

Modeling the Vapor-Liquid Equilibrium of Mixtures Involving Noble Gases, Alkanes, and Refrigerants and some Ionic Liquids Using Perturbed Hard-Sphere Equation of State

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Abstract: The present study is a continuation of our previous work (S.M. Hosseini, J. Moghadasi, M.M. Papari, F. Fadaei Nobandegani, J. Mol. Liq. 160 (2011) 67–71) related to the examination of the ability of the perturbed hard-sphere equation of state (EOS) in predicting thermodynamic properties of pure fluid and mixtures. In our previous study, a perturbed hard-sphere equation of state was developed to predict pressure-volume-temperature-composition surfaces of pure and mixtures of ionic liquids (ILs). The present paper aims to extend the model to vapor-liquid equilibria of some binary mixtures consisting of ionic liquids, refrigerants, hydrocarbons, and monatomic fluids. The novelty of the present work is the application of our perturbed hard-sphere equation of state to model the phase equilibria of various mixtures. The outcomes of the computation are compared with the experimental data. Our results demonstrate that this EOS can properly model phase equilibria of fluid mixtures with acceptable accuracies.

Keywords: Equation of state, Ionic liquids, Phase equilibria.

1. INTRODUCTION

The need for an applicable model for predicting phase equilibria of fluids and fluids mixtures is one of major industrial concern. Measurements are costly and time-consuming. So, it is of vital to have predictive methods to describe thermodynamic properties of pure fluids and their mixtures. Equations of state are important tool in equipment design and have assumed an expanding role in correlating of phase equilibria of fluids. However, most of the EOS suffers from the fact that they fail to represent properties accurately in a vast range of temperature and pressure of operation. In the case of mixtures, there is some mixing and combining rules that allow an EOS to be developed for mixtures. Accuracy in the prediction of properties of mixtures is one of the major concerns in scientific research and engineering calculations.

In our previous work [1], a perturbed hard-sphere equation of state (PHS EOS) was developed to model the volumetric properties of ILs and their mixtures. The structure of the PHS EOS will be introduced in the next section. In the present study, the PHS EOS is employed to predict the phase equilibria of several fluid mixtures. The phase equilibria properties in question are the mixture densities, vapor pressures, excess Gibbs free energies and excess molar volumes. The studied mixtures are noble gas mixtures, noble gas +

alkane mixtures, refrigerant mixtures and some mixtures containing ionic liquids. In this respect, the density and the excess volumetric properties of fluid mixtures, which depend on the composition and/or temperature that are of great importance in understanding the nature of molecular mixtures aggregation that exists in the binary mixtures, have been determined. The outcomes of the computations are compared with literature data. The results demonstrate that the perturbed hard-sphere EOS is capable of modeling phase equilibria of mixtures accurately.

2. THEORY

Equation of state in pure frame of the EOS proposed by Hosseini *et al.* [2, 3] has the following form:

$$\frac{P}{\rho kT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{a(T)\rho}{kT}, \quad (1)$$

Where P is the pressure, ρ is the number (molar) density, kT is the thermal energy per molecule and η is packing fraction defined as:

$$\eta = \frac{b(T)\rho}{4}, \quad (2)$$

Eq. (1) has two parts: 1) the Carnahan–Starling expression [4] taken as reference hard-sphere model into account and 2) van der Waals (vdW) attraction term. Several procedures have been proposed to evaluate two temperature-dependent parameters $a(T)$ and $b(T)$ appeared in Eq. (1) [5-8]. We have

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determined these parameters from the corresponding states correlation. The temperature-dependent parameters of Eq. (1) can be expressed in terms of the following universal functions:

$$a(T) = \frac{2\pi}{3\rho_c} k T_c F_a(T_r) \quad (3)$$

$$b(T) = \frac{2\pi}{3\rho_c} F_b(T_r) \quad (4)$$

Here ρ_c is the critical density, and T_r is the reduced temperature which is scaled by the critical temperature T_c . We have presented an empirical formula for universal functions, $F_a(T_r)$ and $F_b(T_r)$ in terms of the reduced temperature, which can be written as:

$$F_a(T_r) = a_1 \exp(-a_2 T_r) + a_3 \exp[-a_4 (T_r)^{3/2}] \quad (5)$$

$$F_b(T_r) = b_1 \exp(-b_2 T_r) + b_3 \exp[-b_4 (T_r)^{3/2}] \quad (6)$$

We have used a wide experimental data PVT space to re-parameterize Eqs (5) and (6). Once the parameters of Eqs (5)-(6) are known, these equations can be applied to pure and binary mixtures of fluids by knowing just their two critical constants T_c and ρ_c .

