

Evaluation of Cubic EOS Models in near Critical Regions of n-Alkanes

Jibeom Kim¹ and Joonhyeon Jeon^{1,2}

¹ Dept. of Information and Communication Engineering, Dongguk University, Seoul, Korea

² Corresponding author: memory@dongguk.edu

Received 01 Jun. 2011; Revised 21 Jul. 2012; Accepted 11 Sep. 2012

Abstract: The purpose of this paper is to evaluate the prediction accuracy and thoroughness of four well-known Cubic Equation Of State (CEOS) models, which are called Peng-Robinson (PR), Modified Peng-Robinson (MPR), Modified Redlich-Kwong (MRK) and Generalized van der Waals (GvdW), to represent pressure of ten pure *n*-alkane molecules (with a general formula C_nH_{2n+2} , $n=1,2,3, \dots, 8,10,12$) near their critical regions. The performance evaluation results show that in the critical region near the critical point, all four CEOS models have a prediction accuracy that gives results quantitatively similar to the experimental vapor-pressure data, while in the critical region far from the critical point, MPR and MRK give more accurate predictions of vapor pressure than PR and GvdW. In contrast, beyond the critical region, GvdW provides much more accurate and reliable predictions of pressure than the other CEOS models. Especially, it is found that GvdW accurately reproduces the experimental pressure data in and beyond the critical region as the molecular size of the *n*-alkanes increases. The performance evaluation of the CEOS models through this approach gives an additional insight into the physical significance of an accurate prediction in and beyond the critical region for pure alkane molecules with linear carbon chains.

Keywords: Equation of state, Critical point, Critical region, Supercritical region, EOS evaluation.

1 Introduction

The estimation of equilibrium phase behavior of complex mixtures over broad temperature and pressure ranges is an important problem in chemical process design. Major research has been conducted in these phase equilibria studies, whereby an Equation Of State (EOS), which is a thermodynamic equation describing the state of matter under a given set of physical conditions, has been established by van der Waals [1]. The van der Waals EOS has made significant contributions to the development of novel Cubic EOS (CEOS) models [2] as proposed by Redlich-Kwong [3], Soave [4] and Peng-Robinson [5]. These famous CEOS models were universally used in calculating fluid thermodynamic properties due to their simple form, few parameters and analytical solutions [6]. However, their simplified original forms had limited applicability due to their inaccurate liquid densities, poor representations in the near-critical

region and unreliability for fluids with large molecules.

The thermo-physical properties of pure materials near their critical points are indispensable in describing fluid phase behavior, predicting physical properties, developing EOS models, and so on. Many researchers failed to measure properties in the critical region directly, because the density fluctuations have a significant influence on fluid properties [7]. Schmidt and Wenzel concluded several years ago that accurate representation of saturated fluid densities in the critical region always leads to a loss of accuracy in describing saturated vapor densities and vice versa [8]. In order to improve the vapor-pressure prediction of Non-hydrocarbon and Hydrocarbon Compounds, Chorng *et al.* [9, 10] has developed modified Peng-Robinson and Redlich-Kwong CEOS models using a modified alpha function (which is a generalized temperature and acentric factor dependent function

of the attractive term). Recently, a generalized van der Waals (GvdW) CEOS for fluid states was proposed [11]. It has a highly simplified Dieterici's form of $P = [RT/(V-b)] - a(b/V)^c$ that is realized by a new model potential construction that describes intermolecular interactions. On the basis of the model potential construction, it is shown that the parameters a , b , and c have physical interpretations as an internal pressure, a void volume, and a dimensionless value that represents an inharmonic intermolecular cell potential, respectively. However, there is still controversy as to whether GvdW can accurately represent saturated fluid densities in the near-critical region [12]. It is also unclear if it can be applied to the three other CEOS models, namely, Peng-Robinson (PR), Modified Peng-Robinson (MPR) and Modified Redlich-Kwong (MRK).

The main focus of this paper is to evaluate the performance of the four CEOS models in and beyond the critical region of pure molecules. For this purpose, these models are applied to ten pure n -alkane molecules: methane, ethane, propane, butane, pentane, hexane, heptane, octane, decane and dodecane. These pure molecules have unique electronic, optical and physic-chemical properties because of their linear carbon chains. It is well known that most EOS models have difficulties in making accurate predictions of pressure near their critical regions.

