J. Serb. Chem. Soc. 70 (3) 527–539 (2005)
JSCS–3286

UDC 541.121:66.040.47+547.21+547.43
Original scientific paper

Vapour–liquid equilibria of the OPLS (Optimized Potentials for Liquid Simulations) model for binary systems of alkanes and alkanes + alcohols

SLOBODAN P. ŠERBANOVIĆ[#], MILAN LJ. MIJAJLOVIĆ[*], IVONA R. RADOVIĆ[#], BOJAN D. DJORDJEVIĆ[**#], MIRJANA LJ. KIJEVČANIN[#], EMILA M. DJORDJEVIĆ and ALEKSANDAR Ž. TASIĆ

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P. O. Box 35-03, Belgrade, Serbia and Montenegro (e-mail: bojan@tmf.bg.ac.yu)

(Received 29 December 2004)

Abstract: The NpT – Gibbs ensemble Monte Carlo computer simulation method was applied to predict the vapour–liquid equlibrium (VLE) behavior of the binary systems ethane + pentane at 277.55 K and 310.95 K, ethane + hexane at 298.15 K, propane + methanol at 313.15 K and propane + ethanol at 325.15 K and 425.15 K. The optimised potentials for the liquid simulating (OPLS) model were used to describe the interactions of alkanes and alcohols. The simulated VLE predictions are compared with experimental data available for the pressure and phase composition of the analyzed binary systems. The agreement between the experimental data and the simulation results is found to be generally good, although slightly better for system in which both components were nonpolar.

Keywords: Gibbs ensemble, Monte Carlo, molecular simulation, OPLS model, vapour–liquid equilibria, alkanes, alcohols.

INTRODUCTION

During the last decade of the last century, research in the synthesis, rational design and optimization of different processes in the chemical, petrochemical, gas processing and pharmaceutical industry was largely concerned with problems related to succesful correlation and predication of phase equilibria and other thermodynamic properties of binary and multicomponent mixtures. Direct measurements and macroscopic thermodynamic procedure of data were the usual approaches. Also, due to the lack of experimental data, different predictive equations were frequently used to describe the thermodynamic behavior of various systems for indus-

* Coresponding author: Fax: +381-11-3370387.
** Present address: Kenneth Denbigh Building, School of Engineering and Electronics, The University of Edinburgh, Edinburgh EH9 3JL UK.
\# Serbian Chemical Society active member.

trial applications. The accuracy of these equations varies depending on the molecularly complex substances, as well as on the particular equation chosen.

To achieve quantitative description of the behavior of fluids in chemical plants or single unit operations (*e.g.*, separation processes), chemical engineering thermodynamics ensures useful empirical, semi-empirical and theoretical frameworks.[1–5] Examples are empirical and semiempirical equations of state, liquid activity coefficient models, group contribution methods, macroscopic corresponding state correlation and various molecular theories (the corresponding state theory, perturbation theories, density functional theories, the integral equation theory, *etc.*).

In chemistry and chemical engineering, vapour–liquid equilibria (VLE) calculations are traditionally carried out using cubic equation of state (CEOS) and/or liquid activity coefficient models (G^E). Recently, the modern development is based on the combination of CEOSs with excess Helmholtz energy (CEOS/A^E) or excess Gibbs energy models (CEOS/G^E) as very accepted and effective methods foremostly, for correlating phase equilibrium descriptions of highly non-ideal systems. A large number of experimental data is available for binary mixtures over restricted ranges of temperature, pressure and compositions. For multicomponent mixtures, however, experimental data are available only for a limited number of mixtures under experimentally determined conditions.

Also, the measurement of thermodynamic properties of mixtures is usually complex and frequently extensive, hence it would be very useful if the properties of a mixture could be predicted having good agreement with those experimentally determined. Molecular dynamic and Monte Carlo simulations,[6–11] are the grand challenges. Molecular simulation approaches based on reliable intermolecular potential models estimate the corresponding thermodynamic macroscopic properties using relations of statistical mechanics. There are several reasons for the importance of such simulations: (*i*) prediction of VLE and other properties, (*ii*) check of statistical mechanics theories (*iii*) inclusion of an explicit term for the dipolar contribution of Helmoltz free energy to equations of state, (*iv*) comparisons with experiment which could give better information about suggested intermolecular potentials. The molecular models include a clear atomistic description of the mixtures to be studied and functional form of the intermolecular potential for the interactions between encountered molecules. A great variety of potential models of various types (true pair potentials, semi-empirical pair potentials and effective pair potentials) including multibody effects have been studied and tested on different cases. A recent review of potential models is available in the literature.[3,12,13]

The success of molecular simulation mostly depends on the availability of efficient simulation algorithms and accurate force fileds. In a binary mixture, the contributions which result from interactions between dissimilar molecules can be obtained from combining rules.[14–17]

Over the last few years, significant progress has been made in the molecular simulation of VLE, and the study of VLE has been the subject of numerous studies.