2. EXTENSION OF EQUATION OF STATE TO MIXTURES

The mixture version of Eq. (1) has the following structure:

$$\frac{P}{\rho k T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{\rho}{k T} \sum_i^m \sum_j^m x_i x_j a(T)_{ij}, \quad (7)$$

Where x_i and x_j are the mole fractions of i 'th and j 'th components, respectively. η is the packing fraction of mixtures of hard sphere which has been taken from Ref. [9]. This parameter is defined by the following expression:

$$\eta = \frac{\rho}{4} \sum_i^m x_i b(T)_i, \quad (8)$$

In the case of binary mixtures, the hard-sphere co-volumes, $b(T)_{ij}$ are additive according to the following expression:

$$b(T)_{ij} = 1/8 [b(T)_i^{1/3} + b(T)_j^{1/3}]^3 \quad (9)$$

The attractive forces between two hard-sphere species of mixture including i and j components can be written as follows:

$$a(T) = \frac{2\pi}{3(\rho_c)_{ij}} k(T_c)_{ij} (F_a)_{ij} \quad (10)$$

In this study, we have applied the following combining rules for T_c , ρ_c and universalized function F_a :

$$T_{cU} = (T_{ci} T_{cj})^{1/2} \quad (11)$$

$$(\rho_{ci})^{-1/2} = \frac{1}{2} \left[(\rho_{ci})^{-1/3} + (\rho_{cj})^{-1/2} \right] \quad (12)$$

$$(F_a)_{ij} = [(F_a)_{ij} (F_a)_{ij}]^{1/2} \quad (13)$$

Also the excess molar volume, v^E and G^E of binary mixtures were calculated from the mixture version of Eq. (1).

3. RESULTS AND DISCUSSION

As already mentioned a PHS EOS was developed in our previous works and applied to several classes of fluids including ionic liquids. Our results showed that the proposed PHS EOS can predict well the volumetric properties of fluids especially ionic liquids. The aim of the present work was to assess the ability of proposed PHS EOS in modeling vapor-liquid equilibria (VLE) of varieties of mixtures. In this regard, several VLE properties of mixtures consisting of molar densities, vapor pressure, excess molar volumes, and excess Gibbs free energy have been calculated. The systems in questions are binary mixtures containing ionic liquids, noble gases, n-alkanes, refrigerants. The input parameters of PHS EOS for pure studied systems have been listed in Table 1.

In the first step, the coefficients Esq. (5) and (6) were obtained for all classes of fluids studied. The numerical values of these parameters have been listed in Table 2. Then the proposed EOS was employed to perform a comprehensive and extensive comparison of the calculated values of VLE properties for considered mixtures with experimental data over a vast range of temperatures, pressures, and compositions.

3.1. Noble Gas Mixtures

We used the perturbed hard-sphere equation of state to model phase equilibria of noble gas mixtures. So, the molar densities of mixture 0.485 Ar + 0.515 Kr at several temperatures and different range of pressures were calculated and then compared with experimental data [10]. Further, the molar densities of

Table 1: The Input Parameters

Compound	T_c/K	$\rho_c(\text{mol/l})$
Ar	150.69	13.41
Kr	209.48	10.85
He	5.20	17.40
Xe	289.73	8.4
R32	351.26	8.15
R125	339.17	4.78
R134a	374.08	5.02
R143a	345.86	5.13
R290	369.83	5.81
H ₂ O	647.10	17.87
CO ₂	304.13	10.63
Pentane	469.70	3.22
Hexane	507.82	2.71
Heptane	540.13	2.32
Octane	569.33	2.06
Nonane	594.55	1.81
Decane	617.70	1.64
ethane	305.33	6.87
Propane	369.83	5
Toluene	591.750	3.17
C ₁₄ H ₃₀	693.00	5.25
C ₃₂ H ₆₀	855.00	6.84
C ₆ H ₆	562.05	3.96
CH ₃ OH	512.60	8.6
C ₂ H ₅ OH	514.00	5.97
C ₃ H ₇ OH	507.36	4.54
[C ₄ MIM][NTf ₂]	1265.00	0.0986
[C ₄ MIM][N(CN) ₂]	1158.10	0.97
[C ₄ MIM][ClO ₄]	1235.56	1.95
[C ₈ MIM][BF ₄]	1287.30	1.67
[C ₄ MIM] [(CF ₃ SO ₂) ₂ N]	1295.63	1.21

the mixture He-Xe at several mole fractions, temperatures and pressures were computed and compared with the experimental data [11]. Figure 1 plots the relative deviation (in %) of the calculated molar densities of the aforementioned mixtures in terms of pressure at typically two temperatures for each mole fraction from the literature values [10, 11]. The average absolute deviation (AAD) of our computed densities of two above-cited mixtures from literature

ones was found to be of the order of $\pm 2.3\%$. It should be mentioned that the experimental densities of He-Xe have been measured using Burnett apparatus with accuracies $\pm 0.02\%$ [11].

Besides, Table 3 displays the excess molar volume and excess Gibbs free energy of mixture 0.485 Ar + 0.515 Kr in terms of pressure at four temperatures. The experimental data [10] and our results are in good agreement. It should be mentioned that the accuracies associated with the experimental Gibbs free energy reported in Ref. [10] is $\pm 2\%$.

3.2. Noble Gas + Alkane Mixtures

The phase behavior of xenon + ethane and xenon + propane mixtures were predicted using the perturbed hard-sphere equation of state and compared with experimental data [12]. Figure 2 plots the calculated and measured [12] vapor pressures of mixtures xenon + ethane and xenon + propane in terms of mole fraction of xenon. It was found that the errors are within $\pm 3\%$. Also, the excess molar volumes and Gibbs free energy of the studied systems have been computed using the perturbed hard-sphere equation of state and checked against experimental values [12]. The results are listed in Table 4. It is noticeable that our model is able to reproduce accurately the experimental data and deviate negatively from the Raoult's law.

