

Phys. Chem. Res., Vol. 3, No. 1, 16-23, March 2015.

DOI: 10.22036/pcr.2015.7298

VLE Properties from ISM Equation of State: Application to Pure and Mixture

F. Fadaei-Nobandegani^{a,*}, M.M. Alavianmehr^b, A.A. Mohsenipour^c, J. Moghadasi^a and M.A. Faghihi^b

^aDepartment of Chemistry, Shiraz University, Shiraz, 71454, IRAN

^bDepartment of Chemistry, Shiraz University of Technology, Shiraz, 71555-313, IRAN

^cChemical Engineering Department, University of Waterloo, Waterloo, ON, Canada N2L 3G1

(Received 19 May 2014, Accepted 27 October 2014)

In this paper, the vapor-liquid equilibrium (VLE) properties of polar and nonpolar fluids are modeled by the use of a statistically-based equation of state (EOS). The equation of state used in this work is that of Ihm-Song-Mason (ISM) EOS. An alternative approach is to revise the isothermal integration on liquid. In this respect, a temperature-dependent revision factor β (T) is introduced to the liquid fugacity coefficient expression which was already derived from traditional isothermal integration. By this modification, the vapor pressure of pure liquids can be successfully reproduced using ISM EOS. This equation of state originally cannot predict the vapor pressure of fluids. The novelty of the present work is to introduce a method such that the ISM EOS is able to predict vapor pressure of pure substances and mixtures. Furthermore, the revisionzaSX method is extended to represent the VLE properties of binary mixtures including noble gases, refrigerants and hydrocarbons. Our computation results on the VLE and PVT behaviors of 24 pure substances and 9 binary mixtures are impressive.

Keywords: Fugacity coefficient, Vapor-liquid equilibrium, Combining rule

INTRODUCTION

The knowledge of vapor-liquid equilibria (VLE) properties of fluids and fluid mixtures is important task for separation processes and production operations including refinery and petroleum reservoir industries. Under these circumstances there is a strong and current need of a suitable equation of state (EOS) to represent both volumetric and equilibrium properties of pure fluids and fluid mixtures. The main role of an EOS is to describe the PVT behavior accurately. If an EOS can reproduce experimental PVT data well, but fail to describe VLE behavior satisfactorily, it is reasonable to question the validity of the widely accepted isothermal integration to determine liquid fugacity.

Over the years, various encouraging activities have been carried out to improve the application of Ihm-Song-Mason (ISM) EOS to liquids both in theoretical and practical dimensions [1-12]. In case that the second virial coefficient,

the central part of the equation, is not available experimentally, suggested correlations in the form of corresponding states can be applied. The best of these procedures are those which determine the equation from properties that can be measured and correlated at ordinary conditions. Activities have also been devoted to determine this equation of state for industrially important liquid mixtures [10-12]. However, the main problem associated with ISM EOS is that this EOS has limitation to model critical region and vapor-liquid equilibrium properties of pure fluids and mixtures. This EOS cannot be applied to critical region because its theoretical sound is based on mean field approximation. In a two-phase region this EOS produces a van der Waals loop such that the vapor pressure cannot be predicted.

The novelty of the present work is to remove this limitation from ISM EOS. In this paper we apply the revision method of Chen *et al.* [13] to the above-mentioned EOS to predict the saturated liquid volumes and vapor pressures of pure substances and fluid mixtures. We aim to apply a revision method to ISM EOS by using a

*Corresponding author. E-mail: fatima_fadaei_84@yahoo.com

temperature-dependent revision factor $\beta(T)$ and using three correlations for three temperature dependent parameters appeared in the ISM EOS developed by Sheikh *et al.* [9]. The extension of the modified ISM EOS for predicting the VLE of mixtures will be also discussed. Thermodynamic properties of the mixtures are calculated using this model with reasonably good accuracies.

