UNIVERSITÄT PADERBORN
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FAKULTÄT FÜR MASCHINENBAU

Thermodynamik und Energietechnik

ThEt

Considering Dispersive Interactions in the COSMO-SAC Model: A Study on Nonpolar Mixtures

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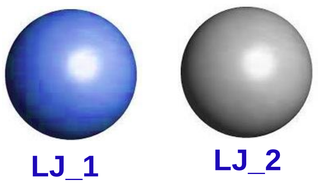
1. Introduction

- **A reliable predictive thermodynamic model is highly desirable to reduce the amount of required experimental data, which are crucial for the design of chemical and pharmaceutical processes.**
- **The COSMO-SAC model, that is exclusively based on the results from quantum chemical calculations, does not contain any species-dependent parameters and thus never suffers with respect to missing parameters. However, the dispersive intermolecular interactions in mixtures are neglected. This is considered as the main reason why the COSMO-SAC model fails to yield good predictions for nonpolar mixtures.**
- **In this study, we propose a new dispersion term to explicitly consider the contribution of the dispersive interactions to the non-ideality of mixtures from classical force field based molecular simulation results.**

2. Theory

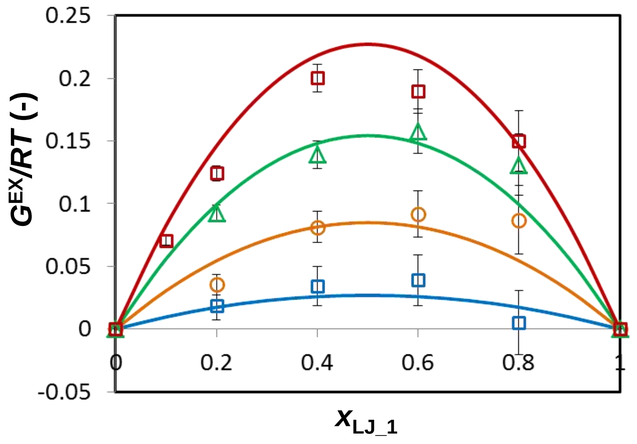
A. Studying Dispersive Interactions with Molecular Simulation

Mixtures of Lennard-Jones fluids



LJ_1 σ_1, ε_1 LJ_2 σ_2, ε_2

ε_1	ε_2	$\varepsilon_1/\varepsilon_2$	σ_1/σ_2	Margules A
100	83.333	1.2	1	0.102
	71.428	1.4	1	0.324
	62.500	1.6	1	0.592
	55.556	1.8	1	0.875



$\varepsilon_1/\varepsilon_2$ = 1.8 $\varepsilon_1/\varepsilon_2$ = 1.4
$\varepsilon_1/\varepsilon_2$ = 1.6 $\varepsilon_1/\varepsilon_2$ = 1.2
Prediction from Margules

➢ Margules equation: $\frac{G^{ex}}{RT} = Ax_1x_2$

with constant A determined from: $A = \frac{\varepsilon_1 + \varepsilon_2}{2} - \sqrt{\varepsilon_1\varepsilon_2}$

Since the single constant Margules equation can well describe G^{EX} for systems containing only dispersive interactions, it was used here to consider the dispersive contribution to the non-ideality of mixtures in COSMO-SAC model.

B. COSMO-SAC-dsp Model

$$\ln\gamma_{i/S} = \frac{\Delta G^{*res}_{i/S} - \Delta G^{*res}_{i/i}}{RT} + \ln\gamma^{SG,comb}_{i/S} + \ln\gamma^{disp}_{i/S}$$

Dispersion contribution

Residual contribution: Electrostatic interactions between molecules in the mixture

$$\frac{\Delta G^{*res}_{i/S}}{RT} = n_i \sum_{\sigma_m} p_i(\sigma_m) \ln\Gamma_S(\sigma_m)$$

Using quantum chemistry results

Combinatorial contribution: Size and shape effect via Staverman−Guggenheim model:

$$\ln\gamma^{comb}_{i/S} = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad \phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

r_i and q_i are the normalized volume and surface area parameters for component i

These two contributions were taken from previous work without any modification or parameter re-optimization.

➢ **Dispersion contribution (for binary mixtures *i* + *j*)**

$$\ln\gamma^{dsp}_{i/S} = Ax^2_{j\neq i} \qquad \text{with constant } A \text{ determined from: } A = \frac{\varepsilon_i + \varepsilon_j}{2} - \sqrt{\varepsilon_i\varepsilon_j}$$

➢ **Dispersion parameter of a molecule**

$$\varepsilon_{Molecule} = \frac{1}{N_{Atom}}\sum_{j=1}^{n}\varepsilon_j N_j$$

where: n : number of atoms in the molecule; N_{atom} : number of atoms in the molecule; N_j : number of type j atoms; ε_j : dispersion parameter of atom j

➢ **Two different approaches were tested for systems containing compounds composed of C, H, N, O, F and Cl**

- ❖ dsp1 (Npar=5, ε_C , ε_O , ε_N , ε_F and ε_{Cl})
- ❖ dsp3 (Npar=10, $\varepsilon_{C(sp3)}$, $\varepsilon_{C(sp2)}$, $\varepsilon_{C(sp)}$, $\varepsilon_{O(-O- \text{ and } -OH)}$, $\varepsilon_{O(=O)}$, $\varepsilon_{N(sp3)}$, $\varepsilon_{N(sp2)}$, $\varepsilon_{N(sp)}$, ε_F and ε_{Cl})

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Alexander von Humboldt Stiftung/Foundation