3.3. Refrigerant Mixtures

There have been reported thermodynamic properties for a couple of refrigerant mixtures in literature. In this study we have evaluated the capability of the perturbed hard-sphere equation of state to model the phase behavior of this class of fluids. Three binary mixtures R32+R143a, R134a+R290, and R32+R125, have been typically selected and their VLE properties have been studied using the present EOS.

Figure 3 shows the relative deviation (in %) of the calculated saturated liquid densities of mixture $xR32 + (1-x) R143a$ at $x=0.0$, $x=0.502$, and $x=0.749$ and also

Table 2: The Values of Coefficients of Eq. (5) and (6)

Refrigerant	Refrigerant	Ionic liquid	Ionic liquid	Noble gas	Noble gas	alkane	alkane
$a_1 = -0.4360$	$b_1 = 2.8562$	$a_1 = -0.5230$	$b_1 = 2.3984$	$a_1 = -0.2369$	$b_1 = 0.1.145$	$a_1 = -0.40263$	$b_1 = 2.1326$
$a_2 = -9.763$	$b_2 = 10.356$	$a_2 = -10.964$	$b_2 = 9.5380$	$a_2 = -5.2369$	$b_2 = 6.258$	$a_2 = -8.5642$	$b_2 = 7.689$
$a_3 = 4.1236$	$b_3 = 0.4635$	$a_3 = 3.9201$	$b_3 = 0.2499$	$a_3 = 2.452$	$b_3 = 0.2489$	$a_3 = 3.9562$	$b_3 = 0.41365$
$a_4 = -10.456$	$b_4 = -1.5698$	$a_4 = -9.9757$	$b_4 = -1.192$	$a_4 = -5.4782$	$b_4 = -4.2365$	$a_4 = -9.2145$	$b_4 = -8.9562$

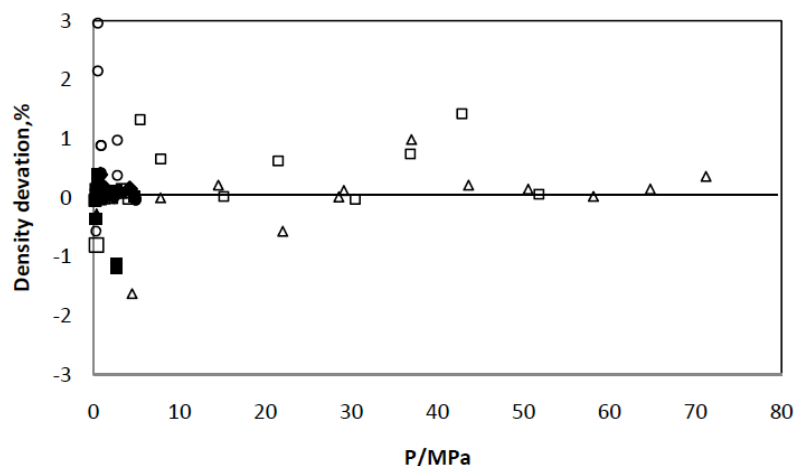


Figure 1: Deviation of the calculated densities of mixture 0.485 Ar + 0.515 Kr in terms of pressure at temperatures $T=129.32$ K (■), 142.68 K (◆), from the experiment [10] and mixture He+Xe at mole fraction $x_{Xe}=0.20120$ and temperatures $T=293.15$ K (□) and $T=373.15$ (Δ) and, mole fraction $x_{Xe}=0.47304$ and temperatures $T=273.15$ K (◇) and $T=373.15$ K (○), and mole fraction $x_{Xe}=0.74128$ and temperatures $T=273.15$ K (×) and $T=373.15$ (*) from the literature values [11].

Table 3: The Excess Molar Gibbs Free Energy and Volume of Mixture 0.485 Ar + 0.515 Kr in Terms of Pressure at Four Temperatures and their Deviations from the Experiment [10]

	T=129.32K									
P(MPa):	2	5	10	15	20	30	40	50	60	70
G^E (Jmole ⁻¹):	-2.33	-5.04	-8.10	-10.10	-11.6	-13.90	-15.40	-16.40	-	-
Dev%:	-150	-1.2	0.36	1.65	1.23	0.25	0.369	0.91	-	-
	T=134.32K									
P(MPa):	2	5	10	15	20	30	40	50	60	70
G^E (Jmole ⁻¹):	-3.90	-7.70	-11.70	-14.20	-16.00	-18.30	-20.00	-21.10	-21.80	-22.50
Dev%:	0.3654	1.58	0.154	0.2658	0	0.94	0	0.2547	0.86	0
	T=142.68K									
P(MPa):	2	5	10	15	20	30	40	50	60	70
G^E (Jmole ⁻¹):	-14.50	-23.60	-30.60	-34.40	-36.90	-40.00	-42.60	-43.20	-44.20	-45.00
Dev%:	0	0.82	0.9587	0	0.5698	0	-1.83	0.63	0.245	0
	T=147.08K									
P(MPa):	2	5	10	15	20	30	40	50	60	70
G^E (Jmole ⁻¹):	-41.30	-59.00	-70.00	-74.00	-76.00	-80.50	-83.00	-84.00	-86.00	-86.00
Dev%:	-0.93	0	-1.85	0.6543	0	-0.83	0.3654	0	-1.28	0
	T=129.32K									
P(MPa):	2	5	10	15	20	30	40	50	60	70
V^E (cm ³ mole ⁻¹):	-1.045	-0.761	-0.499	-0.354	-0.258	-0.173	-0.127	-0.092	-	-
Dev%:	-1.552	-0.76	0	0.68	0.69	0	-0.99	2.13	-	-
	T=134.32K									
P(MPa):	2	5	10	15	20	30	40	50	60	70
V^E (cm ³ mole ⁻¹):	-1.594	-1.016	-0.605	-0.410	-0.296	-0.182	-0.130	-0.097	-0.036	-0.056
Dev%:	0.236	0.550	0.47	0	0.658	1.29	0	-1.14	0	3.45

(Table 3). Continued.