2 Results and Discussions

2.1 Application of EOS models to n -alkanes

Ever since van der Waals proposed the CEOS model in the form of $P = [RT/(V-b)] - (a/V^2)$, several modifications of it have taken place [1]. Out of many evolutions, as mentioned before, PR, MPR, MRK and GvdW have been the most successful in vapor-liquid equilibria calculations of polar as well as non-polar properties of fluids. The major modifications have been as follows: modifications of the second or attractive term or and/or the introduction of temperature dependence on the parameter a or use of the experimental critical compressibility factor Z_{cc} for the parameters a , b and c [5], [9], [10], [11]. Table 1 and 2 show the basic forms of the four CEOS models and related symbols, respectively. Also, Table 3 indicates the critical properties of the ten pure molecules [13]. Table 4 - 7, based on Table 3, denote the calculated parameters of each CEOS used to apply the four CEOS models to the ten pure molecules.

Table 1 : The basic forms of the four CEOS models used in the comparison

PR(Peng Robinson) Equation of State [5]	
$P[\text{bar}] = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2}$	
where,	
$a = 0.457535 \frac{R^2 T_c^2}{P_c}, b = 0.077796 \frac{RT_c}{P_c}$	
and the alpha function is,	
$\alpha = (1 + \kappa(1 - T_r^{0.5}))^2$	
$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$	
$T_r = \frac{T}{T_c}$	
MPR(Modified Peng Robinson) Equation of State [9]	
$P[\text{bar}] = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2}$	
where,	
$a = 0.457235528921 \frac{R^2 T_c^2}{P_c},$	
$b = 0.0777960739039 \frac{RT_c}{P_c}$	
and the alpha function is,	
$a(T) = \alpha(T) \cdot a(T_c)$	
$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)})$	
$\alpha^{(0)} = T_r^{-0.792615} e^{0.401219(1-T_r^{-0.992615})}$	
$\alpha^{(1)} = T_r^{-1.98471} e^{0.024955(1-T_r^{-9.98471})}$	
$\omega = \text{acentric factor defined at } T_r = 0.7$	
MRK(Modified Redlich Kwong) Equation of State [10]	
$P[\text{bar}] = \frac{RT}{V-b} - \frac{a}{V(V+b)}$	
where,	
$a = 0.42748023354 \frac{R^2 T_c^2}{P_c},$	
$b = 0.086640349965 \frac{RT_c}{P_c}$	
and the alpha function is,	
$a(T) = \alpha(T) \cdot a(T_c)$	
$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)})$	
$\alpha^{(0)} = T_r^{-1.10000} e^{0.44141(1-T_r^{-1.30000})}$	
$\alpha^{(1)} = T_r^{-2.31278} e^{0.03258(1-T_r^{-10.31278})}$	
$\omega = \text{acentric factor defined at } T_r = 0.7$	
GvdW(Generalized van der Waals) Equation of State [11]	
$P[\text{bar}] = \frac{RT}{V-b} - a \left(\frac{b}{V} \right)^c$	
where,	
$c = 2Z_{cc} + \sqrt{4Z_{cc}^2 + 1},$	
$a = \left(\frac{c+1}{c-1} \right)^{c+1} \times P_c,$	
$b = \left(\frac{c-1}{c+1} \right) \times V_c$	

Table 2 : List of symbols used in CEOS models in Table 1

Symbol	Meaning of symbol
a, b, c	Parameters for EOS (PR, MPR, MRK and GvdW)

P	Pressure
R	Gas constant
T	Temperature
V	Molar volume
α	Alpha function
ω	Acentric factor
c	Subscript for critical property
r	Subscript for reduced property

Ethane	C_2H_6	5648856.103	45.085046
Propane	C_3H_8	9512166.546	62.698699
Butane	C_4H_{10}	14069881.71	80.665365
Pentane	C_5H_{12}	19346241.63	100.40273
Hexane	C_6H_{14}	25118252.05	120.57173
Heptane	C_7H_{16}	31511269.09	142.21227
Octane	C_8H_{18}	38360099.70	164.24523
Decane	$C_{10}H_{22}$	53616852.80	211.58905
Dodecane	$C_{12}H_{26}$	70439172.04	260.91066