METHOD

The ISM equation of state has been derived based on the statistical mechanical perturbation theory of Weeks-Chandler-Anderson (WCA) [1,2] for the decomposition of potential function. The final form of ISM EOS reads as:

$$\frac{P}{\rho kT} = 1 + \frac{(B_2(T) - \alpha(T))\rho}{1 + 0.22\lambda b(T)\rho} + \frac{\alpha(T)\rho}{1 - \lambda b(T)\rho} \quad (1)$$

where P is the pressure, ρ is the density, kT is the thermal energy per molecule, B_2 is the second virial coefficient, b is an analogous to van der Waals co-volume, and α is the contribution of repulsive side of potential function to the second virial coefficient. Three temperature dependent constants B_2 , α and b can be determined by integration if a promising potential function is known. Besides, λ is an adjustable parameter which can be fixed with the help of volumetric properties of dense fluids. Sheikh *et al.* [9] developed three correlations for B_2 , α and b from speed-of-sound data (hereafter, we name these correlations as SPB correlation). The SPB correlations are:

$$B_2\rho_{nb} = 0.1 - 0.054 \left(\frac{\Delta H_{vap}}{RT}\right)^2 - 0.00028 \left(\frac{\Delta H_{vap}}{RT}\right)^4 \quad (2)$$

$$\alpha\rho_{nb} = a_1 \left\{ \exp\left[-d_1\left(\frac{RT}{\Delta H_{vap}}\right)\right] \right\} + a_2 \left\{ 1 - \exp\left[-d_2\left(\frac{\Delta H_{vap}}{RT}\right)^{1/4}\right] \right\} \quad (3)$$

$$b\rho_{nb} = a_1 \left[1 - d_1\left(\frac{RT}{\Delta H_{vap}}\right) \right] \exp\left[-d_1\left(\frac{RT}{\Delta H_{vap}}\right)\right] + a_2 \left\{ 1 - \left[1 + 0.25d_2\left(\frac{\Delta H_{vap}}{RT}\right)^{1/4} \right] \exp\left[-d_2\left(\frac{\Delta H_{vap}}{RT}\right)^{1/4}\right] \right\} \quad (4)$$

where ρ_{nb} is the density at normal boiling point. The coefficients in Eqs. (2)-(4) are $a_1 = 0.1162$, $a_2 = 2.22572$, $d_1 = 6.58566$, and $d_2 = 0.71472$.

The basic fugacity coefficient equation using classical thermodynamic is given by [14]:

$$RT \ln \phi_{EOS} = \int_v^\infty \left[P - \frac{RT}{v} \right] dv - \ln Z + RT(Z - 1) \quad (5)$$

where ϕ is the fugacity coefficient and Z is the compressibility factor.

A temperature-dependent revision factor can be introduced to modify the liquid fugacity coefficient expression:

$$RT \ln \phi = \int_v^\infty \left[P - \frac{RT}{v} \right] dv - \ln Z + RT(Z - 1) + RT \ln \beta(T_r) \quad (6)$$

For the gas/vapor phase, parameter $\beta(T)$ should be equal to unity. The fugacity coefficient revised in this work, is then formulated for liquid phase as:

$$\phi^L = \beta(T_r) \phi_{EOS}^L \quad (7)$$

The subscript EOS stands for properties determined from the equation of state. By this modification the vapor pressure can be obtained without revising the EOS itself. It means that the traditional method for parameter adjustment of equations of state using vapor pressure data is equivalent to the revision of isothermal integration.

For the liquid phase, $\beta(T)$ plays the role of a revision factor. This parameter is obtained from the vapor pressure data as the following equation:

$$\beta(T_r) = b_1 + b_2(1 - T_r) + b_3(1 - T_r)^2 + b_4(1 - T_r)^3 \quad (8)$$

where $Tr = T/T_c$. The coefficients b_1 - b_4 for 24 pure substances have been reported in Table 1.

