Thermodynamic modeling of PVTx properties for several water/hydrocarbon systems in near-critical and supercritical conditions

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Abstract−Both the equation of state-excess Gibbs energy (EoS/G^E) model and the cubic plus association (CPA) equation of state (EoS) are compared in this study with respect to their accuracy in the correlation of PVTx for systems such as water/methanol, water/ethanol, water/benzene, water/toluene, water/methane, water/n-butane, water/n-pentane, water/n-hexane, water/heptane, and water/octane, in supercritical conditions within temperature and pressure ranges of (573-698 K) and (7.0-276.0 MPa), respectively. In the proposed EoS/G^E model, Peng-Robinson (PR) equation of state, linear combination Vidal-Michelsen (LCVM) and Wong-Sandler (WS) mixing rules in conjunction with UNIQUAC activity coefficient model were used. Correlation of both CPA and EoS/G^E models was evaluated by comparing the results with the experimental data. Average absolute relative deviation (AARD) for WS, LCVM, and CPA was found to be 2.99, 11.11 and 5.14%, respectively, indicating better correlation of WS model with the experimental data.

Key words: CPA Equation of State, EoS/G^E Model, Supercritical Mixture, UNIQUAC Activity Coefficient

INTRODUCTION

Supercritical water remains a subject of intense scientific research due to its potential industrial applications in areas such as hydrothermal production of ultrafine particles, extraction, dry cleaning, biomass conversion, hazardous wastes and effluent treatment. Designing these processes requires accurate knowledge of the thermodynamic properties of the systems involved. In the last two decades, a large number of publications have been presented on supercritical water due to its remarkable anomalous properties as a solvent or reaction medium for a wide range of technological applications. The applications cover fields such as geology, mineralogy (for hydrothermal synthesis), or include oil and gas industries (tertiary oil recovery), new extraction techniques for separation, regeneration of sorbents used in waste water treatment, hazardous waste decontamination of soils or equipment, and oxidation of hazardous chemicals [1-3].

Solvent characteristics of water going through ambient to supercritical conditions change dramatically as solvent for ionic species to solvent for non-ionic ones, primarily due to the reduction of dielectric constant (~2 at 25 MPa and 723 K) [1,4]. Also, electrochemical properties of water such as dipole moment decrease from larger values at ambient conditions, to that of acetone in the critical region [4]. The pH-value too, decreases by 3 units, providing much more hydronium ions for acid catalyzed reactions. On the other hand, the reactivity of water increases near the critical point, irrespective of any catalyst presence [4].

When designing any of these processes in such a wide range of applications, access to reliable thermodynamic properties becomes of paramount importance, especially the knowledge of PVTx for

developing phase diagrams for complicated aqueous mixtures whose applications both in industry and research laboratories are on the increase [5]. Hence, a large number of publications have focused on obtaining such data [1,2,5-10] which present considerable experimental difficulties in measurement techniques, instability of molecules, high temperature/pressure and corrosive medium involved [11]. Employing a reliable EoS, capable of predicting such data, and therefore, avoiding the strenuous testing procedure, seems to be necessary for overcoming the mentioned problems and cost reduction. This is quite a difficult task due to the broad temperature and pressure conditions and the asymmetric nature of the mixtures considered. However, the presence of water as a polar compound with strong associative interactions in any system increases the complexity of the thermodynamic behavior [12].

Recently, a number of models have been developed to correlate high-pressure vapor-liquid equilibrium using PTxy data at subcritical conditions. For instance, water/alcohol (C_1-C_3) or water/acetone systems were studied in temperature and pressure ranges of 473-623 K and 16-185 bar, respectively, by Voutsas et al. [13] and Garduza et al. [14], having used EoS-excess Gibbs energy (EoS/G^E) model. Voutsas et al., however, used SRK/UNIFAC in conjunction with MHV2, PSRK, LCVM and Wong-Sandler (WS) mixing rules, while Graduza employed PR/NRTL, Van Laar, and the UNIFAC model. Folas [15] also modeled the thermodynamic properties for systems such as water/propane, water/butane, water/propylene and water/CO_2 using cubic-plus-association (CPA) EoS. SAFT EoS too, has been employed by Li et al. [16] in the temperature range of 348-427 K.

As can be seen, the above calculations were all made based on vapor-liquid equilibrium at subcritical conditions. This is while in supercritical conditions, phase equilibrium becomes irrelevant (as there is only one single phase) and data should normally be presented in PVTx (x corresponds to the composition of the single phase

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at supercritical condition). Such a study is already reported in the literature for water/CO_2 system using SAFT-LJ EoS [17].

To have a model that could simultaneously apply to high pressures at both polar and hydrogen bonding systems, G^E models are coupled with the cubic equations of state through the EoS-G^E mixing rules. In such an approach a range of possibilities may be considered where different equations of state and G^E models are coupled with various degrees of success [18]. Association EoS, such as the group contribution associating EoS, SAFT [19], APACT [20], and the CPA EoS [21], however, explicitly describes the specific interactions between like molecules (self-association) and unlike molecules (cross-association). These have been considered as a breakthrough in modeling of polar and highly nonideal systems in large temperature and pressure ranges. In particular, the CPA EoS has shown to be the most appropriate model of this kind to deal with complex associating systems, considering the balance between accuracy, predictability, and simplicity [22,23]. These complex associating systems include binary systems containing alcohols and hydrocarbons [24,25], water and hydrocarbons [26], polymers and solvents [27], organic acids [28], amines [29], for multi-component systems containing water/alcohol/alkane [30] and [31], and water/glycol/alcohol/alkane [32].