VLE simulation for simple intermolecular model fluids[4,18] very frequently includes Lenard-Jones (LJ) three and two dimensional fluids, the square-well fluid, Yukawa fluids, dipolar and quadrupolar LJ fluids, associating LJ fluids with square well sites, and the Gay–Besne fluid.

Different methods have been applied for the simulation of VLE with molecular models, for example the Gibbs Ensemble Monte Carlo (GEMC),[19–26] the Gibbs–Duhem integration,[27–33] the NpT + Test Particle Method,[18,34–38] the Grand Equilibrium,[13,39] Histogram-reweighting grand canonical Monte Carlo simulation,[17,40–43] pseudoensemble,[44,45] and direct interfacial simulations.[46–48] Many studies show the possibility of the combination of the mentioned molecular simulations and other techniques to the prediction of VLE of binary systems.[49–51]

Monte Carlo simulations, generally speaking, can be used[23,24,50,52,53] in the canonical (NVT) or the isobaric–isothermal (NpT) ensemble or other ensembles (the grand-canonical (μVT) and micro-canonical (NVE)).

The semi-empirical OPLS (Optimised Potentials for Liquid Simulations) model, as a very suitable model for the study of organic liquid properties was applied here. This model functions quite satisfactorily for completely different types of hydrocarbons, such as alkanes, alcohols, amines, aromatic hydrocarbons, ethers, *etc*.

Numerous computer simulations have been developed for alkanes and alcohols for several model potentials. The main reasons for this interest are their great importance in many technological applications.[54,55] Thermodynamic properties were mostly calculated for pure short linear alkanes and alcohols, while simulations of VLE for binary mixtures of alkanes and alkanes + alcohols were perofmed in only a few cases[17,55–62] (methane + ethane, methane + propane, methane + *n*-pentane, ethane + *n*-heptane, methanol + ethane, *n*-hexane + methanol, *n*-hexane + ethanol).

In this work, VLE of alkanes (ethane + *n*-pentane, ethane + *n*-hexane) and alkanes + alcohols (propane + methanol, propane + ethanol) binary systems were calculated by the Gibbs ensemble simulation technique. The molecules of ethane, propane, *n*-hexane, methanol and ethanol were described with the OPLS model.

OPLS FORCE FIELDS

OPLS united-atom force fields (frequently signed as OPLS-UA) were developed by Jorgensen *et al.*[63–66] They are used to describe interactons between molecular groups (segments) separated by more than three bonds or belonging to different molecules. Here, this force field makes use of the united-atom approach, *i.e.*, methyl and methylene segments are treated as single pseudoatoms centred on the carbon. Non-bonded pseudoatoms in most cases interact through Lennard-Jones (LJ) potentials.[67,68] For molecules with dipolar bonds, the disposition of the electrical charge is represented by the arrangement of point charges. The value of the dipole moment is evaluated from the distance between the points and the values of their electric charge. The interaction between point charges for alcohol molecules is described by the Coulomb expression for electric force.

The OPLS model, here described by the sum of pairwise additive LJ 12–6 potentials, Coulombic interactions of partial charges, angle bending and torsional terms, is given by:

$$E(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + E_{\text{bend}} + E_{\text{tors}} \quad (1)$$

where r_{ij} is the distance between site i and site j, while ε_{ij}, σ_{ij}, q_i and q_j are the LJ depth of the potential well, LJ size and partial electric charge, respectively. ε_0 is the permittivity of vacuum.

For the description of the unlike OPLS interaction in binary mixtures, the unlike interaction parameters ε_{ij} and σ_{ij} were determined using the following standard Lorentz–Berthelot combining rules

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (2)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (3)$$

where ε_i and σ_i are LJ parameters for site i. Thus, no adjustable interaction parameters were used in the calculations.

The OPLS potentials for alkanes and alcohols have been widely determined and used.[54,55,61,64,69–75] The OPLS parameters for the groups of investigated alkanes and alcohols were taken from reference[66] and are listed in Table I.