	T=142.68K									
P(MPa):	2	5	10	15	20	30	40	50	60	70
$V^E(\text{cm}^3\text{mole}^{-1})$:	-4.530	-2.039	-0.953	-0.580	-0.397	-0.233	-0.156	-0.111	-0.082	-0.065
Dev%:	0.1265	0.360	0.2650	0	0.7855	0	0	0.99	0	-1.56
	T=147.08K									
P(MPa):	2	5	10	15	20	30	40	50	60	70
$V^E(\text{mole}^{-1})$:	-9.850	-3.423	-1.221	-0.708	-0.479	-0.275	-0.180	-0.126	-0.095	-0.074
Dev%:	0.850	-0.56	0.66	0	1.236	-0.56	0	0.99	0	0.3256

Dev%=100 X (experiment-calculated)/experiment.

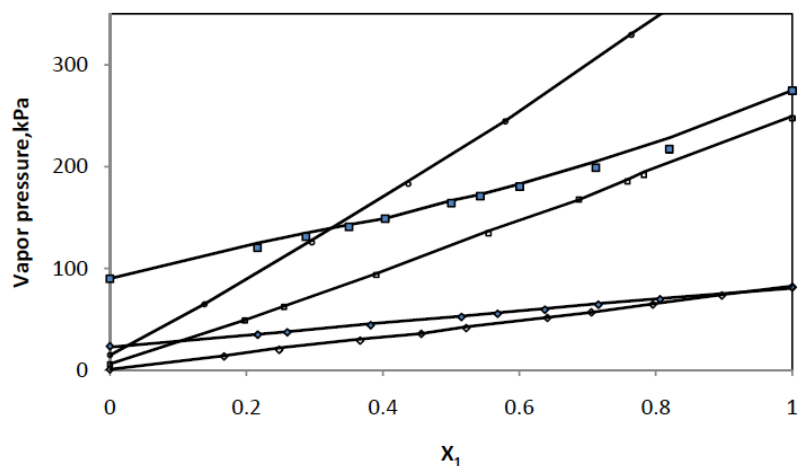


Figure 2: Plot of vapor pressure of liquid mixture xenon (1) + ethane (2) at temperatures $T=161.4\text{ K}(\blacklozenge)$ and $182.34\text{ K}(\blacksquare)$ and liquid mixture xenon (1) + propane (2) at temperatures $T=161.4\text{ K}(\blacklozenge)$, $T=182.34\text{ K}(\blacksquare)$, $T=195.49\text{ K}(\circ)$ in terms of mole fractions of xenon compared with experiment [11]. The solid lines and markers represent the calculated and experimental values [11], respectively.

Table 4: The Average Absolute Deviation of the Calculated Excess Molar Volumes and Excess Molar Gibbs Energy of xenon+ethane and xenon+propane Mixtures at 161.40k, 182.34 and 195.49

Mixtures	Np	AAD (%)
Xe+Ethane(V^E)	10	1.5
Xe+Propane(V^E)	10	1.48
Xe+Ethane(G^E)	21	1.45
Xe+Propane(G^E)	28	1.6

mixture $x\text{R134a} + (1-x)\text{R290}$ at $x=0.25, 0.5, 0.6, 0.78$, at different temperatures, from the experimental data reported by Widiatmo *et al.* [13] and by Naganuma *et al.* [14], respectively. It should be mentioned that the accuracies of the measured densities values for R32+R143a mixture as claimed by Widiatmo *et al.* [13] using magnetic densitometer coupled with a variable cell are $\pm 0.3\%$ and for R134a+R290 mixture using constant volume method coupled with expansion

procedure as reported by Naganuma *et al.* [14] are $\pm 0.085\%$. As the Figure 3 shows, the deviations of the calculated densities fall within $\pm 2.5\%$.

Moreover, a comparison has been made for the calculated vapor pressure of R32+R125 refrigerant mixture in terms of temperature with those reported from the measurement [15] in Figure 4. The experimental temperature ranges from 290 to about 340K and the mass fractions of R32 are 25, 50, and 75%. The estimated measurements uncertainty for the vapor pressure reported by Weber [15] is $\pm 0.03\%$. As the Figure 4 shows deviations of the calculated vapor pressure from those reported in Ref. [15] are not larger than $\pm 1.4\%$.