Considering the above, in this work, the EoS/G^E model and CPA EoS were employed to correlate PVTx for water/methanol, water/ethanol, water/benzene, water/toluene, water/methane, water/n-butane, water/n-pentane, water/n-hexane, water/heptane, and water/octane, in single-phase systems at supercritical conditions within temperature and pressure ranges of (573-698 K) and (7.0-276.0 MPa), respectively. Here, the PR equation of state, LCVM and WS mixing rules in conjunction with UNIQUAC activity coefficient model are used.

THERMODYNAMIC MODELS

Considering water as one of the two components in the supercritical system under investigation, thermodynamic models employed should be capable of describing compounds with association sites at the corresponding high temperatures and pressures. The thermodynamic models used in this study are briefly described below.

1. EoS/G^E Model

This model is developed from a cubic EoS in conjunction with the activity coefficient model in order to correlate thermodynamic properties of both polar and non-polar mixtures, especially at higher pressures [33]. Among the many cubic EoS of van der Waals (VdW) type nowadays available, the model proposed by Peng and Robinson [34] is widely used due to its simplicity and flexibility [35]. Here, an improved PR EoS modified by Gasem [36], as presented in Eq. (1) below, was employed

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)+b(V-b)}. \tag{1}$$

The pure-component parameters (a_i and b_i) are calculated from pure-component critical properties as below:

$$a_i = \frac{0.4572\,\alpha_{(T_r)}(RT_{C,i})^2}{P_{C,i}} \text{ and } b_i = \frac{0.0778RT_{C,i}}{P_{C,i}}, \tag{2}$$

where $\alpha_{(T_r)} = \exp[(2+0.836T_r)(1-T_r^m)]$ and parameter m is defined in terms of acentric factor ω, as

$$m = 0.134 + 0.508\omega - 0.0467\omega^2. \tag{3}$$

To evaluate mixture parameters (a and b), two mixing rules of LCVM [37] and WS [38] were used. LCVM is based on a linear combination of the mixing rules of Vidal [39] and Michelsen [40], and could be expressed as

$$a = bRT\left[\left(\frac{\lambda}{C}+\frac{1-\lambda}{q_1}\right)\frac{G^E}{RT}+\frac{1-\lambda}{q_1}\sum_i x_i \ln\left(\frac{b}{b_i}\right)+\sum_i x_i \frac{a_i}{b_i RT}\right], \tag{4}$$

where G^E is the excess Gibbs energy and λ is an arbitrary parameter selected to give the best results for the particular systems used [41]. For the PR EoS, $\lambda = 0.36$, $C = \ln(\sqrt{2}-1)/\sqrt{2}$ and $q_1 = -0.53$ [18].

The mixture co-volume parameter is also evaluated using the following linear relationship:

$$b = \sum_i x_i b_i. \tag{5}$$

The other mixing rule used here, WS [38], may be expressed as

$$b = \frac{RT\sum_i\sum_j x_i x_j\left(b-\frac{a}{RT}\right)_{ij}}{RT-\left[\sum_i x_i\frac{a_i}{b_i}+\frac{G^E}{C}\right]}, \tag{6}$$

with

$$\left(b-\frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b_i-\frac{a_i}{RT}\right)+\left(b_j-\frac{a_j}{RT}\right)\right](1-k_{ij}), \tag{7}$$

and

$$a = bRT\left[\frac{G^E}{CRT}+\sum_i x_i\frac{a_i}{b_i RT}\right]. \tag{8}$$

The activity coefficient model used in Eqs. (4), (6) and (8) is the UNIQUAC model containing two combinatorial and residual terms described as [42]

$$G^E = G^E \text{ (combinatorial)} + G^E \text{ (residual)}, \tag{9}$$

where

$$\frac{G^E \text{(combinatorial)}}{RT} = x_1\ln\frac{\varphi_1}{x_1}+x_2\ln\frac{\varphi_2}{x_2}$$
$$+\frac{z}{2}\left(q_1 x_1\ln\frac{\theta_1}{\varphi_1}+q_2 x_2\ln\frac{\theta_2}{\varphi_2}\right), \tag{10}$$

and

$$\frac{G^E \text{(residual)}}{RT} = -q_1 x_1\ln(\theta_1+\theta_2\tau_{21})-q_2 x_2\ln(\theta_2+\theta_1\tau_{12}). \tag{11}$$

Here,

$$\varphi_i = \frac{x_i r_i}{\sum_i x_i r_i}, \quad \theta_i = \frac{x_i q_i}{\sum_i x_i q_i},$$
$$\ln\tau_{21} = -\frac{\Delta u_{21}}{RT} \text{ and } \ln\tau_{12} = -\frac{\Delta u_{12}}{RT}, \tag{12}$$

where r and q are VdW volume and area parameters of molecule i calculated through group contribution increments, and x corresponds to the mole fraction of component i.

