the prediction of even small molecules like carbon dioxide becomes possible. The use of COSMO-RS was successful in the selected case. Even the COSMO-RS method could only be classified as a screening tool, the overall prediction capability of the group contribution framework could be extended, and the results are promising. Thus, in some cases the COSMO-RS model might be a useful tool for group contribution methods to obtain missing interaction parameters.

NOMENCLATURE

G	: Gibbs energy
<i>l</i>	: group connectivity parameter
N	: number of lattice sites
P	: pressure
q	: surface area parameter
r	: segment number parameter
R	: gas constant=8.314 J/(mol K)
T	: temperature in K
v	: molar volume
V_H	: molar lattice cell volume
V_{HS}	: lattice hard sphere volume
z	: lattice coordination number=10

Greek Letters

β	: 1/kT
ϵ	: interaction energy parameter
Θ	: surface area fraction
ρ	: reduced density

Superscripts

A, B, C	: parameter identifier
E	: excess
G	: group
HB	: hydrogen bonding

q, r : group index

Subscripts

0 : reference point

i, j : component index, donor group or acceptor group

M : mixture

Abbreviation

COSMO-RS : conductor-like screening model for real solvents

EOS : equation of state

GC : group contribution

HB : hydrogen bonding

KDB : korean thermo physical properties data bank

DDB : dortmund data bank

NLF : nonrandom lattice fluid

VLE : vapor-liquid equilibrium

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