Table 3 : Critical properties of the ten pure molecules used in this work

Formula	ω	M/W (g/mol)	Z_{cc}	T_c (K)	P_c (bar)	V_c (cm ³ /mol)
CH ₄	0.011	16.043	0.288	190.56	45.99	98.6
C ₂ H ₆	0.099	30.069	0.284	305.33	48.72	145.6
C ₃ H ₈	0.152	44.096	0.280	369.83	42.48	220.48
C ₄ H ₁₀	0.199	58.123	0.274	425.12	37.97	254.9
C ₅ H ₁₂	0.249	72.148	0.321	469.70	33.71	310.98
C ₆ H ₁₄	0.305	86.175	0.270	507.82	30.42	369.56
C ₇ H ₁₆	0.351	100.201	0.298	540.13	27.31	431.90
C ₈ H ₁₈	0.369	114.228	0.297	569.32	24.978	486.28
C ₁₀ H ₂₂	0.484	142.281	0.249	617.70	21.030	609.76
C ₁₂ H ₂₆	0.573	170.334	0.242	658.10	18.170	751.86

Table 7 : Parameters used in GvdW for individual molecules

Molecule	Formula	c	a (bar)	b (cm ³)
Methane	CH ₄	1.724973	1697.069580	26.237162
Ethane	C ₂ H ₆	1.704352	1853.259399	37.900089
Propane	C ₃ H ₈	1.695261	1638.075562	51.578754
Butane	C ₄ H ₁₀	1.687634	1480.641724	65.220978
Pentane	C ₅ H ₁₂	1.671981	1347.804443	78.200554
Hexane	C ₆ H ₁₄	1.665549	1228.683716	92.293816
Heptane	C ₇ H ₁₆	1.654927	1122.487305	106.54027
Octane	C ₈ H ₁₈	1.637403	1057.753540	117.49171
Decane	C ₁₀ H ₂₂	1.616515	922.6959230	143.68490
Dodecane	C ₁₂ H ₂₆	1.616339	796.8950200	177.31190

Table 4 : Parameters used in PR for individual molecules

Molecule	Formula	$a(T_c)$ (bar)	b (cm ³)
Methane	CH ₄	2495243.899	26.775275
Ethane	C ₂ H ₆	6046009.089	40.482711
Propane	C ₃ H ₈	10180936.52	56.298342
Butane	C ₄ H ₁₀	15059090.04	72.430948
Pentane	C ₅ H ₁₂	20706413.93	90.153502
Hexane	C ₆ H ₁₄	26884235.92	108.26452
Heptane	C ₇ H ₁₆	33726725.52	127.69507
Octane	C ₈ H ₁₈	41057075.48	147.47888
Decane	C ₁₀ H ₂₂	57386482.04	189.98979
Dodecane	C ₁₂ H ₂₆	75391524.68	234.27659

Table 5 : Parameters used in MPR for individual molecules

Molecule	Formula	$a(T_c)$ (bar)	b (cm ³)
Methane	CH ₄	2493610.683	26.775301
Ethane	C ₂ H ₆	6042051.785	40.482749
Propane	C ₃ H ₈	10174272.78	56.298395
Butane	C ₄ H ₁₀	15049233.40	72.431017
Pentane	C ₅ H ₁₂	20692860.93	90.153587
Hexane	C ₆ H ₁₄	26866639.34	108.26462
Heptane	C ₇ H ₁₆	33704650.32	127.69519
Octane	C ₈ H ₁₈	41030202.33	147.53810
Decane	C ₁₀ H ₂₂	57348920.78	189.98997
Dodecane	C ₁₂ H ₂₆	75342178.55	234.27682