This thermodynamic model includes the PR equation of state, the WS or LCVM mixing rules, and the UNIQUAC model for G^E

Table 1. CPA EoS parameters and structural parameters of UNIQUAC activity coefficient model for the pure compounds considered in this work

Component	r	q	a_0 (bar·l^2·mol^{-2})	b (l/mol)	c_1	$\varepsilon^{A_iB_j}$ (bar.l.mol^{-1})	$\beta^{A_iB_j} \times 10^3$
Water	0.92[a]	1.40[a]	1.228[b]	0.01452[b]	0.6736[b]	166.55[b]	69.2[b]
Methanol	1.43[a]	1.43[a]	4.053[b]	0.03098[b]	0.4310[b]	245.91[b]	16.1[b]
Ethanol	2.11[a]	1.97[a]	8.672[b]	0.04908[b]	0.7369[b]	215.32[b]	8.0[b]
Methane	0.171[c]	0.355[c]	0.2333[b]	0.02985[b]	0.4981[b]	-	-
n-Butane	3.15[d]	2.78[d]	13.143[b]	0.07208[b]	0.7077[b]	-	-
n-Pentane	3.83[d]	3.32[d]	18.198[b]	0.09101[b]	0.7986[b]	-	-
n-Hexane	4.50[a]	3.86[a]	23.681[b]	0.10789[b]	0.8313[b]	-	-
n-Heptane	5.17[a]	4.40[a]	29.178[b]	0.12535[b]	0.9137[b]	-	-
n-Octane	5.85[a]	4.94[a]	34.875[b]	0.14244[b]	0.9942[b]	-	-
Benzene	3.19[a]	2.40[a]	17.876[b]	0.07499[b]	0.7576[b]	-	-
Toluene	3.92[a]	2.97[a]	23.375[b]	0.09214[b]	0.8037[b]	-	-

[a]=[45], [b]=[15], [c]=[46], [d]=[47]

in the mixing rules, and for brevity is referred to here as PR/WS/UNIQUAC and PR/LCVM/UNIQUAC, respectively.

2. CPA Equation of State

This EoS, developed by Kontogeorgis et al. [21], combines the simplicity of a cubic EoS such as SRK and the theoretical background of the perturbation theory, employed for the association part, and is commonly used to describe associating fluids. In terms of pressure P, CPA EoS can be expressed for mixtures as

$$P = \frac{RT}{V-b} - \frac{\alpha(T)}{V(V+b)} - \frac{1}{2}\frac{RT}{V}\left(1+\rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1-X_{A_i}), \quad (13)$$

where the physical terms (i.e., the first two terms) correspond to the same in SRK EoS and the associating term is taken from the SAFT EoS [43]. Here, a Soave-type temperature dependency of the pure component energy parameter, α is used where

$$\alpha(T) = \alpha_0[1+c_1(1-\sqrt{T_r})]^2, \quad (14)$$

and ρ is density, g is a simplified radial distribution function [30], X_{A_i} is the mole fraction of component i not bonded at site A, and finally, x_i is the mole fraction of component i. X_{A_i} is calculated through the association strength, $\Delta^{A_iB_j}$, between two sites belonging to two different molecules, and is obtained by solving the following set of equations:

$$X_{A_i} = \frac{1}{1+\rho\sum_j x_j \sum_{B_j} X_{B_j}\Delta^{A_iB_j}}, \quad (15)$$

where

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)-1\right]b_{ij}\beta^{A_iB_j}, \quad (16)$$

with the radial distribution function $g(\rho)=1/(1-1.9\eta)$ for $\eta=1/4b\rho$ and $b_{ij}=(b_i+b_j)/2$.

In the expression for the association strength $\Delta^{A_iB_j}$, the parameters $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ correspond to the association energy and the association volume, respectively. These two parameters, used only for associating components, as well as the three additional SRK parameters (a_0, b, and c_1), represent the five pure-component parameters of the CPA model [44]. These parameters as well as those from UNI-

QUAC (i.e. r and q) are presented in Table 1.

When CPA EoS is used for mixtures, conventional mixing rules are often employed in the corresponding physical terms (i.e., SRK section of the model) for the energy and co-volume parameters [15]. The interaction parameter k_{ij} appearing in the mixing rules is the only adjustable binary parameter of CPA in the following form:

$$a = \sum_i\sum_j x_i x_j a_{ij} \quad (\text{where } a_{ij}=\sqrt{a_i a_j}(1-k_{ij})). \quad (17)$$

To extend the CPA EoS to mixtures containing associating compounds (for instance alcohols, water, or a mixture of the two), combining rules (CR) for the association energy ($\varepsilon^{A_iB_j}$) and the association volume ($\beta^{A_iB_j}$) should be employed. Here, two specific CRs, CR-1 and Elliott CR (ECR) are used as suggested by Folas [14], where CR-1 may be expressed as

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i}+\varepsilon^{A_jB_j}}{2} \quad \text{and} \quad \beta^{A_iB_j}=\sqrt{\beta^{A_iB_i}\beta^{A_jB_j}}. \quad (18)$$

