

Volumetric properties of high temperature, high pressure supercritical fluids from improved van der Waals equation of state

Seyed Ahmad Razavizadeh*, Fahimeh Alirezapoor

Department of Chemistry, Payame Noor University, P. O. BOX 19395-3697 Tehran, Iran

Received: 16 April 2016, Accepted: 10 April 2017, Published: 10 April 2017

Abstract

In the present work, a modified equation of state has been presented for the calculation of volumetric properties of supercritical fluids. The equation of state is van der Waals basis with temperature and density-dependent parameters. This equation of state has been applied for predicting the volumetric properties of fluids. The densities of fluids were calculated from the new equation of state at different temperatures and pressures in the supercritical region. The predicted densities have been compared with those obtained from the experiment, over a broad range of pressure. It is found that the new equation of state yields excellent results in comparison with 1894 experimental data points with overall average absolute deviation percent (AAD %) of 0.98% in density for the pure studied compound. The studied fluids are: CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂, C₆H₁₄, C₇H₁₆, C₈H₁₈, C₁₀H₂₂, C₁₂H₂₆, C₂H₄, C₆H₆, C₆H₁₂, C₇H₈, O₂, N₂ and CO₂.

Keywords: Equation of state; supercritical; density; high temperature; high pressure; van der Waals.

Introduction

Pressure-volume-temperature (PVT) properties play an important role in various chemical processes such as distillation and extraction in the production and purification of oils, polymers, pharmaceuticals, and other natural materials. In some processes, PVT data at extreme pressures or temperatures are required. In addition, PVT properties provide a fundamental database for the development and examination of thermodynamic models. Fluid densities are necessary for many engineering problems such as process calculations, simulations, equipment and pipeline design. Density is usually

calculated by using the correlation methods or equations of state. A large number of publications deal with the development or improvement of equations of state. The equation of state should be simple and accurate so that it can be used instead of the experimental data that is not available. It is very difficult to obtain experimental data at high pressures, so the development and modification of equations of state are essential to obtain consistent results with experimental data for the supercritical region.

In the present work, 14 hydrocarbons, O₂, N₂, and CO₂ have been studied. The hydrocarbons are the most broadly used organic compounds. The greatest amounts of hydrocarbons are used as the fuel for

*Corresponding author: Seyed Ahmad Razavizadeh
Tel: +98 (713) 6222273, Fax: +98 (713) 6222284
E-mail: razavizadeh@pnu.ac.ir

combustion, particularly in heating and motor fuel applications. Density and phase behavior information of hydrocarbons and their mixtures at different pressures and temperatures are needed for both practical applications and modeling studies.

The volumetric properties of hydrocarbons are of particular interest in connection with production and refining of petroleum. The influences of temperature and pressure on the volumetric properties of hydrocarbons are important for simulating the behavior of the fluid under reservoir conditions [1,2]. The density prediction of hydrocarbons at extreme temperature and pressure conditions are most relevant to petroleum engineering studies of ultra-deep reservoirs. During the past decades, many equations have been used to predict the density and other thermodynamic properties of hydrocarbons [3–9]. Cubic equations of state have been used widely for the density prediction of hydrocarbons. Standard Soave–Redlich–Kwong (SRK) equation of state [4] and Peng–Robinson (PR) equation of state [5] have been used extensively by the petroleum engineering industry and are relatively easy to understand and employ.

In this study, modification of van der Waals equation of state is proposed to calculate the density of the fluid in the supercritical region. This equation of state has been based on the generic van der Waals equation of state [10]. The structure of this equation is almost similar to the van der Waals equation of state, and the difference is that the parameters of this equation of state are not constant for any gas, and these are functions of conditions of each gas, such as the intermolecular force, pressure, and density. The advantage of this equation with respect to temperature and density dependence of the parameters has a good ability to predict the thermodynamic properties of fluids.

This equation of state and its parameters have been studied in the critical region [10]. In this work, modifications have been done on the parameters of this equation of state in the supercritical region and a new equation of state is proposed for pure fluids. The density of these

compounds has been calculated from the new equation of state in the supercritical region.

A supercritical fluid is any substance at a temperature and pressure above its critical point where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid. Unlike liquids in supercritical conditions, little change in temperature or pressure or both creates drastic changes in the physical properties, especially the density of the fluid. The transport properties of the supercritical fluid are similar to a gas in which it has high viscosity and low permeability and in terms of solubility is similar to liquid solvents. These fluids are a good alternative for organic solvents, especially solvents contain chlorine.