To determine the above-mentioned parameters, the following objective function (OF) was minimized using the least-squares method:

$$OF = \min \frac{1}{n} \sum_{i=1}^n \left| \frac{\rho_i^{S.Lit.} - \rho_i^{S.Corr.}}{\rho_i^{S.Lit.}} \right| \quad (9)$$

Table 1. The Coefficients of Eq. (8) for Pure Studied Fluids

Compound	b ₁	b ₂	b ₃	b ₄
Ethene	1.11365	0.96287	-5.66023	2.48021
R32	1.32120	1.81906	0.28590	-10.10153
R134a	1.08264	2.64222	-13.48456	9.63680
Ar	1.08251	0.57051	-1.96430	-1.99786
Benzene	1.10131	1.35933	-7.09600	2.85590
Butane	1.09401	1.26423	-8.19098	5.22534
CO ₂	1.06155	1.06101	-2.64061	-11.28030
Cyclohexane	1.10534	0.80629	-5.95148	2.20180
Cyclopropane	1.08163	0.933140	-1.50117	-8.41201
Decane	1.17813	2.04183	-15.41338	13.71110
Ethane	1.09223	0.81355	-5.41522	2.90032
Kr	1.0614	0.61522	-2.15041	-1.93040
Methane	1.05261	0.64420	-1.94775	-2.67000
Methanol	1.34142	3.88204	-21.53094	18.87050
N ₂	1.07223	0.69214	-3.17120	-0.66051
O ₂	1.11905	0.18832	-2.60552	0.83702
Octane	1.12301	2.04061	-13.60439	11.34700
Propane	1.10195	1.11312	-7.81304	5.64933
Propene	1.08176	0.90603	-6.36432	3.56108
Propyne	1.08708	0.99430	-4.31434	-1.22718
R125	1.09903	1.18812	-8.64623	4.58135
R143a	1.15922	1.61429	-6.02203	-0.08863
Xe	1.04310	0.79386	-1.73400	-3.12523
Toluene	1.10040	1.55503	-8.87867	5.08100

where, $\rho^{\text{Lit.}}$ and $\rho^{\text{Corre.}}$ stand for the saturated liquid density data taken from literature and the correlated values, respectively. n is the number of correlated density data.

Extension to Binary Mixtures

Mixture of liquids is important in practically industrial applications and in modeling theoretical applications such as development of fluctuation theory in which the thermodynamic properties are attributed to the fluctuation in local density at microscopic level. Thus, an equation of state with pronounced statistical mechanical basis for mixtures is appreciably helpful for such purposes. The ISM equation of state has been employed to study the mixture of simple non-polar and slightly polar fluids by elaborating the Eq. (1) as:

$$\frac{P}{\rho kT} = 1 + \rho \sum_{ij} X_i X_j (B_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} X_i X_j G_{ij} \quad (10)$$

where x_i and x_j are the mole fractions of the fluids i and j . B_{ij} and α_{ij} represent the bimolecular interaction between the unlike molecules within the mixture.

Further, G_{ij} and F_{ij} are defined by:

$$G_{ij} = \frac{1}{1-\eta} + \left(\frac{b_i b_j}{b_{ij}} \right)^{1/3} \frac{\rho \sum_k x_k b_k^{2/3} (\lambda_k - 1/4)}{(1-\eta)(1-\rho \sum_k x_k b_k \lambda_k)} \quad (11)$$

$$F_{ij} = \frac{1}{1-\eta_3} - \left(\frac{b_i b_j}{b_{ij}} \right)^{1/3} \frac{\rho \sum_k x_k b_k^{2/3} (0.22\lambda_k + 0.25)}{(1-\eta_3)(1+0.22\rho \sum_k x_k b_k \lambda_k)} \quad (12)$$

$$\eta = \frac{b(T)\rho}{4}, \quad (13)$$

We employed SPB correlations in conjunction with simple combining rules for the heat of vaporization and molar

density to predict the interaction second virial coefficients, as well as the second virial coefficients for single substances.

$$(\Delta H_{vap})_{ij} = \left((\Delta H_{vap})_i \times (\Delta H_{vap})_j \right)^{1/2} \quad (14)$$

$$(\rho_{nb})_{ij}^{-1/3} = \frac{((\rho_{nb})_i)^{-1/3} + ((\rho_{nb})_j)^{-1/3}}{2} \quad (15)$$