The expression for the cross-association strength ($\Delta^{A_iB_j}$) in conjunction with ECR may also be written as

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}}. \quad (19)$$

MODELING BY GENETIC ALGORITHMS

Genetic algorithm (GA) is a reliable method that employs biologically derived techniques such as inheritance, mutation, natural election, and recombination and was used in this study to evolve toward better solutions in satisfying the objective function as defined in the model. The interaction parameter k_{12} and UNIQUAC model parameters of $u_{21}(=\Delta u_{21}/R)$ and $u_{12}(=\Delta u_{12}/R)$ were obtained by predicting PVTx properties from the models, having minimized the following objective function:

$$F = \frac{1}{NP}\sum_i\left|\frac{v_i^{exp}-v_i^{calc}}{v_i^{exp}}\right|, \quad (20)$$

where NP is the number of data points, v is the molar volume, and the superscripts (calc) and (exp) denote the calculated and experimental values, respectively.

Initially, a number of individuals represented by chromosomes

are randomly created, forming a set known as the initial population. Each chromosome consists of a number of "0s" and "1s" and represents the values of the parameters to be calculated [48]. On the whole, GA is conducted using information from this population of candidate solutions. Crossover and mutation operators generate new off-springs, while the mentioned objective function controls the search progress. GA's mutation probability corresponds to the off-spring mutation and to adaptive random searches' control of local/global convergence. Periodic domain expansion and contraction of adaptive random searches is analogous to the increasing diversity of the GA population by using crowding scheme [49]. A competition-cooperation among 'families' in the evolution algorithm is equivalent to (a) avoiding the 'elitism' induced by the 'fitness' function in GA, (b) the continuous switching between local and global search in adaptive random searches, and (c) the multi-start local searches in clustering algorithms [50].

In the GA scheme used here, the number of variables (chromosomes), the number of generations, the length of a chromosome, the search space, the crossover probability and the mutation probability, etc. were all defined according to literature information [48] and are presented in Table 2.

RESULTS AND DISCUSSION

Table 3 illustrates the fitted interaction and UNIQUAC activity coefficient parameters obtained as outlined above for the ten single phase binary systems under investigation in this study (i.e., water/methanol, water/ethanol, water/benzene, water/toluene, water/methane, water/n-butane, water/n-pentane, water/n-hexane, water/heptane, and water/octane) and their corresponding absolute average relative deviation (AARD) for the models employed using GA. Available PVTx relationships for these systems were measured with a constant-volume piezometer surrounded by a precision thermostat as defined in the literature indicated in Table 3 [1,2,5,8,11,51-53].

These measurements included three aqueous ethanol mixtures (0.2, 0.5, and 0.8 mole fraction of ethanol), a H_2O+CH_3OH mixture (0.36 mole fraction of methanol), six compositions from 0 to 0.614 mole fraction of hydrocarbon (n-heptane, n-octane, and benzene), three composition mole fractions of toluene (0.0008, 0.0022, and 0.0085), five composition mole fractions of methane (0.3709, 0.4326, 0.4914, 0.7900 and 0.8424), five composition mole fractions of n-butane (0.02, 0.05, 0.15, 0.25 and 0.35), seven composition mole fractions of n-pentane (0.027, 0.058, 0.075, 0.0967, 0.1185, 0.139 and 0.8898) and four composition mole fractions of n-hexane (0.0021, 0.0050, 0.0085, 0.0138). The operating temperature ranges for these ten mixtures were 573 to 673 K, 588 to 673 K, 647 K, 623 to 673 K, 573 to 653 K, 602 to 698 K, 620 to 679 K and 643 to 651 K, and the corresponding pressures ranges were 5.4 to 48 MPa, 6.6 to 90.9 MPa, 5 to 40 MPa, 11 to 46 MPa, 7 to 63 MPa, 19 to 276 MPa, 7 to 63 MPa and 8 to 35 MPa, respectively.

With the set of data in Table 3, density (ρ) and compressibility factor (Z) in supercritical conditions for the systems could be evaluated. The associated errors presented in Table 3 correspond to the accuracy of both the optimized parameters of EoS as well as capability of the models in correlating ρ and Z. This is because the objective function is defined based on the molar volume v, used directly in assessing ρ and Z. Considering the degree of nonideality and high pressures and temperatures involved, the accuracy of the three models may be considered satisfactory. As expected, the EoS/G^E model is capable of correlating the characteristics of such polar systems as investigated here under high pressure [38]. Despite the PR/LCVM/UNIQUAC model offering reasonable accuracy, the PR/WS/UNIQUAC model showed a much superior compatibility with the experimental data as indicated by its lower AARD. It was not possible to validate our models, primarily because despite the growing interest on the matter, there is limited empirical data on supercritical water systems and little modeling reported on them in the literature so far. The only similar approach to this study reported

Table 2. Variables and parameters for the genetic algorithms method developed in this work to correlate the models parameters from available experimental data