TABLE I. OPLS parameters for alkanes and alcohols

Group	σ/Å	(ε/k_b)/K	q/e
$CH_3(-CH_2R)$	3.905	88.1	–
$(R-)(CH_2)(-R)$	3.905	59.4	–
$CH_3(-OH)$	3.775	104.1	+0.265
$CH_3(-CH_2-OH)$	3.775	104.1	–
$(R-)CH_2(-OH)$	3.905	59.4	+0.265
(R–)O(–H)	3.070	85.6	–0.700
(RO–)H	–	–	+0.435

σ – Lenard-Jones diameter of the group; ε – energy minimum for the Lennard–Jones potential; q – partial electric charge of the group

The bonds between groups were considered to be of constant length with the following values: 1.53, 1.43. and 0.945 Å for C–C, C–O and O–H, respectively. A harmonic potential E_{bend} is used to govern bond angle bending[76]

$$E_{\text{bend}} = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \tag{4}$$

where E_{bend} is the bending potential, k_θ is the force constant which is expressed over Boltzmann's constant k_b and has the values k_θ/k_b: 62500, 50400 and 55440 (K/rad^2) for C–C–C, C–C–O and C–O–H bond angles, respectively; θ is the angle between bonds and θ_0 is the corresponding equilibrium angle with the values 112, 108 and 108.5°, for C–C–C, C–C–O and C–O–H, respectively. The torsional motion of molecules with more than three segments is controlled by the internal rotational potential function.[64,65]

$$E_{\text{tors}} = c_1[1 + \cos\phi] + c_2\,[1 - \cos(2\phi)] + c_3\,[1 + \cos(3\phi)] \tag{5}$$

where c_1, c_2 and c_3 are the constants with the following values: $c_1/k_b = 355.03$, $c_2/k_b = -68.19$ and $c_3/k_b = 791.32$ K for C–C–C–C; $c_1/k_b = 176.62$, $c_2/k_b = -53.34$ and $c_3/k_b = 769.93$ K for C–C–C–O; and $c_1/k_b = 209.82$, $c_2/k_b = -29.17$ and $c_3/k_b = 187.93$ K for C–C–O–H.

SIMULATION DETAILS

The NpT version of GEMC simulations were carried out using the computer program of Errington and Panagiotopoulos.[77] Simulation details for each system are given separately.

Simulations were performed for two types of binary mixtures (i) nonpolar + nonpolar: ethane + *n*-pentane and ethane + *n*-hexane mixtures, (*ii*) nonpolar + polar: *n*-propane + methanol and *n*-propane + ethanol mixtures.

The parameters of isothermal VLE of the ethane + *n*-pentane system were evaluated. Therefore, the simulaton was conducted at two temperatures: 277.55 K and 310.96 K. Since this kind of ensemble represents the behavior of a system at constant pressure, the simulation had to be done several times to gain equilibrium data for several different pressures. However, many of the conditions were kept the same in all of these runs. The total number of molecules was set to 300 and the number of ethane molecules was varied from 110 to 220, depending on the pressure. All of the simulations were started from two simulation boxes containing pure components, while the initial densities were set to values that were sufficiently far away from the expected equilibrium values. The latter condition plays an important role in the verification of the duration of the equilibration period. When the production period was reached, the values of the density in both phases start to stabilize and fluctuate around the final average value. The simulation consisted of 3.5 million Monte Carlo steps, where the equilibration period was 1 million steps long, while the production period consisted of 2.5 million steps. The ratio of the probability of selecting a specific Monte Carlo move was the following: 0.79: 0.01: 0.1: 0.1 for translation (or rotation) of molecules inside the box, volume changes, transfer of molecules from one box to another and regrowth of molecules.

Most of the initial conditions for the ethane + *n*-hexane system at 298.15 K were set to be the same as for the simulation of the ethane + *n*-pentane system (total number of molecules, although in this case the number of ethane molecules was varied between 150 and 285; the initial densities far away from the equilibrium values, the length of the simulation). However, only one isothermal equilibrium was simulated for this system at a temperature of 298.15 K and for several different pressures. In all of these simulations, the temperature and pressure were kept constant during the run.

For the propane + methanol system, isothermal equilibrium was simulated at a temperature of 313.15 K and for 12 different pressures. Most of the initial conditions were identical to those in the previous two examples, the simulation consisted of 3.5 million Monte Carlo steps, 1 million in the equilibration period and 2.5 million in the production period. The probability of selecting specific Monte Carlo moves had the following ratio: 0.75:0.01:0.1:0.1 for translation (or rotation), volume change, transfer of molecules and regrowth of molecules. The total number of molecules was set to 300, whereby the number of propane molecules was varied from 150 to 250, depending on the pressure.

The initial conditions for the propane + ethanol system were set to be the same as for the simulation of the propane + methanol system. The parameters of isothermal VLE were evaluated at two temperatures 325 K and 425 K, and for several different pressurs.