Further, the deviation plots of this property for $\text{CO}_2+\text{R134a}$, propane+ $\text{C}_{32}\text{H}_{66}$, and benzene+ $\text{C}_{14}\text{H}_{30}$ mixtures in terms of mole fraction at different temperatures have been shown in Figures 5-7, respectively. The experimental values of the vapor pressure for benzene+ $\text{C}_{14}\text{H}_{30}$ (tetradecane) mixture

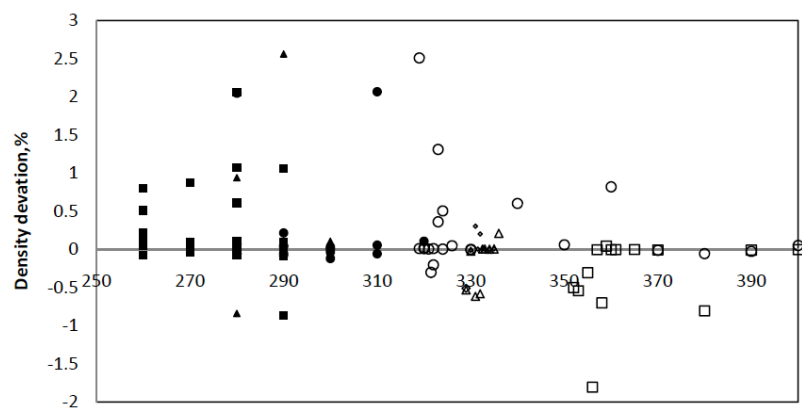


Figure 3: Deviation plot of the calculated saturated liquid densities of refrigerant mixture $xR32 + (1-x) R143a$ at $x=0.000$ (■), 0.502 (●), and 0.749 (▲) in terms of temperatures from the experimental values [11] and mixture $xR134a + (1-x) R290$ at $x=0.25$ (□), 0.50 (○), 0.60 (◇), and 0.78 (Δ) from the experiment [12].

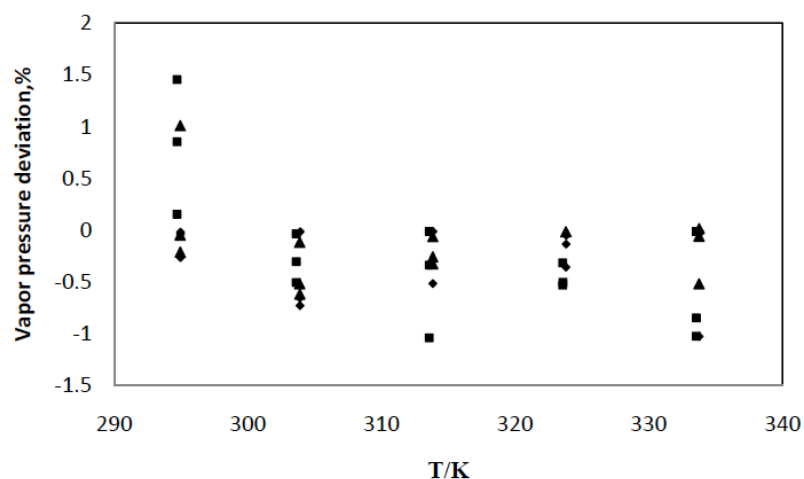


Figure 4: Deviation plot of the vapor pressure for mixture R32+R125 in terms of temperature at mass fractions 25% (◇), 50% (■), and 75% (▲) from the experiment [14].

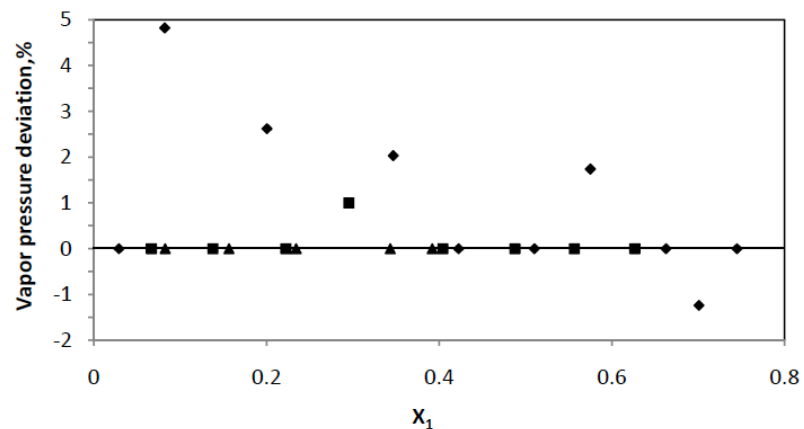


Figure 5: Deviation plot of the calculated vapor pressure of mixture CO_2 (1) + $R134a$ (2) in terms of mole fraction of CO_2 at temperatures $T=329.60K$ (◇), $339.10K$ (■), and $354K$ (▲) from the experiment [15].

were taken from Ref. [18]. The estimated measurement uncertainties of the vapor pressure are $\pm 0.04\%$ for $CO_2+R134a$, 0.06 MPa for propane+ $C_{32}H_{66}$, and $\pm 1\%$ for benzene+ $C_{14}H_{30}$. It should be mentioned that the

phase equilibria measurements were carried out for propane+ $C_{32}H_{66}$ in the region 378-408 K and mass fractions from 0.015 to 0.55. The deviations of the calculated vapor pressure from the experiment [16-18]