The fluids that have been investigated in this study are CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂, C₆H₁₄, C₇H₁₆, C₈H₁₈, C₁₀H₂₂, C₁₂H₂₆, C₂H₄, C₆H₆, C₆H₁₂, C₇H₈ (Toluene), O₂, N₂, and CO₂. The densities of these compounds have been calculated at different temperatures and pressures from the new equation of state in the supercritical region.

In summary, the aim of this work was to develop an equation of state from van der Waals family. The present equation of state is evaluated by examination of 1894 experimental density data for 17 fluids. Our calculations encompass the supercritical temperatures and the pressures up to available experimental pressure. Furthermore, the outcome of the computations is compared with the results of the PR equation of state. The average absolute deviation percent (AAD %) of the density has been calculated. The prediction of the improved equation of state is particularly impressive matching the experimental data at high pressures for studying compounds. Despite its simplicity, this equation of state appears to have the potential to provide more accurate density predictions over a wide range of temperature and pressure.

Generic van der Waals equation of state

The van der Waals equation of state has been serving not only as a practical model for the description of liquids and gasses,

but also as a prototype, and a guide for the equations of state subsequently proposed in the literature, which causes to improve it from the phenomenological standpoints. Besides such older versions of equations of state that appear in the literature, some propositions [10-13] have been made to modify the excluded volume term in the van der Waals equation of state so as to make it perform better at high densities.

Eu and Rah [13] showed that the form of the van der Waals equation of state is generic to all interaction potential models that have a hard core and a finite-ranged attractive potential, or, more generally, a repulsive core and an attractive branch of interaction. Therefore, the form of the equation of state presented in effect amounts to a derivation of an exact van der Waals-type equation of state. This viewpoint enables us to obtain exact statistical mechanical representations of the van der Waals parameters, and thereby investigate the meanings of the original van der Waals parameters in a more precise manner and also to explore modifications of the original van der Waals equation of state to form it more suitable for studying the thermodynamic properties of fluids.

For a pair potential energy $u(r)$, the virial equation of state is given by the following equation [14,15]:

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi}{3} \beta \rho \times \quad (1)$$

$$\int_0^{\infty} dr r^3 u'(r) \exp[-\beta u(r)] y(r, \rho, \beta)$$

where P , ρ , β and $u(r)$ are the pressure, density, $1/k_B T$ and interaction potential, respectively. Furthermore, $u' = du(r)/dr$ and $y(r, \rho, \beta)$ is the cavity function, and the distance between particles is denoted by r . Assume the interaction potential function consists of an attractive and a repulsive branch:

$$u(r) = \begin{cases} \infty & r < \sigma \\ u_a(r) & \sigma < r < \xi \\ 0 & \xi < r \end{cases} \quad (2)$$

the virial EoS takes the following form [13]:

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi\sigma^3}{3} \rho y(\sigma, \rho, \beta) + \frac{2\pi}{3} \rho \int_{\sigma}^{\xi} dr r^3 y(r, \rho, \beta) \frac{d}{dr} f(r) \quad (3)$$

where $f(r)$ is the Mayer function for $u(r)$ that is defined by

$$f(r) = \exp[-\beta u(r)] - 1 \quad (4)$$

Now, define the following functions of density and temperature:

$$A(\rho, \beta) = -\frac{2\pi}{3\beta} \int_{\sigma}^{\xi} dr r^3 y(r, \rho, \beta) \frac{d}{dr} f(r) \quad (5)$$

$$B(\rho, \beta) = \frac{2\pi\sigma^3}{3} \frac{y(\sigma, \rho, \beta)}{1 + \frac{2\pi\sigma^3}{3} \rho y(\sigma, \rho, \beta)} \quad (6)$$

Then the virial EoS can be written in the form

$$(P + A\rho^2)(1 - B\rho) = \rho\beta^{-1} \quad (7)$$

which has formally the same form as the vdW EoS. This will be referred to as the generic van der Waals EoS and the coefficients A and B the generic van der Waals parameters. The advantages of this equation with respect to temperature and density dependence of the coefficient is high precision and good ability to predict the thermodynamic properties of fluids. The parameters of this EoS are not constant and for each fluid, they are a function of conditions such as intermolecular force, pressure, and density.