Variables	Notation/method/formula	Value
Number of experimental data	NP	-
Number of variables	N_V	1, 2 or 3 based on the model used
Number of generations	N_{gen}	30
Length of a chromosome	L_c	20
Total length of an individual	$L_T = N_V \times L_c$	-
Number of individuals	N_I	20
Aptitude definition	Linear	-
Selection scheme	Universal stochastic sampling	-
Crossover operator	Multipoint	
Crossover probability	Pcross	0.8
Mutation operator	Binary	-
Mutation probability	Pmut	0.035
Search space (range of feasible solutions for the parameters k_{12}, u_{12}, u_{21})	SS1 for k_{12}	(−1,1)
	SS2 for u_{12}	(−800,1000)
	SS3 for u_{21}	(−800,1000)
Objective function	$F = \dfrac{1}{NP} \sum_I \left| \dfrac{v_i^{exp} - v_i^{calc}}{v_i^{exp}} \right|$	Minimum positive value

Table 3. Adjustable interaction and UNIQUAC activity coefficient parameters for the ten single phase binary systems investigated and their corresponding relative error (AARD) for the models used

Column groups: PR/LCVM/UNIQUAC = u_{12} (K), u_{21} (K), AARD, k_{ij}; PR/WS/UNIQUAC = u_{12} (K), u_{21} (K), AARD; CPA = k_{ij}, AARD.

Systems	x_1	N.P.	Temp. (K)	Press. range (MPa)	u_{12} (K) [LCVM]	u_{21} (K) [LCVM]	AARD [LCVM]	k_{ij} [LCVM]	u_{12} (K) [WS]	u_{21} (K) [WS]	AARD [WS]	k_{ij} [CPA]	AARD [CPA]	Ref. of data
	0.2	10	673.15	9-48	−200.2877	−119.8188	0.076122	−0.001	−133.7503	−111.6190	0.031974	−0.055	0.042532	[5]
		7	648.15		−105.7468	−63.3722	0.078976	−0.001	−85.7590	−53.6445	0.033535	−0.009	0.045775	
		9	623.15		−107.0129	6.9094	0.095961	−0.001	−8.7804	−4.2098	0.042035	−0.036	0.061177	
		9	598.15		−32.8306	126.1937	0.110348	−0.070	121.3612	124.4888	0.085846	−0.156	0.092685	
		10	573.15		124.8376	222.4453	0.201999	−0.019	360.1155	273.7551	0.200593	−0.164	0.122932	
Water (2)/ ethanol (1)	0.5	10	673.15	6.6-50	−88.5591	−82.0820	0.067224	0.140	−68.4388	−52.5619	0.017430	−0.269	0.030655	
		6	648.15		−82.1843	−74.5032	0.089673	0.245	−68.4388	−49.6752	0.013632	−0.050	0.051814	
		10	623.15		−221.1066	−208.6156	0.079291	0.150	−42.3382	−33.7984	0.016444	−0.265	0.046418	
		12	598.15		−148.9391	−132.2384	0.091197	0.110	−33.9187	−19.8460	0.022202	−0.050	0.076335	
		15	573.15		41.0488	−132.2384	0.124842	0.069	13.8321	11.4265	0.017162	−0.020	0.066016	
	0.8	11	673.15	5.4-43	−316.1414	−303.3654	0.052255	0.096	−190.6423	−173.8032	0.028685	−0.834	0.029563	
		8	648.15		−303.3907	−279.1893	0.056380	0.181	−184.6283	−168.9921	0.020426	−0.747	0.033696	
		12	623.15		−246.7404	−243.1056	0.059527	0.160	−186.3122	−168.9921	0.019401	−0.430	0.030759	
		13	598.15		−199.1087	186.4542	0.068186	0.190	−169.5935	−156.8439	0.017127	−0.290	0.040859	
		15	573.15		−126.9413	−131.1258	0.085330	0.190	−133.3895	−118.4749	0.013424	−0.350	0.041102	
Total							**0.092913**				**0.038661**		**0.054155**	
Water (2)/ methanol (1)	0.36	22	673.15	6.6-90.9	−548.4003	−509.7065	0.149174	−0.921	−256.1944	−232.2588	0.012685	−0.320	0.056450	[11]
		22	663.15		−420.3031	−617.5968	0.159564	−0.771	−141.8090	−127.9769	0.071836	−0.315	0.086032	
		22	647.15		−566.3219	−520.6519	0.227432	−0.982	−230.8155	−199.7835	0.006539	−0.282	0.090197	
		22	623.15		509.7907	−571.4458	0.366228	−0.995	−197.3779	−158.6481	0.009971	−0.013	0.098923	
		22	598.15		−382.0544	−469.4130	0.423847	−0.220	−115.4679	−95.1407	0.045098	−0.480	0.101027	
		22	593.15		−354.6307	−444.9122	0.429955	−0.341	−71.8066	−48.5927	0.063920	−0.556	0.123481	
		22	588.15		−322.1554	−410.3921	0.451202	−0.230	−74.5730	−49.4347	0.090810	−0.485	0.137138	
Total							**0.315343**				**0.043106**		**0.099035**	
Water (2)/ methane (1)	0.4326	5	573.15	6.58-63.24	−243.6179	−214.1173	0.051647	0.631	−62.4248	−49.5550	0.014524	0.314	0.028215	[51]
	0.3709	5	653.15		−479.2168	−421.3417	0.067018	0.731	−421.5781	−240.3175	0.021088	0.592	0.034064	
	0.4914	5			−264.3162	−211.1271	0.056114	0.228	459.3457	278.0852	0.016879	0.187	0.029047	
	0.7900	5			−347.9472	−189.1467	0.024017	−0.664	−211.4265	−121.4337	0.005960	0.522	0.011429	
	0.8424	5			−734.7115	−637.3316	0.018106	−0.034	−273.6589	−244.1080	0.002388	0.294	0.008271	
Total							**0.043380**				**0.012168**		**0.022205**	
Water (2)/ n-butane (1)	0.02	13	615-642	19.3-276.4	−148.9055	−323.7912	0.108491	0.621	−740.4619	−619.3409	0.023333	0.348	0.040391	[52]
	0.05	13	617-644		−642.5307	−363.9644	0.075162	0.271	−582.3911	−351.4554	0.031880	0.326	0.051473	
	0.15	5	602-653		345.9225	147.9432	0.066015	0.437	−685.7391	−627.1394	0.010374	0.615	0.027064	
	0.25	5	616-700		225.6435	147.9432	0.008365	0.381	−576.1336	−499.2414	0.007194	0.587	0.008018	
	0.35	6	600-698		421.9389	347.3659	0.042363	0.519	−761.9131	−664.2197	0.017618	0.682	0.031089	
Total							**0.060079**				**0.018080**		**0.031607**	

