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PREDICTION OF VAPOR-LIQUID EQUILIBRIA OF BINARY MIXTURES USING QUANTUM CALCULATIONS AND ACTIVITY COEFFICIENT MODELS

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PHAM VAN TAT

Department of Chemistry, University of Dalat

ABSTRACT

In this work, the conductor-like screening model COSMO-SAC (segment activity coefficient) obatained from the density functional theory calculations DFT-VWN-BP with basis set DNP (double numerical basis set augmented with polarization function). The molecular-single sigma profiles were generated by using COSMO calculations. The vapor-liquid equilibria (VLE) for three binary mixtures water(1) - ethanol(2), methanol(1) - benzene(2) and toluene(1) - chlorobenzene(2) were calculated from these sigma profiles. The VLE data of these mixtures turn out to be in good agreement with experimental data as far as such data resulting from the activity coefficient models Wilson [1] and NRTL (non-random two-liquid) [2]. RMS error, mean relative deviation of pressure (MRD_p) and mean deviation of vapor composition (MD_y) are less than 0.087, 9.052 and 0.065, respectively.

Keywords: *Vapor-liquid equilibria, conductor-like screening model COSMO-SAC.*

I - INTRODUCTION

Prediction of vapor-liquid equilibria is a important goal in physical chemistry and chemical engineering. Reliable information of vapor-liquid equilibria is most decisive for developing the usual liquid fuels. The experimental measurement of VLE can be expensive and sometimes highly challenging in several industrial applications. Recent years, trustworthy theoretical methods based on *ab initio* quantum calculations [3, 4] and Gibbs ensemble Monte Carlo simulation technique [5, 6] are thus very desirable. The theoretical methods conductor-like screening model for real solvents COSMO-RS proposed by Klamt et al. [3] and the conductor-like screening model COSMO-SAC (segment activity coefficient) developed by Lin et al. [4] were used for prediction of vapor-liquid and liquid-liquid equilibria and solubility property of binary, ternary and multicomponent systems.

This work reports the prediction of vapor-liquid equilibria for binary mixtures by using conductor-like screening model COSMO-SAC and activity coefficient models Wilson and NRTL. The single-molecule sigma profiles water, ethanol, methanol, benzene, toluene and chlorobenzene are calculated from quantum computations DFT-VWN-BP with basis set DNP. These in turn are used to predict VLE data of binary mixtures water(1) - ethanol(2), methanol(1) - benzene(2) and toluene(1) - chlorobenzene(2). The VLE of them are compared with experimental data and those from models Wilson and NRTL.

II - COMPUTATIONAL DETAILS

1. Cosmo-based thermodynamic model

The COSMO-based model is the “solventaccessible surface" of a solute molecule [3, 4]. The activity coefficients resulting from Eq.1 developed by Lin and Sandler [4]:

$$\ln\gamma_{i/s} = \frac{\Delta G_{i/S}^{*\text{res}} - \Delta G_{i/i}^{*\text{res}}}{RT} + \ln\gamma_{i/S}^{\text{SG}} \qquad (1)$$

Where $\Delta G_{i/S}^{*\text{res}}$ and $\Delta G_{i/i}^{*\text{res}}$ free energy of restoring the charges around the solute molecule in a solution and the charges in a pure liquid; $\gamma_{i/S}^{\text{SG}}$ the Staverman-Gugenheim term.

The screening charge densities are derived from COSMO calculations. These new surface-charge densities (ó) of the single molecules are given by the following equation [3, 4]:

$$\sigma_m = \frac{\sum_n \sigma_n^* \frac{r_n^2 r_{av}^2}{r_n^2 + r_{av}^2} \exp\left(-\frac{d_{mn}^2}{r_n^2 + r_{av}^2}\right)}{\sum_n \frac{r_n^2 r_{av}^2}{r_n^2 + r_{av}^2} \exp\left(-\frac{d_{mn}^2}{r_n^2 + r_{av}^2}\right)} \qquad (2)$$

Where σ_m the average surface-charge density on segment m; the summation is over n segments; r_n the radius of the actual surface segment; r_{av} the average radius and d_{mn} the distance between the two segments.

2. Activity coefficient model

The model NRTL was developed by Renon and Prausnitz [2] to improve on the Wilson equation [1]. The activity coefficients of binary mixtures are calculated by the equation:

$$\ln\gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k} + \sum_j^N \frac{x_j G_{ij}}{\sum_k^N G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_k^N x_k \tau_{kj} G_{kj}}{\sum_k^N G_{kj} x_k}\right) \qquad (3)$$

Where $\tau_{ji} = A_{ji} + B_{ji}/T + C_{ji}\ln(T) + D_{ji}T;\ G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$ and $\alpha_{ij} = \alpha_{ji}$ the adjustable and system-specific parameters.