RESULTS AND DISCUSSION

In the present work, the ISM EOS has been employed to model the vapor-liquid equilibria (VLE) of several fluids and fluid mixtures using a revision method. As outlined earlier, the ISM EOS cannot be applied to critical region because the underlying theory of this EOS includes a mean

filed approximation. On the other hand, the analytic nature of the EOS leads to producing van derWaals loops in the sub-critical P-V isotherms instead of the correct first order vapor liquid transition, and, therefore, it cannot be applied to a two-phase region to predict vapor pressure of fluids. In this study, a theoretical revision method was taken such that the ISM EOS can predict properly the VLE properties of several fluids and fluid mixtures. In this regard, the temperature-dependent revision factor β (Eq. (8)) was introduced to modify the liquid fugacity coefficient expression without modifying the ISM EOS. Therefore, one of the two limitations of the ISM EOS was removed by taking this method.

For 24 pure substances with vapor-liquid equilibrium data available, saturated liquid-phase densities, vapor-phase densities and vapor pressures were calculated by the ISM

Table 2. The AAD (in %) of the Calculated VLE Properties for Pure Compound from the Literature Values [15]

Compound	NP ^a	Saturated liquid density	Saturated vapor density	Vapor pressure
Ethene	10	0.86	0.65	4.77
R32	12	0.80	0.65	2.63
R134a	13	0.78	0.62	1.82
Ar	10	1.03	0.80	1.87
Benzene	12	0.68	0.66	1.99
Butane	16	0.98	0.74	2.63
CO ₂	12	0.94	0.76	1.79
Cyclohexane	15	0.85	0.65	2.18
Cyclopropane	10	0.89	0.66	2.96
Decane	14	0.86	0.72	2.19
Ethane	10	0.87	0.68	2.15
Kr	10	0.80	0.66	2.70
Methane	10	0.91	0.59	2.70
Methanol	14	0.76	0.63	2.50
N ₂	10	0.73	0.69	2.06
O ₂	12	0.80	0.63	2.28
Octane	10	0.87	0.61	2.46
Propane	12	0.83	0.63	3.38
Propene	10	0.86	0.66	2.47
Propyne	10	0.80	0.55	2.01
R125	11	0.65	0.55	2.64
R143a	12	0.76	0.52	1.90
Xe	10	0.83	0.64	2.02
Toluene	16	0.77	0.67	1.04

EOS and the revised method. The average absolute deviations (AADs%) of the saturated liquid densities, the saturated vapor densities, and the vapor pressures of studied substances from the literature values [15] are listed in Table 2. For 281 data points examined the overall AAD for saturated liquid densities, vapor densities and vapor pressures were found to be 0.83, 0.65 and 2.38, respectively. Figures 1 and 2 display, respectively, the relative deviations of the calculated liquid and vapor densities of cyclohexane, butane, decane, and methanol in terms of the temperature taken from the literature values [15]. In general, the

maximum relative deviations of the calculated saturated liquid densities, vapor densities and vapor pressures from those given in literature were of the order of $\pm 1.28\%$, $\pm 1.14\%$ and $\pm 6.4\%$, respectively.

As stated before, the ISM EOS and the revision method were further assessed by extension of the EOS to mixtures. The mixture version of the ISM EOS together with combining rules given by Eqs. (14) and (15) and SPB correlation equations were employed to predict the saturated liquid and vapor densities and vapor pressure of 24 pure substances and 9 binary mixtures. Table 3 contains the

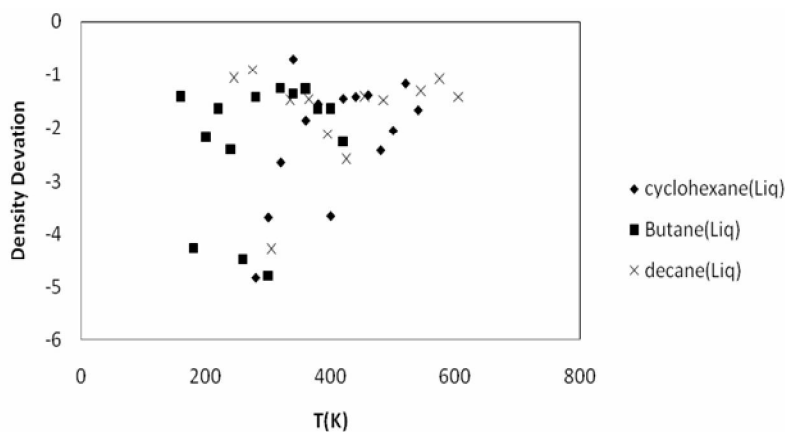


Fig. 1. Deviation Plot of the calculated saturated liquid density for cyclohexane (◆), butane (■), and decane (×) in terms of temperature from the literature data [15].