RESULTS AND DISCUSSION

Ethane + n-*pentane system*

Simulation of the ethane + *n*-pentane system was performed under isothermal conditions, but with two runs at two different temperatures. Experimental data for the mole fraction of ethane in both phases were available over the entire concentration range.[78] Since the system at both temperatures exhibits very similar behavior there was no need to perform separate analysis for each temperature. The results are presented in Table II and Fig. 1a for 277.55 K. The comparison of the pressure dependencies of the difference between the experimental and calculated mole fractions of ethane is shown in Fig. 1b. The differences, Δx and Δy, were calculated using the following equations:

$$\Delta x = \left| x_{exp} - x_{cal} \right| \tag{6}$$

$$\Delta_y = \left| y_{exp} - y_{cal} \right| \tag{7}$$

where x denotes the mole fraction of ethane in the liquid and y is the mole fraction of ethane in the vapour phase.

At both temperatures the ethane + *n*-pentane system deviates substantially from experimental data for the vapour phase with decreasing pressure. Similar re-

sults were expected for the liquid phase. The agreement between the experimental and calculated values could be considered as fair for the whole range of simulation pressures at both temperatures.

TABLE II. Experimental[78] and simulated results of the mole fraction of ethane for the ethane + *n*-alkane systems

p/bar	$x_{exp}(C_2H_6)$	$y_{exp}(C_2H_6)$	$x_{cal}(C_2H_6)$	$y_{cal}(C_2H_6)$	Δx	Δy
			Ethane + n-*pentane*			
T = 277.55 K						
3.4	0.1432	0.9158	0.1679	0.9523	0.0247	0.0365
6.9	0.2891	0.9504	0.3792	0.9847	0.0901	0.0343
10.3	0.4316	0.9659	0.4713	0.9822	0.0397	0.0163
13.8	0.5959	0.9763	0.6196	0.9898	0.0237	0.0135
17.2	0.6950	0.9838	0.6901	0.9931	0.0049	0.0093
20.7	0.8141	0.9901	0.7972	0.9940	0.0169	0.0039
24.1	0.9235	0.9960	0.9167	0.9945	0.0068	0.0015
T = 310.95K						
6.9	0.1519	0.8448	0.1997	0.9079	0.0478	0.0631
10.3	0.2371	0.8897	0.3205	0.9476	0.0834	0.0579
13.8	0.3201	0.9134	0.3512	0.9438	0.0311	0.0304
17.2	0.4002	0.9284	0.4738	0.9737	0.0736	0.0453
20.7	0.4774	0.9389	0.4874	0.9719	0.0100	0.0330
24.1	0.5511	0.9472	0.6497	0.9752	0.0986	0.0280
27.5	0.6219	0.9548	0.6997	0.9796	0.0778	0.0248
31.0	0.6879	0.9609	0.7959	0.9865	0.1080	0.0256
34.4	0.7465	0.9673	0.8342	0.9873	0.0877	0.0200
41.3	0.8503	0.9782	0.8506	0.9854	0.0003	0.0072
48.2	0.9274	0.9854	0.8947	0.9040	0.0327	0.0814
52.1	0.9778	0.9778	0.9163	0.8998	0.0614	0.0780
			Ethane + n-*hexane*			
T = 298.15 K						
5.1	0.1497	0.9544	0.1161	0.9760	0.0336	0.0216
9.0	0.2698	0.9722	0.1890	0.9811	0.0808	0.0089
11.1	0.3306	0.9776	0.2810	0.9850	0.0496	0.0074
15.2	0.4502	0.9825	0.3127	0.9867	0.1375	0.0042
19.9	0.5833	0.9854	0.4232	0.9891	0.1601	0.0037
29.7	0.8097	0.9869	0.6523	0.9909	0.1574	0.0040
35.5	0.9135	0.9886	0.7884	0.9923	0.1251	0.0037

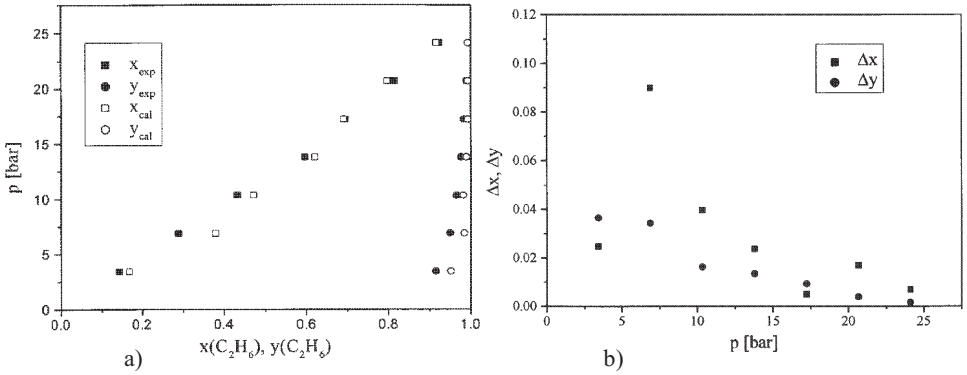

Fig. 1. a) The pressure – composition diagram for the ethane + *n*-pentane system at 277.55 K: experimental[78] and simulated results for the mole fracton of ethane in the liquid and the vapour phase; b) Dependence of the diference between the experimental data and the calculated results on the simulation pressure for the ethane + *n*-pentane system at 277.55K.