3. Calculation of vapor-liquid equilibria

The vapor-liquid equilibria of binary mixtures are generated by using the molecular activity coefficients. The vapor mole fractions y_i are calculated by using the relations [3, 4]:

$$\begin{aligned} y_i &= p_i^0 x_i \gamma_i / p^{tot} \qquad (i = 1,2) \\ p^{tot} &= p_1^0 x_1 \gamma_1 + p_2^0 x_2 \gamma_2 \end{aligned} \qquad (4)$$

Where p_i^0 the vapor pressures of pure component at given temperature; x_i the mole fractions of the compounds in the liquid phase; $\tilde{a}_i$ the activity coefficient of the compound i.

The *RMS* error calculations can be carried out using the equation:

$$RMS = \sqrt{\frac{1}{n}\sum_1^n (y_{\exp} - y_{cal})^2} \qquad (5)$$

Here n the number of data points; y_{cal} the calculated vapor fraction from COSMO-SAC.

The mean relative deviation of pressure (MRD_p) and mean deviations of vapor composition (MD_y) are given in the equations:

$$MRD_p, \% = (100/n)\sum_i^n \left(\left|p_{i,cal} - p_{i,\exp}\right| / p_{i,\exp}\right)$$

$$MD_y = (1/n)\sum_i^n \left(\left|y_{i,cal} - y_{i,\exp}\right|\right) \qquad (6)$$

III - RESULTS AND DISCUSSION

1. Computation of Sigma Profiles

The molecular structures were carried out to optimize with the density functional theory (DFT) at the level of theory GGA/VWN-BP with basis set DNP (Double Numerical basis with Polarization functions) [7, 9, 10]. The surface screening charge densities surrounding the molecule are generated from an energy calculation DFT VWN-BP/DNP. The single-molecule sigma profiles were resulted from these surface charge densities, as depicted in Fig 1.

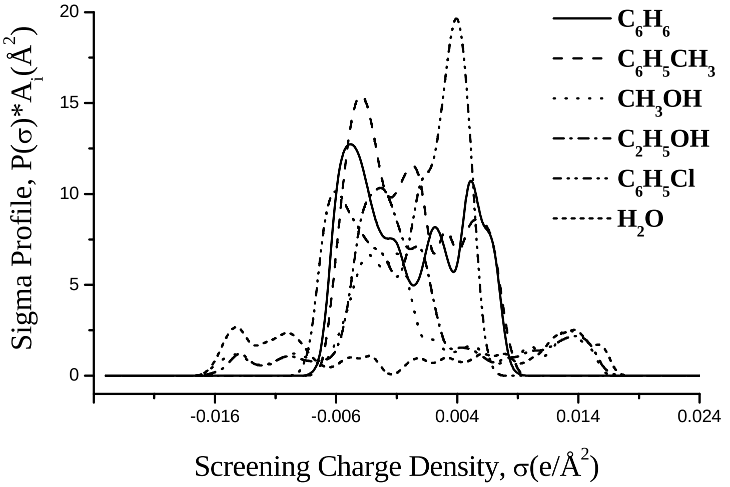


Figure 1: Sigma profiles for the single molecules

2. Vapor-liquid equilibria

The vapor-liquid equilibria for mixture ethanol(1) - water(2) at P = 1.01325 bar was obtained using the relations (4) over a temperature range 350 K to 370 K as shown in Fig 2.