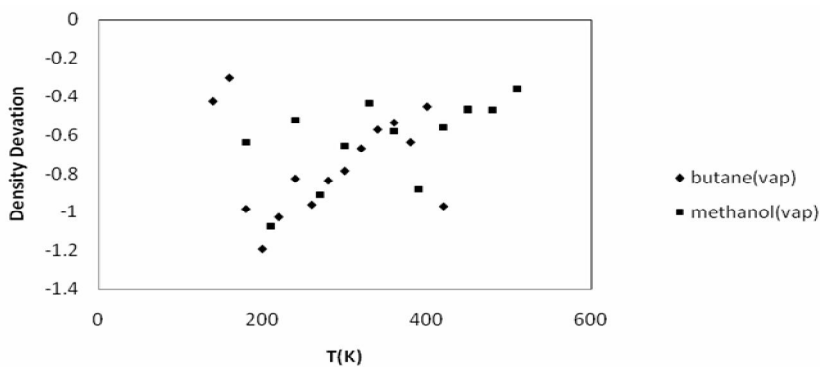
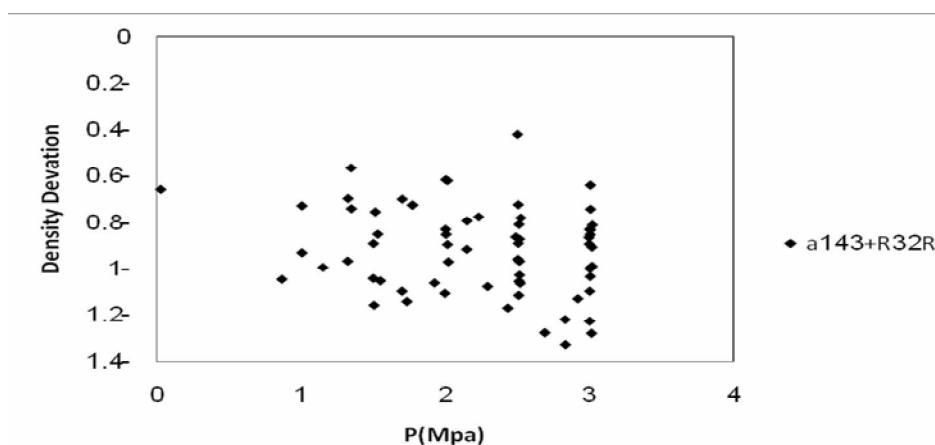


Fig. 2. Deviation Plot of the calculated saturated vapor density for butane (◆) and methanol (■) in terms of temperature from the literature data [15].

Table 3. The AAD (in %) of the Calculated VLE Properties for Mixtures from the Literature Values

Mixture	NP ^a	Saturated liquid density	Vapor pressure	Ref.
Ar+Kr	43	0.61	-	[17]
R32+R143a	120	0.82	-	[16]
R32+R125	44	0.84	2.68	[18]
R125+R143a	35	-	2.88	[16]
R32+R134a	50	-	2.44	[19]
N ₂ +CH ₄	20	0.89	3.03	[16]
Xe+Ethane	20	-	2.85	[20]
Xe+Propane	28	-	3.14	[20]
CO ₂ +R134a	24	-	2.98	[21]

**Fig. 3.** Deviation of the calculated liquid densities of mixture R32+R143a in terms of pressure from the experimental ones [16].