Ethane + n-*hexane system*

The results of the simulation for the ethane + hexane system are presented in Table II and Fig. 2. For the liquid phase, the deviations from the experiments[78] are larger than those for the ethane + *n*-pentane system, particularly with increasing pressure. For vapour phase, good agreement with the experimental data was obtained for lower and higher pressures, although slightly better for the higher pressures.

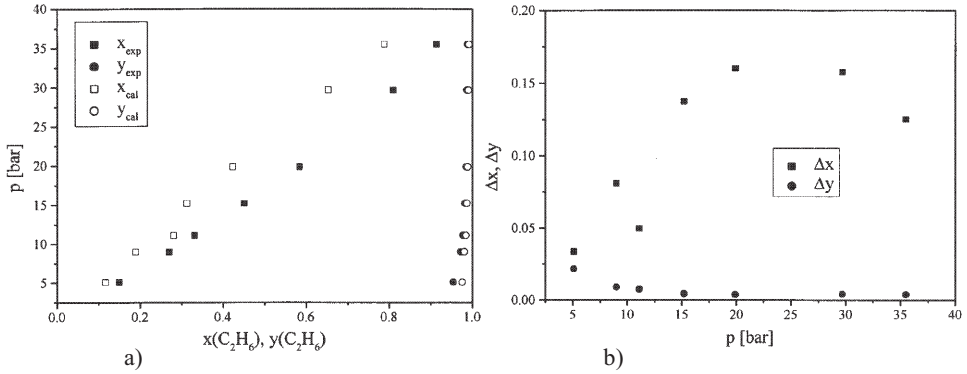

Fig. 2. a) The pressure – composiiton diagram for the ethane + *n*-hexane system at 298.15 K: experimental[78] and simulated results for the mole fraction of ethane in the liiquid and the vapour phase; b) Dependence of the difference between the experimental data and the calculated results on the simulation pressures for the ethane + *n*-hexane system at 298.15K.

Propane + methanol system

The simulation data of the vapour–liquid equilibrium of the propane + methanol system was carried out for twelve different pressures. The results are presented in Ta-

ble III. As can be seen, the simulation results are in good agreement with the experimental values for the liquid phase only for low pressures, while the results for the vapour phase show the opposite tendency, *i.e.*, increasing deviation with decreasing pressure. A possible explanation for this situation is the difference in the interaction forces among the molecules of the different species. For the propane + methanol system, nonpolar–polar interactions exhibit high deviation from ideal behaviour, while in the ethane + pentane and ethane + hexane mixture the molecules of the different components belong to the same class of organic compounds and the deviation from ideal behaviour is much less. The general conclusion that can be drawn from these results is that the Gibbs ensemble method, in its original form, is not powerful enough to accurately represent the behavior of non-ideal mixtures with nonpolar–polar interactions. Interaction parameters of the OPLS model are, also, necessary.

TABLE III. Experimental[78,79] and simulated results of the mole fraction of propane for propane + alcohol systems

p/bar	x_{exp} (C_3H_8)	y_{exp}(C_3H_8)	x_{cal}(C_3H_8)	y_{cal}(C_3H_8)	Δx	Δy
Propane + methanol						
T = 298.15 K						
3.5	0.0252	0.8780	0.0341	0.9357	0.0089	0.0577
5.1	0.0386	0.9000	0.0142	0.9448	0.0244	0.0448
6.2	0.0520	0.9270	0.0335	0.9586	0.0185	0.0316
7.1	0.0750	0.9370	0.0460	0.9644	0.0289	0.0274
8.4	0.0840	0.9470	0.0706	0.9673	0.0134	0.0203
10.6	0.1460	0.9560	0.0642	0.9724	0.0818	0.0164
11.5	0.1950	0.9650	0.0528	0.9727	0.1422	0.0077
12.5	0.2630	0.9660	0.0433	0.9797	0.2197	0.0137
13.1	0.3870	0.9690	0.0692	0.9756	0.3178	0.0066
13.2	0.4110	0.9720	0.0459	0.9780	0.3651	0.0060
13.3	0.4490	0.9680	0.1305	0.9846	0.3185	0.0166
Propane + ethanol						
T = 325.15 K						
5.7	0.1050	0.9210	0.0528	0.9544	0.0522	0.0334
9.9	0.2830	0.9550	0.1793	0.9719	0.1037	0.0169
11.9	0.4120	0.9640	0.2574	0.9809	0.1546	0.0169
T = 425.15 K						
24.9	0.1610	0.5040	0.0676	0.6728	0.0934	0.1688
47.7	0.4470	0.7130	0.1733	0.7643	0.2737	0.0513