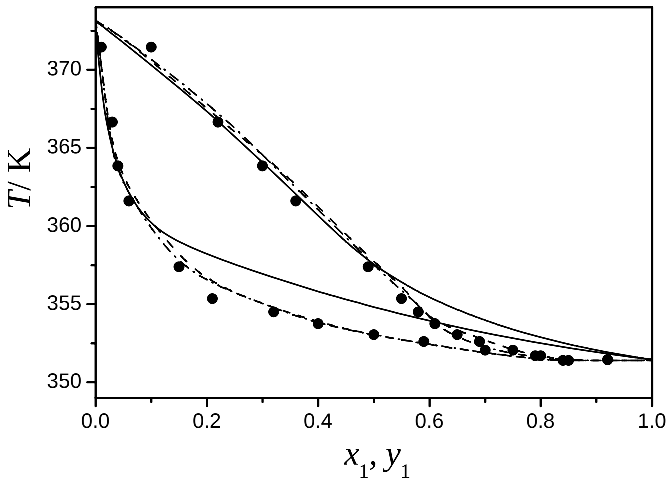
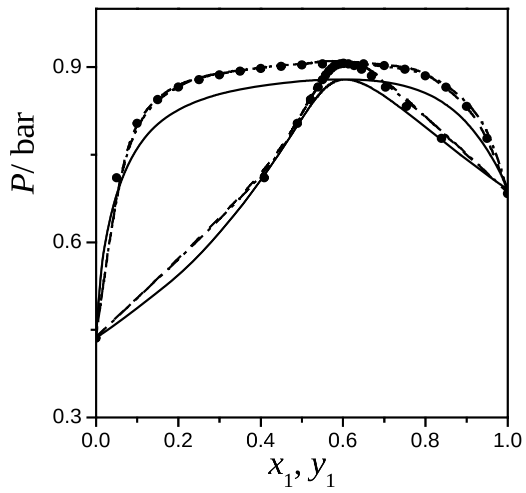


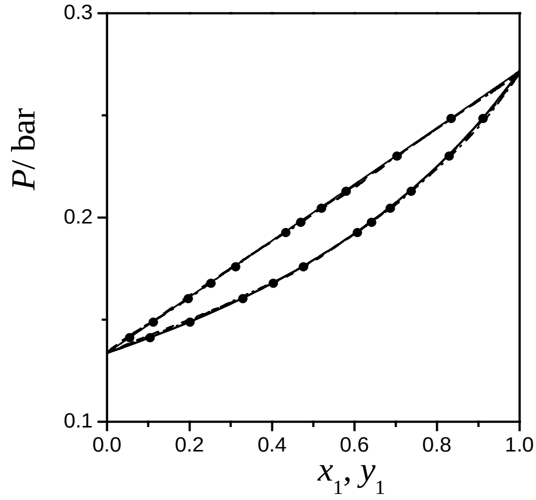
Figure 2: VLE diagram T-x-y of mixture ethanol(1) - water(2) at P = 1.01325 bar; #: experimental data [11]; –: COSMO-SAC; ——— : model Wilson; #####: NRTL.

The VLE data P-x-y of two binary systems methanol(1) - benzene(2) and toluene(1) - chlorobenzene(2) at T = 333.15 K and T = 343.15 K obtained over the pressure ranges from 0.4 to 0.7 bar and from 0.1 to 0.3 bar, respectively.

For the three binary systems in this work the VLE data resulting from COSMO-SAC calculation were compared with experimental data [11] as well as those from the models Wilson and NRTL. This is illustrated in Figs 2, 3. The COSMO-SAC VLE data are very close to experimental data. They agree also well with those from models Wilson and NRTL. The values of *RMS* error, the mean relative deviation of pressure (MRD_p) and mean deviation of vapor composition (MD_y) in table 1 are less than 0.087, 9.052 and 0.065, respectively. So the discrepancies between models are insignificant.



a)



b)

Figure 3: VLE diagram *P*-*x*-*y* of mixtures: a) methanol(1) - benzene(2) at T = 333.15 K and b) toluene(1) - chlorobenzene(2) at T = 343.15 K; for an explanation see Fig. 2.

Table 1: Comparison between the values *RMS*, MRD_p and MD_y of the models

NRTL			Wilson			COSMO-SAC		
RMS	MRD_p, %	MD_y	*RMS*	MRD_p, %	MD_y	*RMS*	MRD_p, %	MD_y
ethanol(1) + water(2) at P = 1.01325 bar								
0.013	6.021	0.013	0.011	5.045	0.045	0.005	7.865	0.01
methanol(1) + benzene(2) at T = 333.15 K								
0.017	5.987	0.007	0.015	6.965	0.065	0.087	9.052	0.03
toluene(1) + chlorobenzene(2) at T = 343.15 K								
0.014	8.753	0.034	0.043	7.132	0.021	0.032	8.343	0.05

IV - CONCLUSIONS

We conclude that the molecular-single sigma profiles water, ethanol, methanol, benzene, toluene and chlorobenzene obtained from quantum calculations are reliable. The activity coefficients of them were calculated from accurately the sigma profiles. The vapor-liquid equilibria of the binary systems water(1) - ethanol(2), methanol(1) - benzene(2) and toluene(1) - chlorobenzene(2) resulting from model COSMO-SAC turn out to be in good agreement with experimental data and those from models Wilson and NRTL. These are pointed out in the *RMS* error, the relative deviations MRD_p and MD_y.

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