Table 6 : Parameters used in MRK for individual molecules

Molecule	Formula	$a(T_c)$ (bar)	b (cm ³)
Methane	CH ₄	2331335.186	29.819261

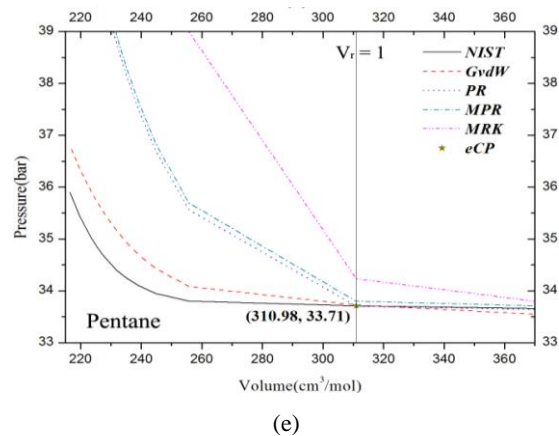
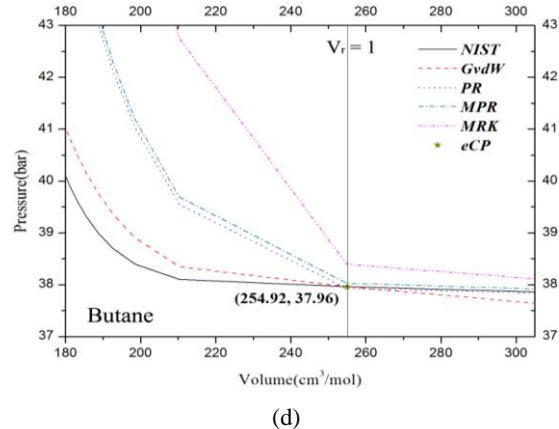
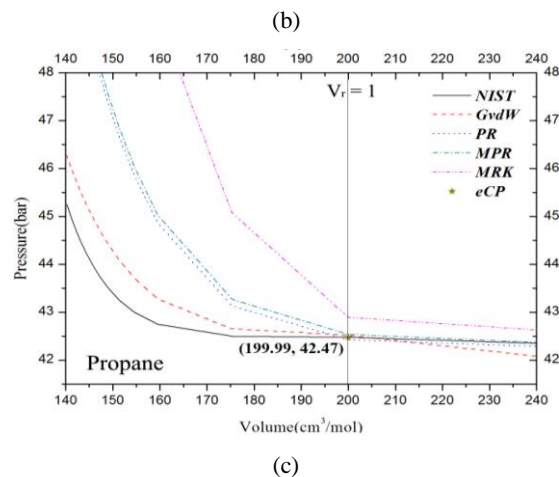
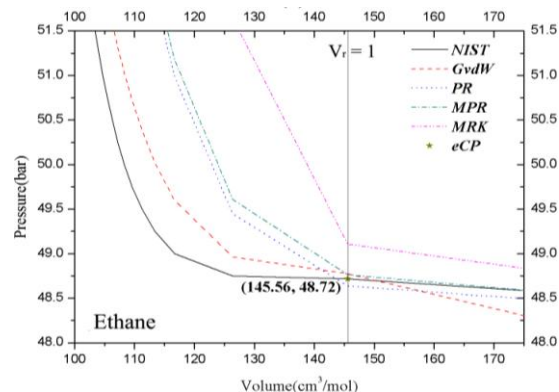
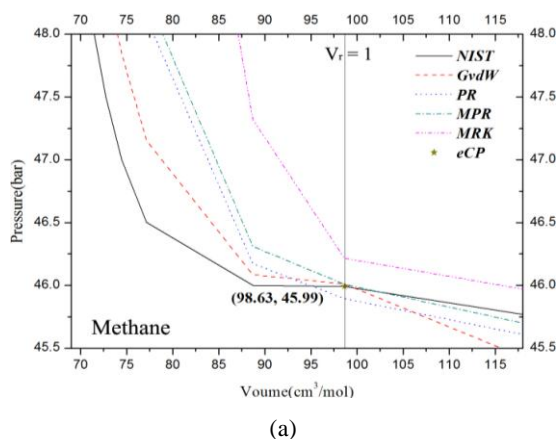
2.2 Comparison near the critical-point region

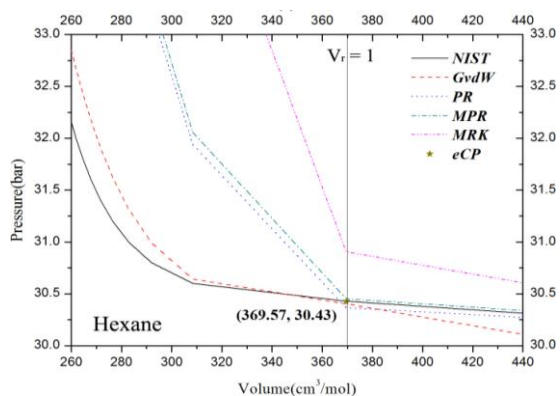
This study made a comparison of four CEOS models, which are PR, MPR, MRK and GvdW. It was performed by evaluating the prediction accuracy of these models in the near-critical regions of the aforementioned ten pure alkane molecules. All of the highly accurate experimental data on the pure molecules used in this work was obtained from the National Institute of Standards and Technology (NIST) [13]. The performance evaluation of the CEOS models is performed in and beyond the critical region of the reduced volume range $0.7 < V_r < 1.2$ (: the reduced temperature is then $T_r = 1$), where $0.7 < V_r < 1.0$ and $1.0 < V_r < 1.2$ correspond to the supercritical and critical regions, respectively.