predicted saturated liquid densities and vapor pressures of several binary mixtures compared with experiment [16-21]. The total AAD of the saturated liquid densities and vapor pressures for 383 numbers of examined data points from the experiment are within 1.39% and 3.6%, respectively. Figure 3 shows the deviation of the calculated density of mixture R32+R143a from the experimental ones [16]. Obviously, the error associated with the calculated liquid densities is within $\pm 1.5\%$. Furthermore, Fig. 4 illustrates the relative deviations of the calculated vapor pressure of Xe+ethane and Xe+propane in terms of mole fraction of xenon at two temperatures and also Fig. 5 shows the relative deviations of the calculated vapor pressure CO₂+R134a from the

experiment [20-21] in terms of the mole fraction of carbon dioxide. In general, for mixtures, the accuracies of the calculated densities and vapor pressures are within 0.79% and 3%, respectively.

The results shown in Figs. 1-5 and Tables 1-3 indicate that the proposed model can reproduce successfully the literature values of VLE properties of the pure and mixtures in a broad range of temperatures and pressures.

Finally, the calculated densities for several mixtures using ISM EOS were compared with those obtained from Peng-Robinson (PR) and Tao-Mason (TM) EOS. As obviously seen in Table 4, the ISM EOS is superior with respect to PR EOS. Further, the ISM EOS is as accurate as

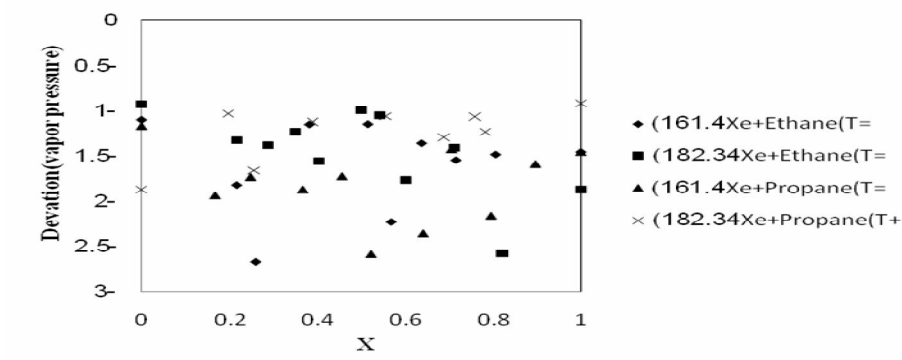


Fig. 4. Deviation Plot of vapor pressure of mixture xenon (1) + ethane (2) at temperatures $T = 161.4 \text{ K}$ (\blacklozenge) and 182.34 K (\blacksquare) and mixture xenon (1) + propane (2) at temperatures $T = 161.4 \text{ K}$ (\blacktriangle), $T = 182.34$ (\times) in terms of mole fractions of xenon from the experiment [20].

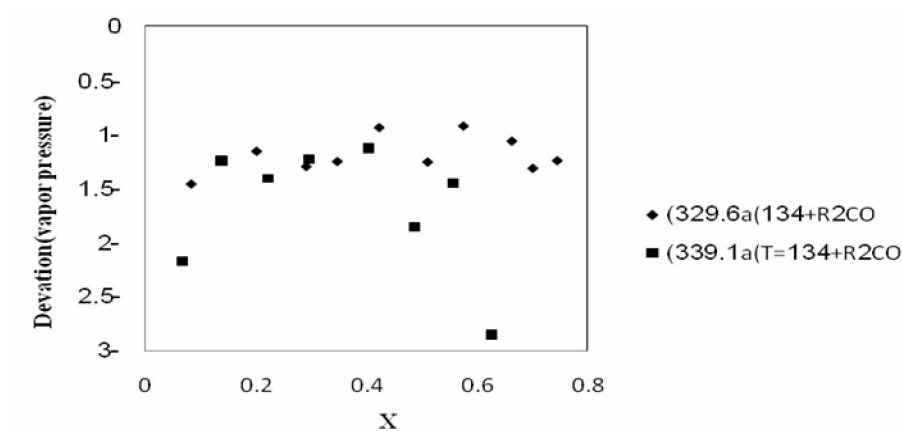


Fig. 5. Deviation plot of the calculated vapor pressure of mixture CO_2 (1) + R134a (2) in terms of mole fraction of CO_2 at temperatures $T = 329.60 \text{ K}$ (\blacklozenge), 339.10 K (\blacksquare) from the experiment [21].

