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Group Contribution Parameters for Nonrandom Lattice Fluid Equation of State involving COSMO-RS

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***Abstract*—**Group contribution based models are widely used in industrial applications for its convenience and flexibility. Although a number of group contribution models have been proposed, there were certain limitations inherent to those models. Models based on group contribution excess Gibbs free energy are limited to low pressures and models based on equation of state (EOS) cannot properly describe highly nonideal mixtures including acids without introducing additional modification such as chemical theory. In the present study new a new approach derived from quantum chemistry have been used to calculate necessary EOS group interaction parameters. The COSMO-RS method, based on quantum mechanics, provides a reliable tool for fluid phase thermodynamics. Benefits of the group contribution EOS are the consistent extension to hydrogen-bonded mixtures and the capability to predict polymer-solvent equilibria up to high pressures. The authors are confident that with a sufficient parameter matrix the performance of the lattice EOS can be improved significantly.

***Keywords*—**COSMO-RS, Equation of State, Group contribution, Lattice Fluid, Phase equilibria.

I. Introduction

GROUP contribution excess Gibbs function models such as UNIFAC [1] have long been utilized. On the other side group contribution equation of state (GC-EOS) are still in developing stages. The EOS based approach includes the advantage of providing information about residual properties such as volume, enthalpy and phase equilibria. Especially for the high pressure region an equation of state model is needed since Gibbs function models are generally not adequate [2].

Lattice based statistics have been proven to be a convenient basis for GC-EOS approaches [3-7] as well as for group contribution excess Gibbs function approaches. Danner and coworkers obtained molecular segment numbers from corresponding group parameters, but molecular surface area parameters and corresponding group parameters were reported to be not related [4,6]. The *ij* group interactions were defined as a geometric mean of *ii* and *jj*. The group contribution lattice fluid formulation proposed by Victorov et al. avoids the problem of the surface area parameters [3], for the cost of introducing a bulkiness factor as fitting parameter. All these approaches have in common that they only include physical interactions. But without association contribution GC-EOS calculations lead to excessive errors in the calculation of phase equilibria for mixtures containing associating components [3,5,7]. It should be also noted that group segment numbers add up to give the molecular segment number but that group surface parameters do not add up to the corresponding molecular surface area parameters in most approaches.

In a non-group contribution version of the lattice fluid equation of state (NLF EOS) based on Guggenheim's combinatory theory [8] developed by Yoo, Lee and coworkers [9,10], the implicit nonrandom contribution was made explicit by an expansion method and the association contribution derived from Veytsmann statistics [11] was extended to include dimer formation [12]. The resulting hydrogen bonding nonrandom lattice fluid equation of state (NLF-HB EOS) has proven to accurately describe fluid properties [13], making it a suitable foundation for the group contribution approach.

The association contribution used in NLF-HB EOS is formulated in a suitable way for group contribution approaches. Park et al. [7] suggested mean values to overcome the incompatibility of the surface area parameters. These considerations forming the foundation for the GC-EOS approach utilized in this paper.

II. Group contribution Equation of State

The configurational Helmholz free energy of a mixture containing N_1, N_2, …, and N_c moles of components 1, 2, …, and C can be represented by summing the physical and association contributions

$$A^C = A_{phys} + A_{ass} \ . \tag{1}$$

The physical contribution is characterized by the molecular segment number r_i and the mean value energy of interactions between segments ε_{ij}. The surface are parameter q_i is related to the segment number by

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$$zq_i = r_i(z-2)+2, \tag{2}$$

where z stands for the coordination number. In addition the unit lattice cell volume V_H must be provided. There are also N_0 holes in the mixture where r_0=1 and $\varepsilon_{0i}=\varepsilon_{0i}$=0. Expressions for the Helmholz free energy are given elsewhere [9].

To evaluate the association contribution, the number of donor type k, d_k^i, the number of acceptor type l, a_l^i in species i, and the
Association free energy between donor type k and acceptor type l, A_{kl}^H, are required. The resulting relation can be expressed by

$$A_{kl}^H = U_{kl}^H - TS_{kl}^H, \tag{3}$$

where U_{kl}^H and S_{kl}^H are the energy and entropy of association. In addition the active segment number of a donor or an acceptor, r_H is needed, which is independent of the species. Expressions for the association contribution were provided by Park and coworkers [12].