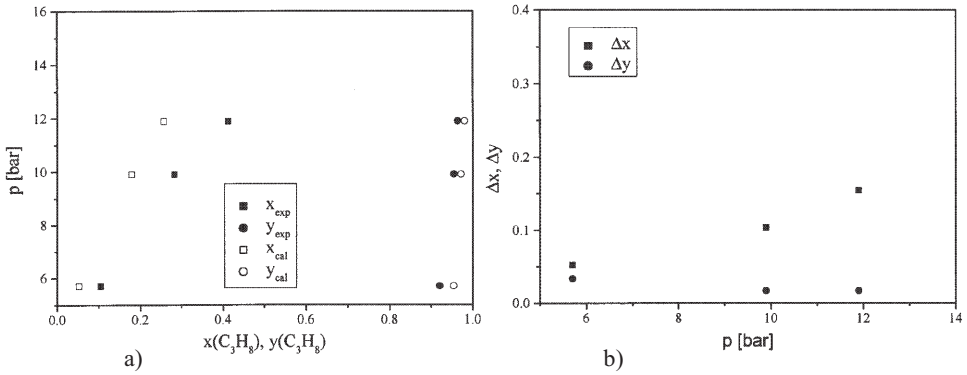

Fig. 3. a) The pressure – composition diagram for the propane + ethanol system at 325.15 K: experimental[79] and simulated results for the mole fraction of propane in the liquid and the vapour phase; b) Dependence of difference between the experimental data and calculated results on simulations pressures for the propane + ethanol system at 325.15K.

Propane + ethanol system

The simulation for this system was carried out for several different pressures and two different temperatures.[79] The results are presented in Table III and Figure 3 at 325.15 K and at 425.15 K. Since the propane + ethanol system is also a system with polar–nonpolar interactions, all the statements made for the propane + methanol mixture could be applied here; the calculated results of the liquid phase are in better agreement with the experimental values at lower pressures, while for the vapour phase, the differences between the experimental and calculated results are lower at higher pressures. For both temperatures, the deviations from the experimental data are larger in comparison with the previously analyzed systems with nonpolar components (ethane + *n*-pentane and ethane + *n*-hexane mixtures). As a result, for example, further refinements might be desirable for the OPLS force field, requiring special binary interaction parameters.

CONCLUSIONS

The general conclusion which can be made from the results obtained for the two nonpolar + nonpolar *n*-alkanes (ethane + *n*-pentane, ethane + *n*-hexane) and the two nonpolar + polar (propane + methanol, propane + ethanol) systems is that reasonably satisfactory agreement with experimental data can be attained in the NpT–GEMC simulation using OPLS united–atom force fields.

It can also be stated that the NpT–GEMC simulations as applied in this work are much more reliable in predicting VLE equilibria in nonpolar systems, the behavior of which are closer to ideal mixtures.

Acknowledgements: This work was supported by a grant from the Ministry of Science and Environmental Protection of Serbia and the Faculty of Technology and Metallurgy, University of Belgrade.

ИЗВОД

РАВНОТЕЖА ПАРА–ТЕЧНОСТ OPLS (ОПТИМИЗОВАЊЕ ПОТЕНЦИЈАЛА ЗА ТЕЧНУ СИМУЛАЦИЈУ) МОДЕЛА БИНАРНИХ СИСТЕМА АЛКАНА И АЛКАНА + АЛКОХОЛА

СЛОБОДАН П. ШЕРБАНОВИЋ, МИЛАН Љ. МИЈАЈЛОВИЋ, ИВОНА Р. РАДОВИЋ, БОЈАН Д. ЂОРЂЕВИЋ, МИРЈАНА Љ. КИЈЕВЧАНИН, ЕМИЛА М. ЂОРЂЕВИЋ и АЛЕКСАНДАР Ж. ТАСИЋ

Технолошко-металуршки факултет, Универзитет у Београду, Карнегијева 4, 11000 Београд

Метод NpT–Gibbs-ових ансамбла и Monte Carlo молекулска симулација су примењени на предсказивање равнотежа пара–течност (VLE) бинарних система етан + пентан на 277.55 K и 310.95 K, етан + хексан на 298.15 K, пропан + метанол на 313.15 K и пропан + етанол на 325.15 K и 425.15 K. Оптимизовани параметри за течну симулацију (OPLS) су коришћени да опишу интеракцију алкана и алкохола. Добијени резултати симулације равнотеже пара–течност су упоређени са доступним експерименталним подацима за одговарајуће притиске и саставе испитиваних бинарних система. Може се рећи да је добијено добро слагање са експерименталним подацима, мада нешто боље код система у којима су обе компоненте неполарне.