Table 4. The AAD of the Calculated Densities for Several Mixtures Using ISM, PR, and TM Equations of State

Mixtures	ISM	TM	PR	NP ^a
Ar+Kr	0.61	0.58	0.95	43
R32+R125	0.84	0.82	1.63	44
R32+R143a	0.82	0.80	1.89	120
N2+CH4	0.89	0.85	2.4	20
Overall	0.79	0.76	1.72	227

^aNP: no. of data point examined

TM EOS in the liquid phase.

CONCLUSIONS

Simplicity and generality of the modified ISM EOS combined with reasonable accuracy makes this EOS useable for predicting volumetric and VLE properties of pure substances and mixtures.

ACKNOWLEDGMENTS

We thank the Shiraz University and Shiraz University of Technology for supporting this project.

REFERENCES

- [1] G. Ihm, Y. Song, E.A. Mason, *J. Chem. Phys.* 94 (1991) 3839.
- [2] G. Ihm, Y. Song, E.A. Mason, *Fluid Phase Equilib.* 75 (1992) 117.
- [3] F.M. Tao, E.A. Mason, *Int. J. Thermophys.* 13 (1992) 1053.
- [4] A. Boushehri, E.A. Mason, *Int. J. Thermophys.* 14 (1993) 685.
- [5] M.H. Ghatee, A. Boushehri, *Int. J. Thermophys.* 17 (1996) 945.
- [6] N. Mehdipour, A. Boushehri, *Int. J. Thermophys.* 19 (1998) 331.
- [7] Y. Song, E.A. Mason, *J. Chem. Phys.* 91 (1989) 7840.
- [8] G. Ihm, Y. Song, E.A. Mason, *Mol. Phys.* 75 (1992).
- [9] S. Sheikh, M.M. Papari, A. Boushehri, *Ind. Eng. Chem. Res.* 41 (2002) 3274.
- [10] M.M. Papari, A. Razavizadeh, F. Mokhberi, A. Boushehri, *Ind. Eng. Chem. Res.* 42 (2003) 3802.
- [11] B. Haghghi, M.M. Papari, M. Niafari, H. Ghasemi, *J. Mol. Liq.* 123 (2006) 134.
- [12] M.M. Papari, S.M. Hosseini, F. Fadaei Noabandegani, J. Moghadasi, *Korean J. Chem. Eng.* 29 (2012) 1628.
- [13] G. Chen, C.Y. Sun, T.M. Guo, *Chem. Eng. Sci.* 55 (2000) 4913.
- [14] B.E. Polling, J.M. Prausnitz, J.P.O. Connell, McGraw-Hill, New York, 2001.
- [15] E.W. Lemmon, M.O. McLinden, D.G. Friend, in: W.G. Mallard, P.J. Linstrom (Eds.), November, 2005. *Thermophysical Properties of Fluid Systems in NIST Chemistry Web book*, NIST Standard Reference Database Number 69. National Institute for Standards and Technology, Gaithersburg, MD20899.<http://webbook.nist.gov>.
- [16] J.V. Widiatmo, T. Fujimine, H. Ohta, K. Watanabe, *J. Chem. Eng. Data* 44 (1999) 1315.
- [17] S.F. Barrelros, Calado, J.C.G. Clancy, M.N. da Panta, W.B. Streett, *J. Phys. Chem.* 86 (1982) 1722.
- [18] F. Weber, *Fluid Phase Equilib.* 174 (2000) 165.
- [19] V.W. Jidiatmo, T. Fujimine, H. Sato, K. Watanabe, *J. Chem. Eng. Data* 42 (1997) 270.
- [20] E.J.M. Filipe, E.J.S. Gomes de, Azevedo, V.A. Martins, M. Soares, J.C.G. Calado, C. McCabe, G. Jackson, *J. Phys. Chem. B* 104 (2000) 1315.
- [21] G. Silva-Oliver, L.A. Galicia-Luna, *Fluid Phase Equilib.* 199 (2002) 213.