The improved equation of state for supercritical region

For the purpose of carrying out the desired analysis, it is convenient to use nondimensionalized variables. We define the reduced variables:

$$T_r = \frac{T}{T_c}, \quad \rho_r = \frac{\rho}{\rho_c}, \quad P_r = \frac{P}{P_c} \quad (8)$$

We also define the following parameters:

$$\tau = (\rho_c^2)/P_c, \quad \nu = \rho_c, \quad \zeta = (R\rho_c T_c)/P_c \quad (9)$$

Upon using the aforementioned reduced variables and parameters τ , ν , and ζ , we can reduce the canonical equation of state (eq. 7) with respect to the critical parameters and express them in the nondimensional form [11,12]:

$$[P_r + \tau \rho_r^2 A(\rho_r, T_r)][1 - \nu \rho_r B] = \zeta \rho_r T_r \quad (10)$$

The reduced generic van der Waals equation of state requires values for the critical temperature (T_c), critical pressure (P_c), and critical density (ρ_c) of each component.

In order to improve the predictive power of the mentioned equation of state for the calculation of the density of fluids, we modified the parameters of this equation of state in the supercritical region. In this equation, the B parameter, which is an effective molecular volume in the hard sphere repulsive term, was considered as constant, while the parameter A in the mean-field attractive term was considered as the function of temperature and density. The parameter B was assumed to be constant similar to the b parameter of original van der Waals equation of state and it is the only function of critical constants of each compound. We determine the parameter A by fitting the equation of state to experimental data. For this purpose, we employ a simple law of corresponding states which relates the reduced form of A to the reduced temperature and density through universal functions. We use the critical temperature, T_c , and the critical density, ρ_c , of compounds as two scaling constants. Hence, the equation of state can be used to analyze PVT behavior of the considered compounds with an alternative law of corresponding states for parameter A .

The temperature and density dependence of parameters should be characterized. By investigating some

types of equations, we can conclude that the following relations for A and B will give better results. The following forms were considered for A and B in the region of $T > T_c$:

$$B = b'(RT_c/16P_c) \quad (11)$$

$$A = A_{vdw} \cdot \alpha(T, \rho) \quad (12)$$

where

$$A_{vdw} = \frac{27R^2T_c^2}{64P_c} \quad (13)$$

The parameter B is a function of critical temperature and pressure, while b' is a constant. $\alpha(T, \rho)$ is dependent on temperature and density. Also function of the universal critical constants of temperature and density should be determined. The following empirical form was considered for $\alpha(T, \rho)$.

$$\alpha(T, \rho) = [a_0 + a_1(\frac{1}{T_r^{0.5}}) + a_2 T_r \rho_r + a_3 \rho_r^4] \quad (14)$$

By fitting of experimental data on the A and B relations, the coefficients in the equations (11) and (14) are determined for fluids in the supercritical region.

We obtained:

$$a_0 = -0.3981 \quad a_1 = 1.3194 \quad a_2 = -0.1131 \quad a_3 = -0.0121 \quad b' = -0.3981$$

By determining the coefficients and then replacing in equation (10), a new equation of state was proposed in the supercritical region for fluids, and density was calculated from this equation of state over a broad range of pressure, for which the experimental data were available in the literature. In addition, the density of compounds has been calculated from Peng - Robinson equation of state [5].

Results and discussion

In recent decades, many studies have been performed to improve the equations of state and their parameters in a more convenient form. The generic van der Waals equation of state is a modified equation of state whose

structure is quite similar to van der Waals except that their parameters are functions of temperature and density. It is necessary to modify the parameters of the equation of state to achieve the best accordance between experimental and computational values. The present study is done in this spirit.

The appropriate estimation of *PVT* properties is essential for accurate prediction of fluids behavior. In this regard, the modified equation of state has been used to predict the densities of some pure fluids. The investigated fluids in this study are the batch of hydrocarbons, including CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂, C₆H₁₄, C₇H₁₆, C₈H₁₈, C₁₀H₂₂, C₁₂H₂₆, C₂H₄, C₆H₆, C₆H₁₂ (Cyclohexane), C₇H₈ (Toluene) and O₂, N₂, CO₂.

In order to modify the generic van der Waals equation of state, some models were examined for the parameters in the canonical equation of state in the supercritical region. By investigating the types of equations, we can obtain relations for parameters *A* and *B* that gives better results. In this study, a fitting procedure was employed to determine the temperature and density-dependent parameters of the proposed equation of state. Generally, we have regarded the parameters of *A* and *B* as parameters which depended on temperature and density, then the temperature and density dependence of parameters of the proposed equation of state were obtained by determining just the critical constants of the studied fluids. This means that the selection of three proper scaling constants, *T_c*, *ρ_c*, and *P_c* was sufficient to develop an accurate equation of state for fluids in supercritical region.