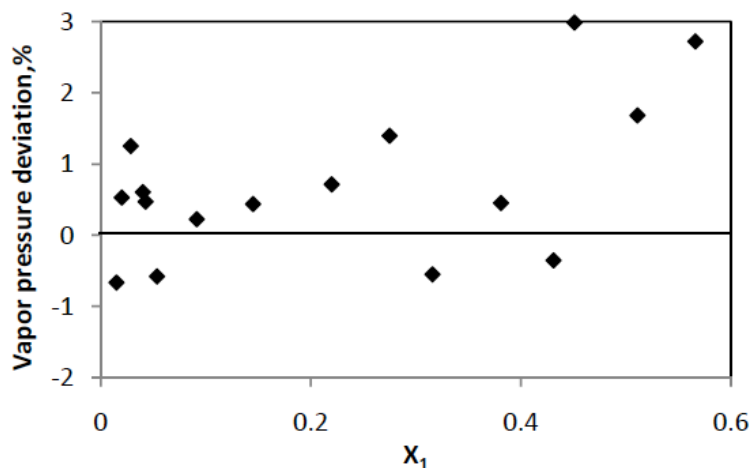


Figure 6: Deviation plot of the calculated vapor pressure of mixture propane(1)+C₃₂H₆₆(2) in terms of mole fraction of propane at T=408.2K from the experiment [16].

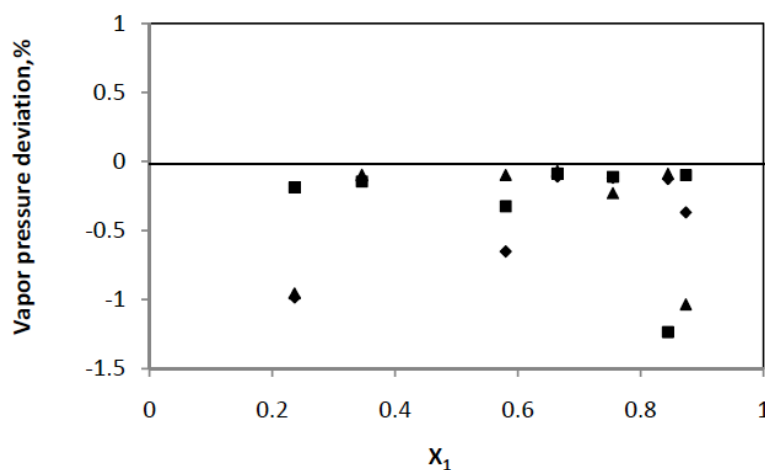


Figure 7: Deviation plot of the calculated vapor pressure of mixture benzene(1)+C₁₄H₃₀(2) in terms of mole fraction of benzene at T=298.15K (♦), 303.15 K (■), and T=313.15K (▲), from the experiment [17].

are to within $\pm 2\%$. It is of important to mention that ability of the perturbed hard-sphere equation of state in modeling the vapor pressure of mixture propane and long chain alkane dotriacontane (C₃₂H₆₆) at temperature 408.2 K and various mole fractions is remarkable.

The perturbed hard-sphere equation of state has further been checked by extending the calculations to excess molar volumes and Gibbs free energy of toluene with n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane. The calculated excess molar volumes and Gibbs free energy have been compared with experimental values [19]. The AAD of the results are listed in Table 5.

3.4. Mixtures Containing Ionic Liquids (ILs)

It is desirable to extend our study to new organic solvents known as ionic liquids. These fluids have

recently received much attention from theoretical and experimental point of view. Figures 8-10 display a deviation plot of vapor pressure of several mixtures containing ionic liquid [C₄MIM] [NTf₂] in terms of mole fractions of n-alcohols at temperatures from 298.15 to 313.15 K. The experimental vapor pressures are those of Verevkin *et al.* [18]. These authors have claimed that the experimental vapor pressures are reliable to within $\pm 1\%$.

Furthermore, Figure 11 shows the deviation plot of the calculated vapor pressure at T=353.15 K from the experimental data [20] for the mixtures benzene + [C₄MIM] [(CF₃SO₂)₂N] and cyclohexane + [C₄MIM] [(CF₃SO₂)₂N]. The estimated accuracies claimed by Kato *et al.* are $\pm 1\%$. Besides, The deviation of the vapor pressure of mixture benzene with ionic liquid [C₄MIM] [NTf₂] from the experimental ones [18] at temperatures 298.15 K, 303.15 K, and 313.15 K have been illustrated