Figure 1 shows the prediction results obtained from applying the four CEOS models to the ten pure *n*-alkanes in the near-critical region. The solid line indicates the experimental data given by NIST and the "★" symbol is used to mark the experimental critical point on the solid line. From these results, it is clear that in the calculation volume range beyond the critical region, GvdW provides much more reliable and accurate prediction of supercritical pressure than the other three CEOS models. Whereas, in the critical region, the prediction graphs of PR and MPR are generally closer to the experimental curves than MRK and GvdW. Especially, the predicted line obtained from

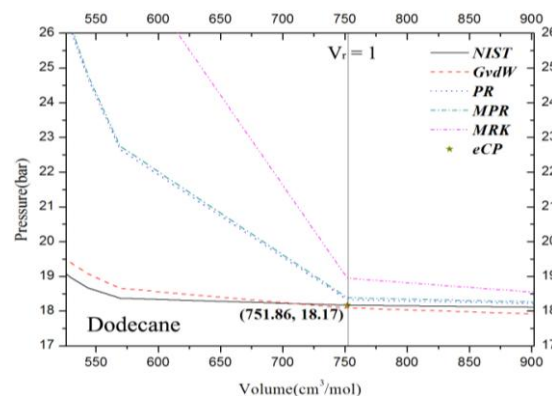
GvdW exhibits the largest representation error in the critical region far from the critical point, although it is most exact in the region near the experimental critical point. However, GvdW shows more improved accuracy in and beyond the critical region as the molecular size of the alkanes increases (i.e., as the number of carbons in the carbon backbone increases and their boiling and melting points also increase). Table 8 shows the average absolute deviation percentage (AAD%) between the experimental and predicted data in and beyond the critical regions.

Based on the performance evaluation results so far, the prediction accuracy of the four CEOS models to represent vapor pressure in the critical region for pure *n*-alkanes is similar and lies within allowable error limits, while for supercritical pressure beyond the critical region, the prediction accuracy of GvdW is much better than the other CEOS models. This is because PR, MPR and MRK were realized by introducing an alpha function, which is a linear function of the acentric factor at a constant reduced temperature, whereby parameter *a* is introduced to improve the prediction accuracy from the triple point to before the critical point. On the other hand, GvdW was optimized by introducing the critical compressibility factor Z_{cc} into three parameters, which can be physically interpreted as an internal pressure, a void volume, and a dimensionless value that represents an inharmonic intermolecular cell potential.

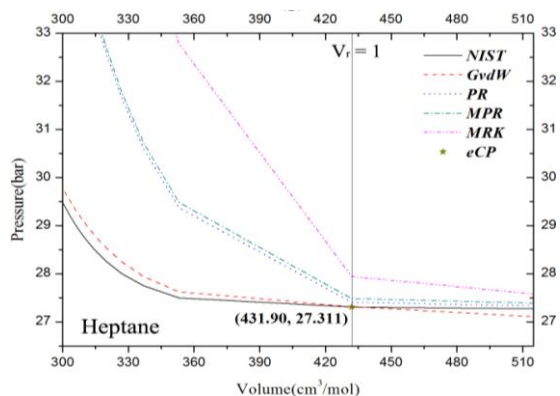




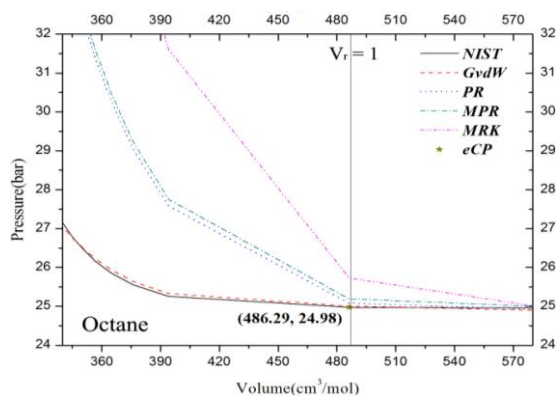
(f)