The experimental *PVT* data of 17 compounds, including some hydrocarbons, and also nitrogen, oxygen, and carbon dioxide, were used

to investigate the validity of improved equation of state [16-20].

The densities of the studied fluids were calculated from the new equation of state. The obtained densities were compared with experimental data at different temperatures and pressures. Table 1 shows the average absolute deviation, percent (*AAD%*) of density obtained from the new equation of state and also the PR equation of state with experimental data [16-20]. In addition, the numbers of the point, pressure and temperature ranges of the examined data are represented in Table 1. The results show that the predicted *PVT* properties of the above mentioned fluids from the new equation of state are in a good agreement with experimental data.

As it is clear from the results in Table 1, the new equation of state can accurately predict the density of the studied fluids over a broad range of temperatures and pressures in the subcritical region. For 1894 data points, the overall % *AAD* was found to be 0.98 and 5.34 from the new equation of state and the PR equation of state, respectively.

The largest %*AAD* of 1.49 was obtained for octane and the smallest %*AAD* of 0.52 was obtained for toluene. As shown in Table 1, most compounds have %*AAD* of less than 1.0%.

The acceptable agreement between the calculated and experimental densities of the studied fluids reveals that the modifications made on the parameters of generic van der Waals make this equation of state a promising tool for the density production of fluids in the supercritical region.

We can easily present isotherms of pressure versus density from the new equation of state for fluids in the supercritical region.

Figures 1 and 2 show the isotherms of CH₄ and CO₂ as typical examples of the studied fluids in the supercritical temperatures and the experimental pressures that are available in the

literature. In each of these figures, the points are experimental results and solid lines are fit to the proposed equations.

Table 1. Critical parameters and average absolute deviation percent (AAD%) of density for fluids from new equation of state at supercritical region

Compound	NP ^a	T_c (K)	P_c (MPa)	ρ_c (mol.m ⁻³)	T Range (K)	P Range (MPa)	AAD% of density of fluids	
							This work	PR
CH ₄	165	190.56	4.599	10139.0	191-300	10-590	0.99	7.79
C ₂ H ₆	37	305.33	4.872	6870.0	306-350	10-60	0.81	6.00
C ₃ H ₈	92	369.83	4.248	5000.0	370-500	5-100	0.61	6.37
C ₄ H ₁₀	75	425.13	3.796	3922.8	430-570	4-70	0.80	5.30
C ₅ H ₁₂	78	469.70	3.370	3125.6	470-600	5-97	1.24	5.41
C ₆ H ₁₄	72	507.82	3.034	2705.9	510-600	5-97	0.89	5.02
C ₇ H ₁₆	54	540.13	2.736	2315.3	550-600	6-100	1.26	4.40
C ₈ H ₁₈	67	569.32	2.497	2056.4	570-600	5-97	1.49	4.25
C ₁₀ H ₂₂	69	617.70	2.103	1640.0	620-675	15-445	0.58	2.91
C ₁₂ H ₂₆	67	658.10	1.817	1330.0	670-700	5-400	1.25	4.40
C ₂ H ₄	118	282.35	5.042	7637.0	290-400	5-300	0.57	8.37
C ₆ H ₆	68	562.05	4.894	3243.8	565-635	5-75	1.22	5.61
Cyclohexane	82	553.64	4.075	3956.1	555-700	10-75	1.41	6.59
Toluene	245	591.75	4.126	11183.9	595-700	10-490	0.52	4.31
N ₂	183	126.92	3.396	13630.0	126-2000	7-220	0.96	8.31
O ₂	93	154.58	5.043	10624.9	155-1000	10-80	0.91	4.46
CO ₂	329	304.13	7.377	3169.0	305-1100	10-780	0.78	6.37
Overall	1894						0.98	5.34

^aNP represents the number of data points examined.

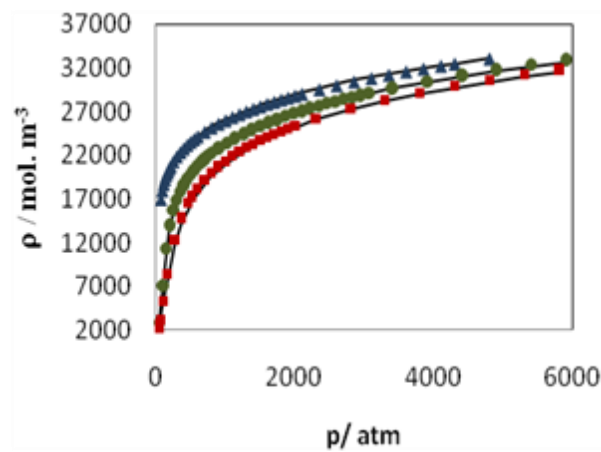


Figure 1. Isotherms of the pressure, P versus density, ρ for methane. The symbols refer to the experimental data: \blacktriangle , 191 K; \bullet , 250 K; \blacksquare , 300 K; --- calculated by the new equation of state.