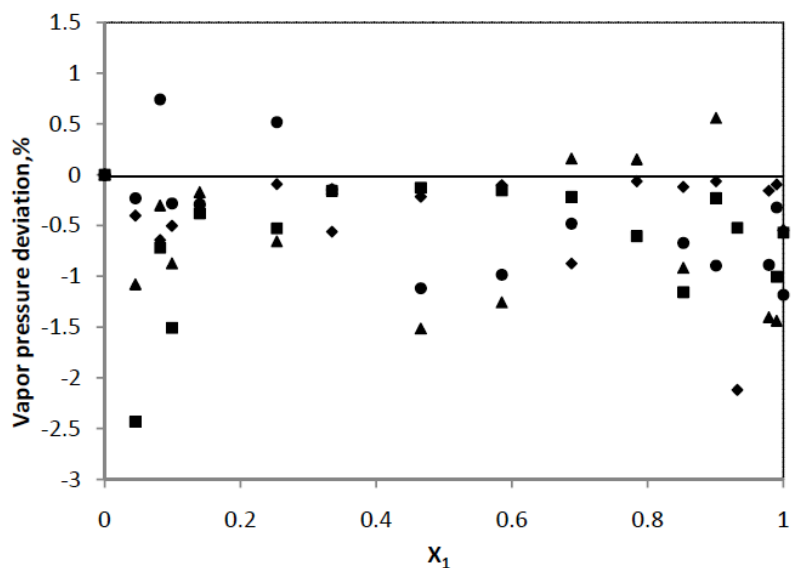


Figure 8: Deviation plot of vapor pressure for mixture methanol (1) + [C₄MIM] [NTf₂] (2) in terms of mole fraction of CH₃OH at T=298.15K (◆), 303.15K (■), 308.15K (▲), and 313.15K (●) from the experiment [17].

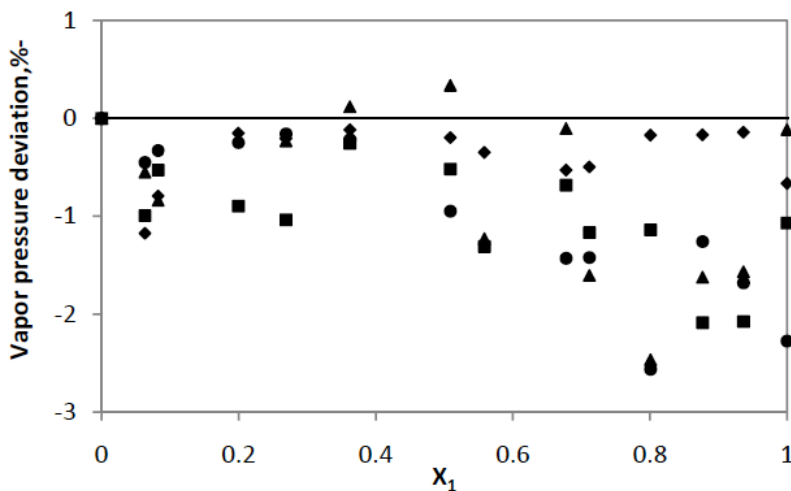


Figure 9: Deviation plot of vapor pressure for mixture ethanol (1) + [C₄MIM] [NTf₂] (2) in terms of mole fraction of C₂H₅OH at T=298.15K (◆), 303.15K (■), 308.15K (▲), and 313.15K (●) from the experiment [17].

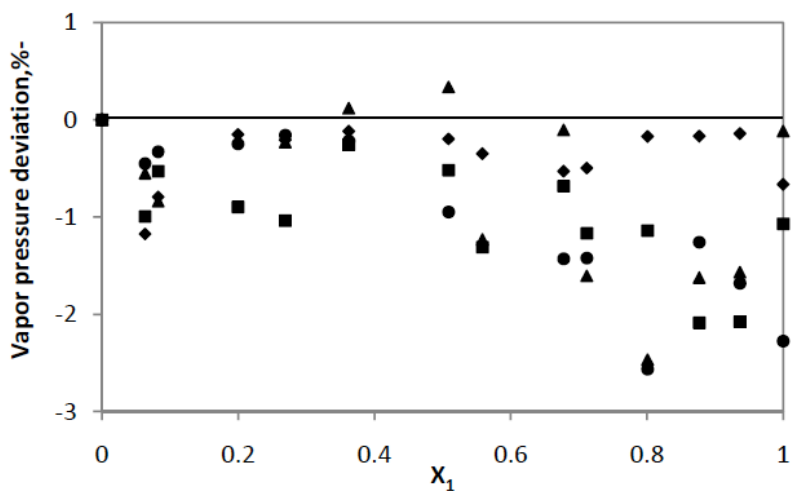


Figure 10: Deviation plot of vapor pressure for mixture propanol (1) + [C₄MIM] [NTf₂] (2) in terms of mole fraction of C₃H₇OH at T=298.15K (◆), 303.15K (■), 308.15K (▲), and 313.15K (●) from the experiment [17].

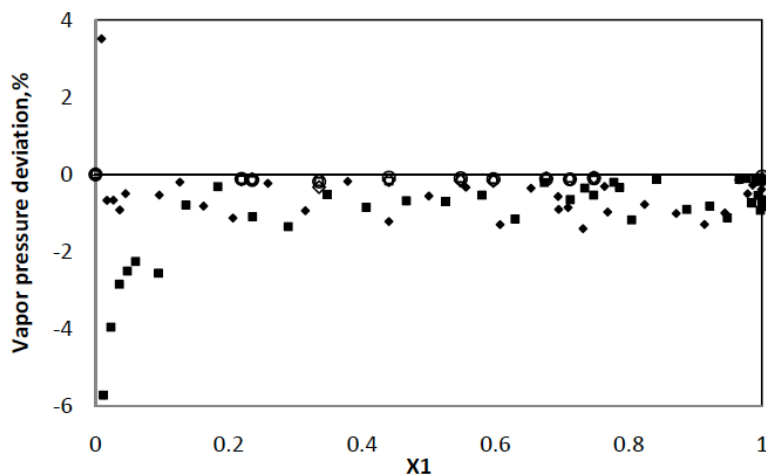


Figure 11: Deviation plot of the calculated vapor pressure for mixtures cyclohexane (1) + [C₄MIM] [CF₃SO₂)₂N] (2) (◆) and benzene (1) + [C₄MIM] [CF₃SO₂)₂N] (2) (■) in terms of mole fraction at T=353.15K from the experimental ones [13] and benzene (1) + [C₄MIM] [NTf₂] (2) in terms of mole fraction of benzene at T=298.15K (◇), 303.15K (□), and 313.15K (○) from the experimental ones [17].