The molecular physical interaction parameters need to be obtained from corresponding group parameters,

$$r_i = \sum v_i^q r_q^G \tag{4}$$

and

$$\varepsilon_{ij} = \sum\sum \theta_i^q \theta_j^r \varepsilon_q^G \tag{5}$$

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

$$\theta_i^q = v_i^q q_q^G \Big/ \sum_m v_i^m q_m^G \cdot \tag{6}$$

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

$$zq_q^G = r_q^G(z-2)+2(1-l_q^G) \tag{7}$$

where l_q^G is the group connectivity parameter and represents the number of contact 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, U_{kl}^H, S_{kl}^H for fitted group variables, l_q^G for group connectivity constants, d_k^i and a_l^i for species dependent association constants, and z and V_H for universal lattice constants. As in previous studies the lattice coordination number z was set to 10 and the lattice cell volume V_H was set to 9.75 cm^3/mol. The values for d_k^i and a_l^i are usually known from the structure of the group. The association parameters U_{kl}^H and S_{kl}^H are mentioned in the literature for some donor-acceptor pair. In this study the size and energy group parameters were considered to be temperature dependent in the following form

$$p = p^A + p^B(T-T_0) + p^C(T\ \ln T_0/T + T - T_0) \tag{8}$$

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 with a breath database at the same time to include as much interaction information as possible. Since appropriated VLE datasets are not available for all parameter groups, the missing data gaps were filled using the COSMO-RS [14,15] method implemented in the program COSMOtherm [16].

III. COSMO-RS

The COSMOtherm program is based on "Conductor-like Screening Model for Real Solvents" (COSMO-RS) theory of interacting molecular surface charges [17,18]. 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 be 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 through

$$p(\sigma) = \sum_i x_i p_i(\sigma) \tag{9}$$

where x_i stand for the mole fraction of the component i. The chemical potential has been derived by Klamt [18] through the sum of N different ensembles of charged surface segments

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

The expression $\mu(\sigma)$ appears on both sides of the equation so that it has to be solved iterative. Thus with the implementation of COSMO-RS in COSMOtherm it possible to calculate mixtures equilibrium properties such as vapor pressure, solubility, activity coefficients, phase diagrams etc.

As described before, in this study the focus was to fill up missing equilibrium data for the group parameter correlation using COSMOtherm.

IV. Results and Discussion

The presented formulation of the GC-EOS based on the Guggenheim combinatory is far-reaching generalized in the sense that both nonrandom and association contribution are included in the model. The first physical parameter determinations were made with alkanes form C3 to C10. Temperature independent segment numbers and interaction energy parameters were fitted to isothermal data set at different temperatures. Then the segment numbers were regressed to group parameters and listed in Table I. Light molecules such as

methane and ethane are usually not composed into groups instead they are treated as one group in total.

TABLE I
SEGMENT NUMBERS FOR SELECTED GROUPS

Group	r_a^G	r_b^G	r_c^G	l_q^G
CH2	1.5525	-7.0335E-5	6.0318E-4	1.0
CH3	2.6293	-3.5423E-4	3.0078E-3	0.5
CH4	4.5818	3.7682E-3	3.7754E-3	0.0
$CH2_{Cyclic}$	1.6515	-0.0001E-4	1.2100E-3	1.0
ACH	1.4008	1.7078E-4	9.7940E-4	1.0
ACCH3	2.9927	-8.5680E-4	-5.9319E-4	1.0
CH2O	2.2951	-9.7000E-4	8.6200E-3	1.0
CH3O	3.3010	4.4000E-4	1.1240E-2	0.5
CH2CO	3.1120	1.9800E-3	7.2100E-3	1.0
CH3CO	4.2677	1.3100E-3	5.5100E-3	0.5
CH2OH	2.5101	9.6975E-4	-2.2452E-3	0.5
CH2OCH	3.9168	2.2400E-3	5.9200E-3	0.5

Group interaction energy parameters were fitted to VLE datasets at several different temperatures in the same temperature interval using the size parameter from Table I. The regressed parameters are listed in Table II.