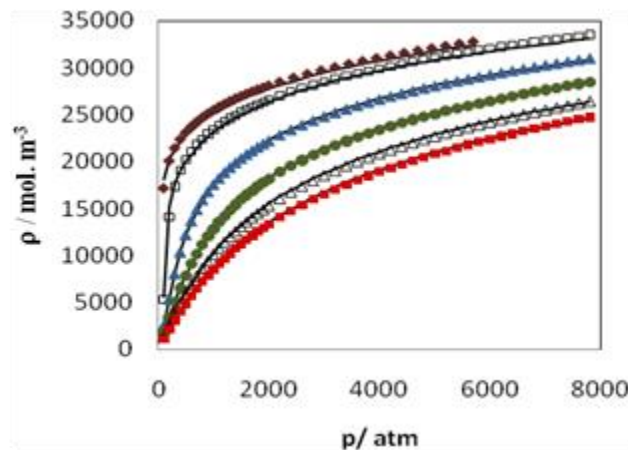


Figure 2. Isotherms of the pressure, P versus density, ρ for CO_2 . The symbols refer to the experimental data : \blacklozenge , 305 K; \square , 350 K; \blacktriangle , 500 K; \bullet , 700 K; \triangle , 900 K; \blacksquare , 1100 K; --- calculated by the modified equation of state.

Figures 1 and 2 show that the obtained results of density are in good agreement with the experimental data [16-19]. In addition, the regularity of linearity associated with isotherms of CH_4 and CO_2 can be shown well by the present equation of state. A closer look at these figures reveals that the densities of fluids decrease as temperature increases because of weakening molecular interactions. According to these figures, although a wide range of density, temperature and pressure are considered, the deviation is very low. The temperature and density

dependencies of the parameter A in equation (12), namely, $\alpha(T, \rho)$, can be presented well using equation (14).

To check the predictive power of the proposed equation of state, the experimental density [16-20] versus the calculated density from the new equation of state was plotted, as shown in Figure 3 for all studied compounds. This figure displays the overall performance of the new equation of state in predicting the density of fluids over supercritical temperatures range. As Figure 3 shows, the calculated densities are well distributed along the

diagonal. Figure 3 reconfirms the reliability of the proposed equation state to predict the *PVT* properties of fluids in the supercritical region. As this figure shows, the diagram has an excellent fit to the data and the

correlation coefficients, R^2 , of the diagram is very good over a wide pressure and density ranges in the supercritical region.

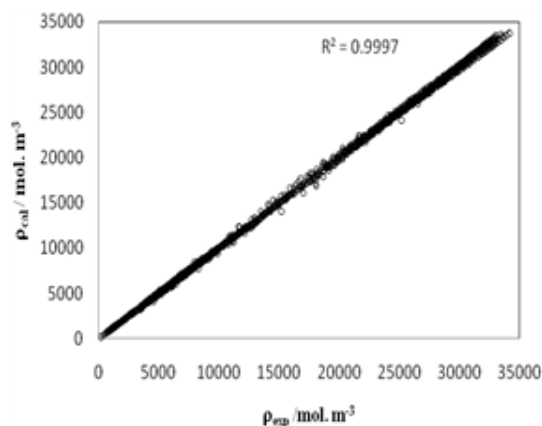


Figure 3. The predicted densities from the new equation of state at various temperatures and pressures in the supercritical region compared with the experimental densities for all studied compounds

Furthermore, Figure 4 presents the distribution of the relative deviation for toluene as a typical example of the studied fluids in this work [16,20]. This figure shows that the maximum deviations were found in the low pressure and with increasing pressure the deviations decreased. The majority of deviations has been distributed at less than $\pm 1\%$.

As the figures show, the present equation of state can predict the *PVT* properties of the aforementioned fluids with a good accuracy. It should be noted that most of the equations of state cannot represent the fluid behavior over a wide range of pressure.