3. Preliminary Results

A. Overview on Vapor-Liquid Equilibrium Predictions

Comparing VLE predictions from COSMO-SAC-dsp, COSMO-SAC and modified UNIFAC

	VLE_nhb (Optimization)			VLE_hb (Prediction)		
	Nbinary	AARD-P	AAD-y1	Nbinary	AARD-P	AAD-y1
mUNIFAC(1998)	198	2.48	0.96	164	3.37	1.39
COSMO-SAC(2010)	221	4.66	1.59	170	6.22	2.17
COSMO-SAC-dsp1 (Npar: 5)	221	4.19	1.54	170	5.98	2.09
COSMO-SAC-dsp3 (Npar: 10)	221	3.84	1.47	170	6.07	2.14

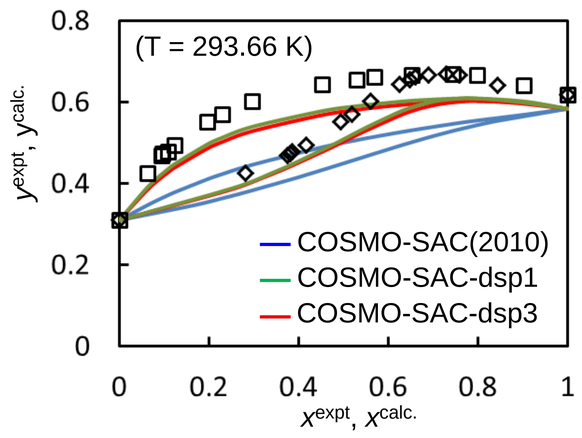
PS. (1) VLE_nhb: in total 7831 VLE data points; (2) VLE_hb: in total 8598 VLE data points;
(3) Different isotherms of the same binary mixture were considered as one binary;
(4) Npar is the number of newly introduced dispersion parameters in the model

➢ **A reduction of 15% in AARD-P can be achieved for non-hydrogen bonding systems!**
➢ **For hydrogen-bonding systems, dominated by electrostatic interactions, a reduction of 3% in AARD-P can be observed.**

B. Improvement of VLE prediction for systems containing fluoro-compounds

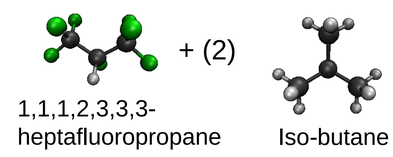
Comparing VLE predictions from COSMO-SAC-dsp, COSMO-SAC and modified UNIFAC

	VLE		
	Nbinary	AARD-P	AAD-y1
mUNIFAC(1998)	**3**	4.57	2.03
COSMO-SAC(2010)	16	11.22	3.97
COSMO-SAC-dsp1	16	6.53	3.65
COSMO-SAC-dsp3	16	6.88	3.70

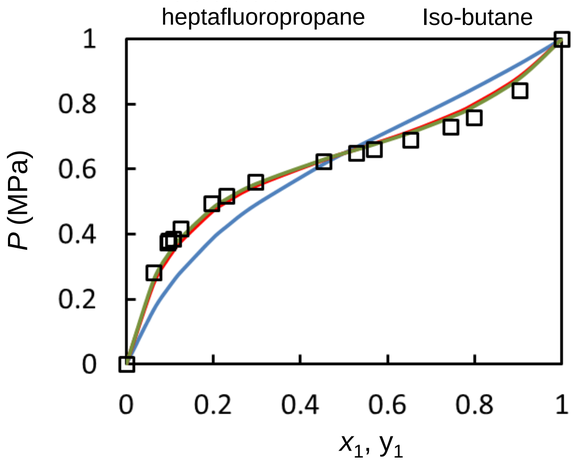


➢ **Modified UNIFAC has a severe issue of missing parameters for this type of system (only 3 out of 16 binary mixtures can be described).**
➢ **COSMO-SAC-dsp could be a good candidate for this type of mixtures.**

(1) + (2)



1,1,1,2,3,3,3-heptafluoropropane Iso-butane

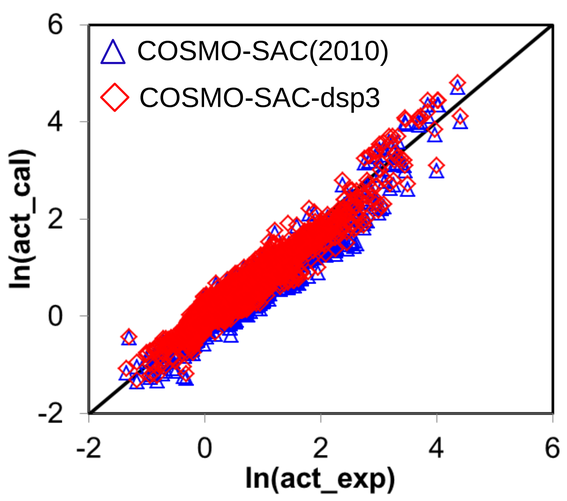


C. Prediction of Infinite Dilution Activity Coefficient (IDAC)

Comparing prediction of IDAC from COSMO-SAC-dsp, COSMO-SAC and modified UNIFAC (in total 728 nhb binary mixtures)

	IDAC_nhb (Prediction)	
	Ndata	Error
mUNIFAC(1998)	1923	0.104
COSMO-SAC(2010)	1923	0.255
COSMO-SAC-dsp1	1923	0.219
COSMO-SAC-dsp3	1923	0.192

$$Error = \frac{1}{N}\sum_{j=1}^{N}\left|\ln\gamma_i^{\infty,expt} - \ln\gamma_i^{\infty,calc}\right|$$



➢ **A reduction of 25% in terms of overall deviation can be achieved for non-hydrogen-bonding systems!**

4. Conclusions

- **A new dispersion contribution to the activity coefficient was proposed in the COSMO-SAC model.**
- **New COSMO-SAC-dsp model can provide better predictions, especially for non-hydrogen-bonding systems.**

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