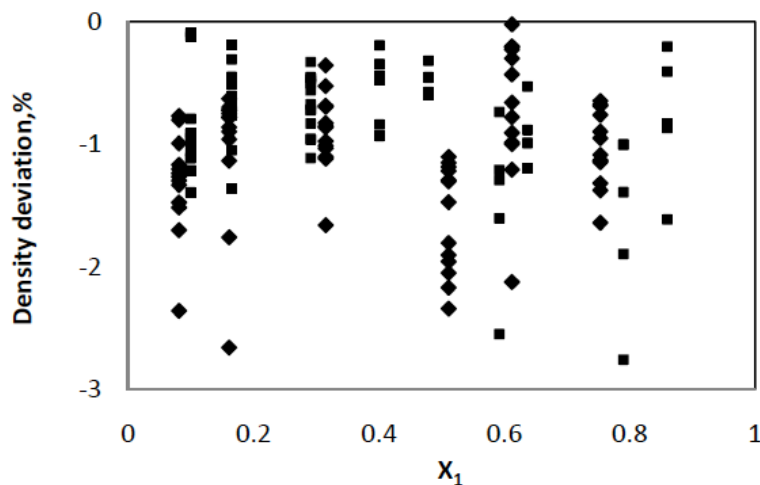


Figure 12: Deviation plot of the calculated density for mixtures ethanol (1) + [C₄MIM] [CLO₄] (2) (■) and ethanol (1) + [C₈MIM] [BF₄] (2) (◆) in terms of mole fraction of C₂H₅OH at temperatures from 283.15K to 343.15K from the experiment [20].

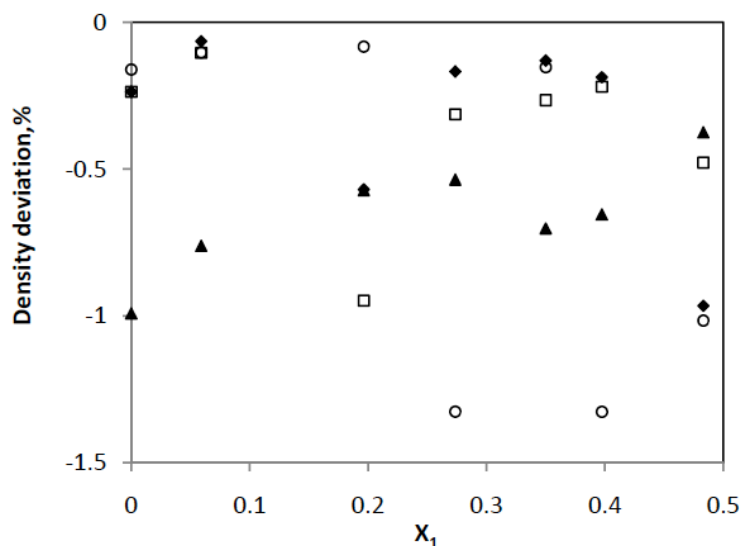


Figure 13: Deviation plot of the calculated density for mixture water (1) + [C₄MIM][N(CN)₂] (2) in terms of mole fraction of H₂O at temperatures 278.15 K(◆), T=308.15 K(□), 348.15 K(▲), 358.15 K(○), from the experiment [20].

in Figure 11. In general, from the Figures 8-11, it is obvious that the accuracies of our calculations are to within $\pm 2.5\%$.

Finally, Figure 12 depicts the relative deviations of the calculated densities of mixtures $C_2H_5OH + [C_8MIM][BF_4]$ and $C_2H_5OH + [C_8MIM][ClO_4]$ in terms of mole fraction of ethanol in temperature range 283.15K to 343.15K from the experiment [21]. Further, Figure 13 shows the density deviation of mixture $H_2O + [C_4MIM][N(CN)_2]$ in temperature range from 278.15K to 358.15K from the experiment [22]. The deviations are to within $\pm 2\%$.

CONCLUDING REMARKS

This study demonstrated that the perturbed hard-sphere equation of state is able to provide reliable information on the VLE properties of different classes of the fluids. The novelty of the present calculations is the successful application of the perturbed hard-sphere equation of state to VLE properties of mixtures. The accuracy of the results obtained from the perturbed hard-sphere EOS is remarkable in low and high density regions.

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NOMENCLATURE

a	= strengths of attractive forces, J/m^3
b	= van der Waals co-volume, m^3
η	= packing fraction
x	= mole fraction
VE	= excess molar volume
M	= molar mass
P	= pressure, P_a
R	= gas constant, $J/mole\ K$
T	= absolute temperature, K
k_B	= Boltzmann constant, J/K
Z	= compressibility factor

F_a = and F_b universal functions

a_1 - b_4 = coefficients used in Eqs. (5) and (6)

Greek Letters

ρ = molar density

η = packing fraction

Subscripts

c = critical

r = reduced

mix = mixture

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