Table 3. Continued

Systems	x_1	N.P.	Temp. (K)	Press. range (MPa)	PR/LCVM/UNIQUAC u_{12} (K)	PR/LCVM/UNIQUAC u_{21} (K)	PR/LCVM/UNIQUAC AARD	PR/WS/UNIQUAC k_{ij}	PR/WS/UNIQUAC u_{12} (K)	PR/WS/UNIQUAC u_{21} (K)	PR/WS/UNIQUAC AARD	CPA k_{ij}	CPA AARD	Ref. of data
	0.027	47	620-675		200.3849	173.5627	0.113852	-0.312	539.9326	446.4758	0.032118	0.217	0.050174	
	0.058	52	620-675		-75.5352	-54.8472	0.109612	0.449	132.7881	124.2483	0.038050	0.084	0.049138	
Water (2)/	0.075	48	620-676	6.99-63.04	362.6413	321.3856	0.102541	0.711	206.1583	183.1850	0.024526	0.413	0.042061	[53]
n-pentane (1)	0.0967	47	620-677		77.9408	64.7101	0.109000	0.286	218.5470	179.8172	0.026002	0.522	0.040369	
	0.1185	38	620-677		110.8973	80.3464	0.085382	0.189	267.8614	251.9846	0.012946	0.241	0.038271	
	0.139	26	624-677		136.1559	102.2372	0.099282	0.202	260.8853	242.8434	0.010180	0.337	0.030649	
	0.8898	12	625-679		-275.7999	-231.7777	0.049160	-0.152	200.7457	136.9978	0.009850	0.164	0.014837	
Total							**0.095547**				**0.021953**		**0.037928**	
		9	643.05		-224.4407	-194.8521	0.162996	0.471	-413.6396	-393.5530	0.062416	-0.719	0.085167	
		9	645.05		-519.0281	-504.4624	0.142197	-0.656	-357.1085	-333.4135	0.054637	-0.561	0.079128	
	0.0021	9	647.05	11.30-31.37	-708.4436	-682.8362	0.138364	-0.504	-442.3863	-429.6368	0.051276	-0.638	0.074137	[8]
		9	649.05		-669.2326	-635.1936	0.130355	0.247	-528.9873	-504.2098	0.050168	-0.291	0.071223	
		9	651.05		-665.5280	-688.1164	0.129567	-0.319	-591.5324	-566.7549	0.043647	-0.095	0.067431	
		10	643.05		-181.1643	-140.1371	0.116308	0.263	-305.3885	-273.2740	0.041375	0.167	0.064389	
		10	645.05		-256.3356	-232.8723	0.120949	0.106	-393.1922	-357.4693	0.040684	0.264	0.061873	
	0.0050	10	647.05	11.37-33.52	-305.8696	-286.5047	0.115553	0.264	-478.4701	-453.6926	0.039149	0.219	0.060769	
		10	649.05		-347.1253	-327.2793	0.113288	0.662	-565.0709	-540.2935	0.037648	0.672	0.057113	
		10	651.05		-418.0899	-366.9714	0.125045	0.518	-615.5882	-590.8107	0.034712	0.762	0.056148	
		10	643.05		-148.0876	-161.7873	0.118815	0.246	-308.9969	-297.3298	0.038647	0.496	0.059176	
		10	645.05		-217.5848	-207.6016	0.119644	0.443	-429.2759	-393.5530	0.036129	0.617	0.056154	
	0.0085	10	647.05	8.48-34.74	-281.8138	-257.3972	0.119086	0.582	-526.5817	-489.7763	0.032167	0.371	0.053279	[8]
		10	649.05		-58.4556	-38.6096	0.118124	0.653	-577.0989	-552.3214	0.029716	0.638	0.051048	
Water (2)/		10	651.05		-151.0705	-125.2105	0.115537	0.674	-639.6440	-614.8665	0.030641	0.314	0.049627	
n-hexane (1)		8	643.05		124.3685	118.6072	0.113836	0.556	-296.9690	-285.3019	0.028649	0.148	0.050192	
		8	645.05		114.0486	90.9430	0.115425	0.714	-430.3584	-393.6733	0.028162	0.034	0.049176	
	0.0138	8	647.05	8.63-33.43	91.8932	69.8821	0.116726	0.642	-478.4701	-453.6926	0.030486	0.864	0.048707	
		8	649.05		83.7142	50.6495	0.115781	0.759	-566.2738	-541.4963	0.031149	0.316	0.052371	
		8	651.05		30.7915	16.9593	0.112207	0.787	-640.9670	-617.2721	0.027168	0.283	0.050118	
Total							**0.122990**				**0.038431**		**0.059861**	
	0.028	7			261.1378	133.819	0.099769	0.410	64.1087	17.3202	0.041782	-0.013	0.061676	
	0.048	7			190.2694	104.9074	0.108414	0.469	148.0635	168.8718	0.015852	-0.026	0.044958	
Water (2)/	0.082	8	647.05	4.70-40.29	457.6858	316.0332	0.091343	0.481	378.8790	252.1049	0.016992	-0.032	0.041660	[2]
heptane (1)	0.173	6			347.8711	383.7022	0.086486	0.565	440.3416	551.2389	0.023484	-0.056	0.056961	
	0.474	6			365.8528	573.8513	0.050798	0.584	960.3079	803.4640	0.023484	-0.066	0.049132	
	0.706	5			378.8910	440.7866	0.026768	0.473	828.0010	706.1583	0.022462	-0.061	0.048662	
Total							**0.077263**				**0.023855**		**0.050508**	