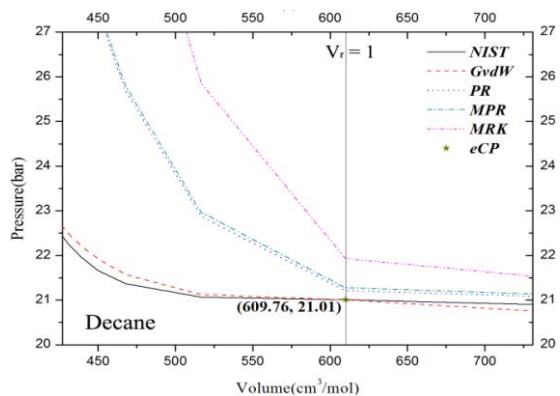
(j)



(g)



(h)



(i)

Figure 1: The CEOS-evaluation results near the critical region of pure *n*-alkane molecules:

(a) Methane, (b) Ethane, (c) Propane, (d) Butane, (e) Pentane, (f) Hexane, (g) Heptane, (h) Octane, (i) Decane, (j) Dodecane

Table 8 : Average absolute deviation percentage (AAD%) of predicting alkane pressures in the range of $0.7 < V_r < 1.2$ from CEOS models

formula	Range (V_r)	GvdW	PR	MPR	MRK
CH ₄	0.7 ~ 1.0	1.378E00	4.094E00	4.471E00	15.43E00
	1.0	4.377E-2	2.113E-1	3.749E-2	4.886E-1
	1.0 ~ 1.2	1.698E00	5.166E-1	3.826E-1	3.827E-1
C ₂ H ₆	0.7 ~ 1.0	1.706E00	7.690E00	8.105E00	24.44E00
	1.0	1.150E-1	1.64E-1	9.509E-2	7.995E-1
	1.0 ~ 1.2	1.041E00	2.094E-1	5.183E-2	3.223E-1
C ₃ H ₈	0.7 ~ 1.0	1.715E00	8.023E00	8.435E00	23.93E00
	1.0	1.005E-1	1.315E-1	1.331E-1	9.759E-1
	1.0 ~ 1.2	1.260E00	1.953E-1	4.037E-2	3.738E-1
C ₄ H ₁₀	0.7 ~ 1.0	1.654E00	9.488E00	9.914E00	27.30E00
	1.0	7.037E-3	9.516E-2	1.748E-1	1.149E00
	1.0 ~ 1.2	9.193E-1	3.237E-2	1.352E-1	3.800E-1
C ₅ H ₁₂	0.7 ~ 1.0	2.066E00	13.36E00	13.81E00	35.61E00
	1.0	5.324E-2	1.807E-2	2.601E-1	1.554E00
	1.0 ~ 1.2	4.318E-1	7.832E-2	1.154E-1	1.486E-1
C ₆ H ₁₄	0.7 ~ 1.0	1.504E00	14.55E00	15.01E00	38.85E00
	1.0	8.417E-2	2.073E-1	7.520E-2	1.562E00
	1.0 ~ 1.2	1.237E00	6.226E-2	1.014E-1	3.945E-1
C ₇ H ₁₆	0.7 ~ 1.0	9.152E-1	16.28E00	16.74E00	264.4E00
	1.0	1.382E-2	3.413E-1	6.298E-1	2.313E00
	1.0 ~ 1.2	9.948E-1	1.103E-1	2.918E-1	4.004E-1
C ₈ H ₁₈	0.7 ~ 1.0	9.067E-1	17.86E00	18.65E00	46.19E00
	1.0	1.150E-1	4.065E-1	8.561E-1	2.997E00
	1.0 ~ 1.2	2.567E-1	1.712E-1	1.420E-1	1.086E-1
C ₁₀ H ₂₂	0.7 ~ 1.0	7.572E-1	22.14E00	22.62E00	53.18E00
	1.0	2.869E-2	9.375E-1	1.252E00	4.354E00
	1.0 ~ 1.2	1.643E00	7.558E-1	9.217E-1	1.207E00
C ₁₂ H ₂₆	0.7 ~ 1.0	1.865E00	30.37E00	30.89E00	70.16E00
	1.0	4.724E-1	8.282E-1	1.143E00	4.24E00
	1.0 ~ 1.2	1.725E00	2.452E-1	4.253E-1	5.482E-1

3 Conclusion

Herein we have described the performance evaluation of four famous CEOS models in the near-critical regions of ten pure *n*-alkane molecules with linear carbon chains. It has been shown that the prediction accuracy of all four CEOS models to represent the vapor pressure in the critical region is similar and lies within allowable error limits. Remarkably, GvdW gives much more accurate and reliable prediction of supercritical pressure than the other three CEOS models, and it represents an improved accuracy in and beyond the critical region as the molecular size of the *n*-alkanes increases.