TABLE II
ENERGY PARAMETERS FOR SELECTED GROUPS

Group	ε_a^G	ε_b^G	ε_c^G	T [K]
CH2+CH2	115.78600	0.05460	0.01010	250-500
$CH2+CH2_{Cyclic}$	108.45250	-1.09102	-17.22395	298-333
CH2+CH2O	132.11466	-3.55692	-31.77778	308-363
CH2+CH2OH	117.18200	0.00473	-0.11360	260-400
CH2+CH3O	103.29245	0.01574	-0.29218	283-387
CH2+CH3CO	116.29271	-0.02344	-0.34842	258-398
CH2+CH2CO	126.14786	0.01530	-0.31909	313-368
$CH2_{Cyclic+}$+CH2	108.88568	0.02105	0.02640	298-333
CH3+CH2	93.98270	0.01590	-0.01680	250-500
CH3+CH3	79.82060	0.01520	-0.07620	250-500
$CH3+CH2_{Cyclic}$	95.82072	1.53396	22.24828	298-333
CH3+CH2O	129.72961	-1.94069	-19.11111	308-363
CH3+CH2OH	97.18030	0.00023	0.21710	260-400
CH3+CH3O	95.55920	-0.05918	-0.05541	283-387
CH3+CH2CO	147.88560	-1.03841	-7.46620	313-368
CH3+CH3CO	109.52975	-0.04010	-0.09778	258-398
CH4+CH2	78.22460	0.04560	0.08050	200-500
CH4+CH3	61.21730	-0.01910	-0.17690	200-500
CH4+CH4	49.38360	-0.00233	-0.02160	200-500
ACH+ACH	119.8611	-0.00855	-0.08540	300-400
ACH+CH2	114.3613	0.03340	-0.34650	300-400
ACH+CH3	96.32140	0.01620	0.43260	300-400
ACH+CH2OH	124.03540	0.04960	0.22790	278-348
ACCH3+ACCH2	116.78300	0.02350	-0.04850	300-400
ACCH3+ACCH3	116.03150	0.06660	0.17060	300-400
ACCH3+ACH	116.78300	0.02350	-0.04850	300-400
ACCH3+CH2	119.22890	0.20930	1.45540	300-400
ACCH3+CH3	92.20290	-0.19620	-1.34860	300-400
ACCH3+CH2OH	125.49840	-0.19830	-2.16420	300-400
CH2OH+CH2OH	138.03300	0.01580	-0.21970	260-400
CH2O+CH2O	180.45509	-3.44975	-16.00000	308-363
CH3O+CH3O	115.44244	0.02406	-0.28943	283-387
CH2CO+CH2CO	162.49662	2.87826	22.66323	313-368
CH3CO+CH3CO	163.81531	-0.08961	-0.24368	258-398

Pure component properties were taken from the Korean thermo physical properties Data Bank (KDB) [19], and binary datasets were taken from the electronic version on the Dortmund Data Bank DDB and from COSMOtherm. The Table III gives and current snapshot of the group-group interaction matrix. The gaps are caused by the lack of appropriated experimental datasets. Since the results with COSMOtherm are promising, as shown below, the authors believe that the gaps in the matrix can be filled using VLE data created by the COSMO-RS method.

TABLE III
GROUP-GROUP INTERACTION MATRIX

		1	2	3	4	5	6	7	8	9	10	11	12	13
1	CH2	x												
2	CH3	x	x											
3	CH4	o	o											
4	$CH2_{Cyclic}$	o	o											
5	ACH			o	o	x								
6	ACCH2		x											
7	ACCH3	x	x	o	o	x								
8	CH2O	o	o											
9	CH3O	o	o											
10	CH2CO	o	o											
11	CH3CO	o	o											
12	CH2OH	x	x			x		x						
13	EPOXY	o	o			o	o	o						

x Previous Publication
o Data: DDB
o Data: COSMOtherm

Fig. 1 shows the correlated Hexane + Pentane binary mixture at 298.15 K. In Fig. 2 the results for the Heptane + Xylene at 348.15 K are shown.