Table 3. Continued

Systems	x_1	N.P.	Temp. (K)	Press. range (MPa)	PR/LCVM/UNIQUAC			k_{ij}	PR/WS/UNIQUAC			k_{ij}	CPA		Ref. of data
					u_{12} (K)	u_{21} (K)	AARD		u_{12} (K)	u_{21} (K)	AARD		k_{ij}	AARD	
Water (2)/ octane (1)	0.031	9	647.05	4.61-43.21	213.5434	355.0036	0.109807	0.480	184.2675	150.2285	0.022166	-0.022	0.048507		[2]
	0.048	8			110.0794	236.6250	0.104895	0.495	307.6738	128.5783	0.018243	-0.036	0.038818		
	0.078	8			399.9880	242.1097	0.106880	0.487	303.8249	263.1706	0.023857	-0.049	0.044774		
	0.263	5			539.5598	452.3214	0.091052	0.816	955.5208	913.5915	0.024818	-0.096	0.042518		
	0.425	6			484.8569	374.2362	0.060387	0.509	854.8232	962.1121	0.018807	-0.081	0.032089		
	0.614	5			344.9122	270.5677	0.038007	0.457	756.4349	812.1241	0.022041	-0.067	0.040189		
Total							**0.085171**				**0.021655**			**0.041149**	
Water (2)/ toluene (1)	0.0085	7	647.10	11-46	-160.9694	-234.0991	0.105312	0.434	-571.9269	-563.5073	0.055441	0.432	0.078214		[1]
		7	648.15		-177.8085	-281.7296	0.103603	0.513	-637.3587	-736.7092	0.049672	0.580	0.060036		
		7	653.15		-341.6286	-446.8727	0.095216	0.785	-738.0563	-623.6709	0.026488	0.647	0.047824		
		7	663.15		-618.2704	-687.0700	0.084827	0.814	-726.4133	-658.2151	0.015675	0.927	0.031298		
		7	673.15		-809.3938	-796.6442	0.084594	0.947	-792.8795	-677.3154	0.012739	0.914	0.025427		
	0.0022	7	623.15	13-42	-733.8465	-613.4472	0.208710	0.385	-760.9045	-721.9353	0.128035	0.619	0.147913		
		7	628.15		-755.4967	-686.9858	0.189494	0.417	-767.8374	-698.7763	0.107953	0.528	0.139724		
		7	633.15		-796.0548	-638.5855	0.175993	0.527	-758.5583	-701.1003	0.084463	0.289	0.118534		
		7	638.15		-637.8157	-714.2891	0.175852	0.297	-787.2326	-724.3096	0.093245	0.313	0.127519		
		7	643.15		-683.5458	-782.2227	0.166898	0.369	-789.5117	-731.8124	0.086100	0.740	0.120065		
		7	647.15		-603.8249	-716.5985	0.161991	0.327	-706.5109	-768.3608	0.086497	0.715	0.112282		
		7	648.15		-603.8249	-794.8039	0.173659	0.572	-714.1742	-691.0041	0.099223	0.967	0.121824		
		7	653.15		-499.2783	-598.9896	0.140081	0.948	-769.2326	-615.1070	0.038433	0.867	0.068549		
	0.0008	7	647.10	14-43	-725.7638	-664.3373	0.106455	0.990	-742.0014	-766.3700	0.076432	-0.754	0.093589		
		7	648.15		-786.3844	-622.0351	0.106523	-0.821	-725.7397	-768.7034	0.066829	-0.927	0.088769		
		7	653.15		-789.1268	-769.4527	0.117665	-0.541	-702.0447	-730.3825	0.034788	-0.654	0.063247		
		7	663.15		-652.4176	-769.8581	0.117733	-0.478	-738.5855	-796.0548	0.020080	-0.768	0.031247		
		7	673.15		-601.1787	-738.9464	0.113070	-0.624	-752.5018	-650.2646	0.017838	-0.457	0.025664		
Total							**0.134871**				**0.061329**			**0.083429**	
Water (2)/ benzene (1)	0.028	7	647.05	4.62-37.68	-131.5131	-268.1381	0.127339	0.546	-317.4164	-634.1111	0.030769	-0.017	0.049154		[2]
	0.043	8			-68.7275	-177.8566	0.086829	0.502	-398.7250	-241.4000	0.029833	-0.020	0.046023		
	0.063	9			22.8410	-37.3827	0.078179	0.521	88.0443	-247.0532	0.021456	-0.024	0.033883		
	0.075	8			254.1015	138.7419	0.094464	0.470	-107.2889	-87.4429	0.012638	-0.026	0.020411		
	0.222	6			226.0645	204.3421	0.071473	0.467	166.5865	131.7056	0.021402	-0.037	0.038894		
	0.439	6			97.8229	65.8408	0.046696	0.404	243.6854	245.0084	0.007928	-0.032	0.014876		
Total							**0.084163**				**0.020671**			**0.033873**	
Global AARD:							*0.111172*				*0.029991*			*0.051375*	