Acknowledgements

This work was supported by the Dongguk University Research Fund of 2012

References

- [1] D. Johannes and V. D. Waals, On the Continuity of the Gaseous and Liquid States (doctoral dissertation), Universiteit Leiden, (1873).
- [2] J. O. Valderrama, The State of the Cubic Equations of State, *Ind. Eng. Chem. Res.*, (2003), 42(8), 1603-1618.
- [3] O. Redlich and J. N. S. Kwong, On the Thermodynamics of Solutions, V. An Equation of States. Fugacities of Gaseous Solutions. *Chem. Rev.*, (1949), 44(1), 233-244.
- [4] G. Soave, Equilibrium Constants from a Modified Redlich-Kwong Equation of State, *Chem. Eng. Sci.*, (1972), 27, 1197-1203.
- [5] D. Y. Peng and D. B. Robinson, A New Two-Constant Equation of State, *Ind. Eng. Chem. Fundamen.*, (1976), 15, 59-64.
- [6] P. Perrot, A to Z of Thermodynamics, Oxford University Press, (1998).
- [7] A. N. Vulfson and N. A. Skibitskaya, On the Use of the Henry Law for the Description of the Sorption of Methane and Ethane by Asphaltenes under Supercritical Temperature and High Pressure Conditions, *IEEE Russian J. Phys. Chem. B.*, (2009), 3(7), 1082-1089.
- [8] G. Schmidt and H. Wenzel, A modified van der Waals type equation of state, *Chem. Eng. Sci.*, (1980), 35(7), 1503-1512.
- [9] H. T. Chorng, E. C. John and R. C. John, A new generalized alpha function for a cubic equation of state Part 1. Peng-Robinson equation, *Fluid Phase Equilib.*, (1995), 105(1), 49-59.
- [10] H. T. Chorng, E. C. John and R. C. John, A new generalized alpha function for a cubic equation of state Part 2. Redlich-Kwong equation, *Fluid Phase Equilib.*, (1995), 105(1), 61-69.
- [11] L. Sukbae, J. Joonhyeon, K. Wonsoo and C. Tong-Seek, A New Model Approach for the Near-Critical Point Region: 1. Construction of the Generalized van der Waals Equation of State, *J. Phys. Chem. B.*, (2008), 112(49), 15725-15741.
- [12] W. Yong, H. Guo-bo and G. Chang-hua, Saturated Properties Prediction in Critical Region by a Quartic Equation of State, *Bull. Chem. Soc. Ethiop.*, (2011), 25(2), 287-294.
- [13] NIST, Chemistry Web Book, National Institute of Standards and Technology, <http://webbook.nist.gov/chemistry/>, (2011).

Jibeom Kim was born in Incheon, Korea in 1982. He received the B.S. and M.S degrees in the department of information and communication engineering, Dongguk University in Seoul, Korea, in 2008 and 2010, respectively. He is currently working to get Ph.D. degree in the Department of Information and communication Engineering, Dongguk University in Seoul, Korea. His research interests include lithium-ammonia and calcium-ammonia solutions, and the theory and application of Equation of State (EOS).



Joonhyeon Jeon was born in Seoul, Korea in 1961. He received the B.S. degree in electronic engineering from Dongguk University, Korea, in 1984 and the M.S and Ph.D. degrees in electric and electronic engineering from Korea Advanced Institute of Science Technology, Korea, in 1986 and 1991, respectively. Since 2002, he has been an Associate Professor in the Department of Information and communication Engineering, Dongguk University in Seoul, Korea. He was a Research Scientist at Korea Telecom Research Center from 1991 to 1999. His current research interests are in the area of thermoelectric materials, in particular, metal-Ammonia and metal-amine solutions, thermoelectric cell design, the theory and application of Equation of State (EOS), and the application of thermoelectric cells.