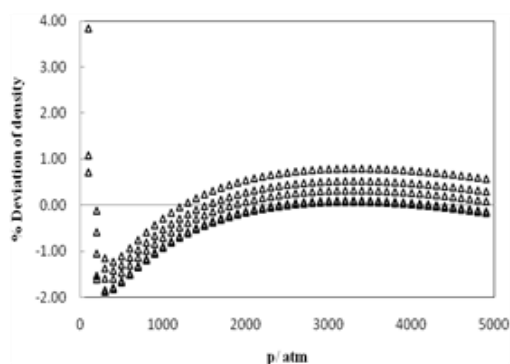


Figure 4. Distribution of relative deviations between the calculated densities and experimental values for toluene versus pressure in the supercritical temperatures

In general, the obtained results show the high capability of the proposed equation of state to predict

PVT properties of fluids in the supercritical region. The present equation of state provides reasonable

densities in the supercritical temperature and high pressures.

Conclusion

A new equation of state has been proposed to improve the predictive power of *PVT* properties of fluids in the supercritical region. In summary, the main purpose of this work was to develop an equation of state from van der Waals family. This equation of state has been obtained with the modification of the parameters of generic van der Waals equation of state. The density of pure fluids has been calculated at different temperatures and pressures in the supercritical region. The obtained results were compared with experimental data. The present equation of state was evaluated by examination of 1894 experimental density data for 17 fluids. This new equation of state predicted the densities of fluids with an overall average absolute deviation percent of the density (*AAD%*) about 0.98%. In addition, the density of these fluids was calculated from PR equations of state. The overall *AAD%* of the density was obtained about 5.34%. Comparison of the obtained results with experimental data and PR equation of state indicates the high capability of the proposed equation of state for prediction of the *PVT* properties of pure fluids at different temperatures and pressures in the supercritical region.

Acknowledgments

The authors are grateful to Payame Noor University for supporting this work.

References

[1] J.L. Daridon, H. Carrier, B. Lagourette, *Int. J. Thermophys.*, **2002**, *23*, 697-708.
[2] D. Pecar, V. Dolecek, *Fluid Phase Equilibria*, **2003**, *211*, 109-127.

[3] K. Liu, Y. Wu, M.A. McHugh, H. Baled, R.M. Enick, B.D. Morreale, *J. Supercrit. Fluids*, **2010**, *55*, 701-711.
[4] G. Soave, *Chem. Eng. Sci.*, **1972**, *27*, 1197-1203.
[5] D.Y. Peng, D.B. Robinson, *Ind. Eng. Chem. Fundam.*, **1976**, *15*, 59-64.
[6] L.S. Wang, J. Gmehling, *Chem. Eng. Sci.*, **1999**, *54*, 3885-3892.
[7] M.R. Riazi, G.A. Mansoori, *Oil Gas Journal*, **1993**, *12*, 108-111.
[8] E.A. Brignole, M. Cismondi, J. Mollerup, *Fluid Phase Equilibria*, **2005**, *234*, 108-121.
[9] H. Baled, R.M. Enick, Y. Wu, M.A. McHugh, W. Burgess, D. Tapriyal, B.D. Morreale, *Fluid Phase Equilibria*, **2012**, *317*, 65-76.
[10] B.C. Eu, K. Rah, *J. Phys. Chem., B* **2003**, *107*, 4382-4391.
[11] S.A. Razavizadeh, F. Alirezapoor, *J. Mol. Liq.*, **2014**, *198*, 358-363.
[12] S.A. Razavizadeh, F. Alirezapoor, *Ext. J. App. Sci.*, **2015**, *3*, 243-251.
[13] B.C. Eu, K. Rah, *Phys. Rev. E.*, **2001**, *63*, 031203-031209.
[14] T.L. Hill, *Statistical Mechanics*, McGraw-Hill, New York, **1956**.
[15] J.P. Hansen, I.R. McDonald, *Theory of Simple Liquids*, 2nd ed. Academic, San Diego, **1986**.
[16] P.J. Linstrom and W.G. Mallard, Eds., *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899.
[17] B.A. Younglove, J.F. Ely, *J. Phys. Chem. Ref. Data*, **1987**, *16*, 577-798.
[18] B.A. Younglove, *J. Phys. Chem. Ref. Data*, **1982**, *11*, 1-11.
[19] R. Span, W. Wagner, *J. Phys. Chem. Ref. Data*, **1996**, *25*, 1509-1596.
[20] N.F. Glen, A.I. Johns, *J. Chem. Eng. Data*, **2009**, *54*, 2538-2545.