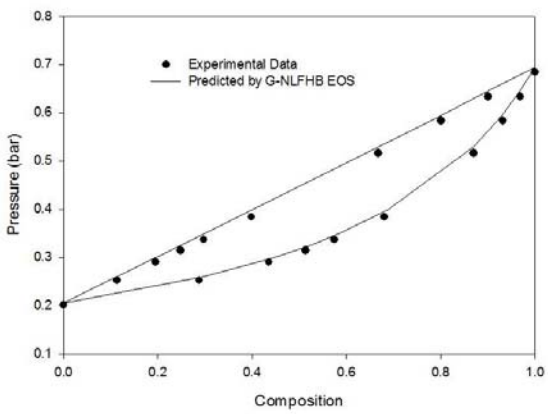

Fig. 1 Hexane + Pentane system at 298.15 K.

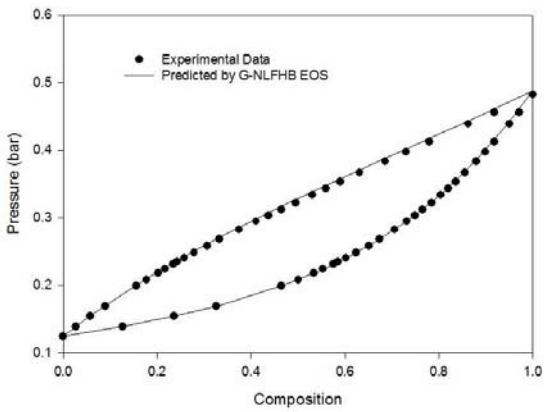

Fig. 2 Hexane + Xylene system at 348.15 K, group energy parameters calculated by using VLE datasets produced by COSMOtherm.

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Fig. 3 shows the Hexane + Ethanol VLE system at 313.15 K, were Ethanol is considered to be an associating component.

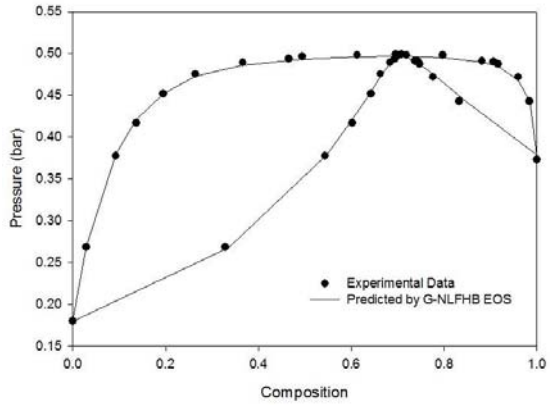

Fig. 3. VLE of the Hexane + Ethanol system at 313.25 K.

In Fig. 4 the a binary VLE system of Hexane and 1,2-Propylene Oxide in shown. The Data for this system was created using COSMOtherm, since there is no experimental data available

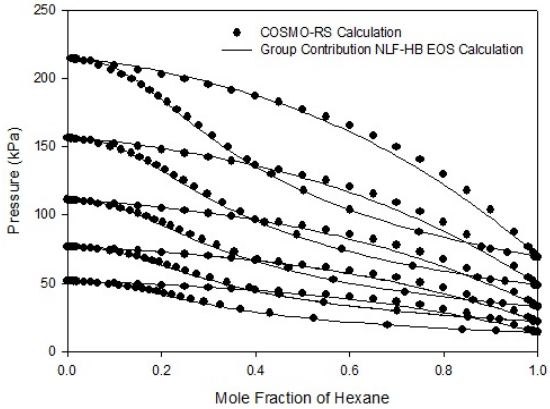

Fig. 4. Hexane + 1,2-Propylene Oxide System at different Temperatures.

All figures show an excellent agreement with the provided datasets. The results using the COSMOtherm provided data are also satisfying.

V. Conclusion

The presented group contribution approach could be proven to be reliable. Since association terms were considered mixtures containing polar components could be predicted. The use of COSMOtherm has been proven to be practically in the presented test cases.

COSMOtherm will be used in the future to predict missing binary data needed for creating a group interaction parameter matrix.

With a comprehensive interaction parameter matrix for a group contribution equation of state, fast solvent screening method become applicable at higher pressures.

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