(Примљено 29. децембра 2004)

REFERENCES

1. J. M. Prausnitz, R. N.Lichtenthaler, E. G. de Azevedo, *Molecular Thermodynamics of Fluid–Phase Equilibria,* Prentice-Hall Inc., Englewood Cliffs, New Yersey 1986
2. S. Malinowski, A. Anderko, *Modeling Phase Equilibria, Thermodynamic Background and Practical Tools*, Wiley, New York, 1992
3. S. I. Sandler, *Models for Thermodynamic and Phase Equilibria Calculations,* Marcel-Dekker, New York, 1994
4. *Equation of State for Fluids and Fluid Mixtures, Part I and II*, J. V. Sengers, R. F. Kayser, C. J. Peters, H. J. White Jr., Eds., IUPAC, Elsevier, Amsterdam, 2000
5. B. E. Poling, J. M. Prausnitz, J. P. O'Connell, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 2001
6. F. F. Abraham, *Adv. in Phys.* **35** (1986) 1
7. (a) K. E. Gubbins, *Mol. Simul.* **2** (1989) 223, (b) K. E. Gubbins, *Pure & Appl. Chem.* **65** (1993) 935
8. K. Binder, *Rep. Prog. Phys*. **60** (1997) 487
9. M. W. Deem, *AlChE J.* **44** (1998) 2569
10. J. I. Siepmann, *Adv. Chem. Phys.* **105** (1999) 443
11. A. Z. Panagiotopoulos, *J. Phys.: Condens. Matter.* **12** (2000) R25
12. R. J. Sadus, *Molecular Simulation of Fluids: Theory, Algorithms and Object-Orientation*, Elsevier, Amsterdam, 1999
13. J. Stoll, J. Vrabec, H. Hasse, *AIChE J.* **49** (2003) 2187
14. B. E. F. Fender, G. D. Hasley, Jr., *J. Chem. Phys.* **36** (1962) 1881
15. F. T. Smith, *Phys. Rev. A* **5** (1972) 1708
16. C. L. Kong, *J. Chem. Phys.* **59** (1973) 2464
17. J. J. Potoff, J. R. Errington, A. Z. Panagiotopoulos, *Mol. Phys.* **97** (1999) 1073
18. J. Vrabec, J. Fischer, *Mol. Phys.* **85** (1995) 781
19. A. Z. Panagiotopoulos, *Mol. Phys.* **61** (1987) 813
20. A. Z. Panagiotopoulos, N. Quirke, D. J. Tildesley, *Mol. Phys.* **63** (1988) 527
21. A. Z. Panagiotopoulos, *Int. J. Thermophys.* **10** (1989) 447
22. B. Smit, Ph. de Smedt, D. Frenkel, *Mol. Phys.* **68** (1989) 931

23. A. Z. Panagiotopoulos, M. R. Stapleton, *Fluid Phase Equilibria* **53** (1989) 133
24. A. Z. Panagiotopoulos, *Mol. Sim.* **9** (1992) 1
25. E. Marcelli, R. J. Sadus, *J. Chem. Phys.* **111** (1999) 1533
26. S. D. Moon, *Bull. Korean Chem. Soc.* **23** (2002) 811
27. D. A. Kofke, *Mol. Phys.* **78** (1993) 1331
28. D. A. Kofke, *J. Chem. Phys.* **98** (1993) 4149
29. M. Mehta, D. A. Kofke, *Chem. Eng. Sci.* **49** (1994) 2633
30. M. Lisal, V. Vacek, *Mol. Sim.* **17** (1996) 27
31. M. Lisal, V. Vacek, *Mol. Sim.* **18** (1996) 75
32. M. Lisal, R. Budinsky, V. Vacek, *Fluid Phase Equilibria* **135** (1997) 193
33. D. A. Kofke, *Adv. Chem. Phys.* **105** (1999) 405
34. D. Moller, J. Fischer, *Mol. Phys.* **69** (1990) 463
35. D. Moller, J. Fischer, *Mol. Phys.* **75** (1992) 1461
36. A. Lotfi, J. Vrabec, J. Fischer, *Mol. Phys.* **76** (1992) 1319
37. J. Vrabec, J. Stoll, H. Hasse, *J. Phys. Chem. B* **105** (2001) 12126
38. J. Stoll, J. Vrabec, H. Hasse, *Fluid Phase Equilibria* **209** (2003) 29
39. J. Vrabec, H.Hasse, *Mol. Phys.* **100** (2002) 3375
40. A. M. Ferrenberg, R. H. Swensen, *Phys. Rev. Lett.* **61** (1988) 2635
41. A. M. Ferrenberg, R. H. Swensen, *Phys. Rev. Lett.* **63** (1989) 1195
42. J. J. Potoff, A. Z. Panagiotopoulos, *J. Chem. Phys.* **109** (1998) 10914
43. J. Potoff, J. I. Siepmann, *AIChE J.* **47** (2001) 1676
44. P. J. Camp, M. P. Allen, *Mol. Phys.* **88** (1996) 1459
45. P. Ungerer, A. Bontin, A. H. Fucks, *Mol. Phys.* **97** (1999) 523
46. A. D. Mackie, A. Z. Panagiotopoulos, S. K. Kumar, *J. Chem. Phys.* **102** (1995) 1014
47. J. Alejandre, D. J. Tildesley, G. A. Chapela, *J. Chem. Phys.* **102** (1995) 4574
48. E. Diaz-Herrera, J. Alejandre, G. Ramirez-Santiago, F. Forstmann, *J. Chem. Phys.* **110** (1999) 8084
49. J. Delhommelle, A. Boutin, A. H. Fucks, *Mol. Sim.* **22** (1999) 351
50. J. Vorholz, B. Rumpf, G. Maurer, *Phys. Chem. Chem. Phys.* **4** (2002) 4449
51. A. Van't Hof, S. W. De Leeuw, C. K. Hall, C. J. Peters, *Mol. Phys.* **102** (2004) 301
52. G. Kronome, T. Kristof, J. Liszi, I. Szalai, *Fluid Phase Equilibria* **155** (1999) 157
53. J. Vorholz, V. I. Harismiadis, B. Rumpf, A. Z. Panagiotopoulos, G. Maurer, *Fluid Phase Equilibria* **170** (2000) 203
54. B. Chen, M. G. Martin, J. I. Siepmann, *J. Phys. Chem. B* **102** (1998) 2578
55. B. Chen, J. J. Potoff, J. I. Siepmann, *J. Phys. Chem. B* **105** (2001) 3093
56. (a) J. J. de Pablo, J. M. Pausnitz, *Fluid Phase Equlibria* **53** (1989) 177, (b) J. J. de Pablo, N. Bonnin, J. M. Pausnitz, *Fluid Phase Equilibria* **73** (1992) 187
57. I. Yu. Gotlib, E. M. Piotrovskaya, S. W. de Leeuw, *Fluid Phase Equilibria* **129** (1997) 1
58. S. K. Nath, F. A. Axobedo, J. J. de Pablo, I. Patramai, *Ind. Eng. Chem. Res.* **37 (1998) 3195**
59. M. G. Martin, J. I. Siepmann, *J. Am. Chem. Soc.* **119** (1997) 8921
60. A. Liu, T. L. Beck, *J. Chem. Phys. B* **102** (1998) 7627
61. M. Lisal, W. R. Smith, I. Nezbeda, *Fluid Phase Equilibria* **181** (2001) 127
62. J. M. Stubbs, B. Chen, J. J. Potoff, J. I. Siepmann, *Fluid Phase Equilibria* **183**–**184** (2001) 301
63. W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, M. L. Klein, *J. Chem. Phys.* **79** (1983) 926
64. W. L. Jorgensen, J. D. Madura, C.J. Swenson, *J. Am. Chem. Soc.* **106** (1984) 6638
65. W. L. Jorgensen, *J. Phys. Chem.* **90** (1986) 1276
66. W. L. Jorgensen, J. Tirado-Rives, *J. Am. Chem. Soc.* **110** (1988) 1657
67. D. J. Adams, *Mol. Phys.* **37** (1979) 211
68. J. J. Nocolas, K. E. Gubbins, W. B. Street, D. J. Tildesley, *Mol. Phys.* **37** (1979) 1429
69. W. L. Jorgensen, *J. Am. Chem. Soc.* **103** (1981) 4721

70. J. Fischer, R. Lusting, H. Breitenfelder-Manske, W. Lemming, *Mol. Phys.* **52** (1984) 485
71. M. Mezei, *Mol. Sim.* **9** (1992) 257
72. J. I. Siepmann, S. Karaborni, B. Smit, *Nature* **365** (1993) 330
73. M. E. van Leeuwen, B. Smit, *J. Phys. Chem.* **99** (1995) 1831
74. W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.* **118** (1996) 11225
75. R. Agrawal, E. P. Walls, *Fluid Phase Equilibria* **131** (1997) 51
76. P. van der Ploeg, A. Berendsen, *J. Chem. Phys.* **76** (1970) 3271
77. http://kea.princeton.edu/jerring/gibbs/ (2004)
78. K. Ohgaki, F. Sano, T. Katayama, *J. Chem. Eng. Data* **21** (1976) 55
79. M. Gomez-Nieto, G. Thodos, *AlChE J.* **24** (1978) 672.