$$\text{AARD} = \frac{1}{NP} \sum_i \left| \frac{v_i^{exp} - v_i^{calc}}{v_i^{exp}} \right|$$

[17], dealt with H_2O-CO_2 system and SAFT-LJ EoS, which could not be used here. However, as far as high pressure and temperature data are concerned, similar results have also been reported for high pressure vapor-liquid equilibria (VLE) in water/ethanol and water/methanol systems [54], where the PR/WS/UNIQUAC model has proved to be more reliable in predicting high-pressure phase behavior than PR/MHV2/UNIQUAC model. This might be because PR/WS/UNIQUAC uses a non-linear relationship (Eq. (6)) for evaluating the co-volume parameter, and hence compared with both PR/LCVM/UNIQUAC and PR/MHV2/UNIQUAC, it deals with an extra binary interaction adjustable parameter of k_{ij}.

As for the CPA EoS, results in Table 3 indicate that its prediction accuracy is higher than PR/LCVM/UNIQUAC but less than that of the PR/WS/UNIQUAC model. However, having in mind its simplicity in structure with only one adjustable parameter, and consequently less demand for CPU time calculation, this reasonable accuracy may be considered as justifiable. Folas et al. have already demonstrated the good capability of CPA EoS in predicting VLE systems involving high pressures and temperatures; this is particularly true for cross associating systems [55] where other commonly used association EoS, such as SAFT-type (applied extensively in polymers), are rarely employed. The investigations of Suresh and Beckman [56] (SAFT for water-alcohol and acid alkanes), Fu and Sandler [57] (simplified SAFT and SAFT for various binary systems), Gross and Sadowski [58] (PC-SAFT for alcohol-alcohol and water-pentanol), and Paragand et al. [59] (SAFT-VR for water-ethanol) can be mentioned among the few such applications.

Another point worth mentioning here is that when either alcohol or water are present in the system mixtures, complex structures and unusual thermodynamic behavior are expected, primarily due to produced H-bonded molecular associations. These present serious challenges in studying them, both from the theoretical and experimental points of views. Contrary to physical interactions, H-bonding interactions, whether between molecules of the same species (self-association), or those of different species (solvation), in aqueous alcohol solutions are short ranged and highly directional [5,45]. Hence, the associated errors in water/methanol and water/ethanol systems, as indicated in Table 3, are higher than other systems investigated here. Even the influence of H-bonding seems to be more significant in water/methanol system as compared with that of water/ethanol; consequently, the models are less capable of correlating the former. This is perhaps because methanol is a small but highly polar molecule and is expected to interact strongly with water (itself, a polar molecule) in the H-bonded network [11,60].

As far as the number of carbon atoms in the alkenes under investigation is concerned, although Table 3 indicates that increasing this from methane (1C) to hexane (6C) has increased error in all three models, for other systems involving water and either heptane, octane and benzene, the error is very near to that of water/hexane. Hence, it is difficult to link the error and the number of carbon atoms in the alkenes. The system mole fraction may play a significant role in here, and this is not the same for the systems investigated. Again, according to Table 3, increasing water mole fraction increases AARD in almost all models investigated here, confirming higher influence of water related H-bond and its associated molecular interactions. This point is quite evident in the dilute water/toluene mixture, where even for the PR/WS/UNIQUAC model, which presents a very good fit with the experimental data, there is a considerable maximum error of 6.13%.

Verifying the accuracy of the models, could also be demonstrated by their ability in calculating (Z) and (ρ) when plotted against pressure. Figs. 1-4 illustrate a typical trend of these plotted for the models used here and water/ethanol system. Other systems investigated here
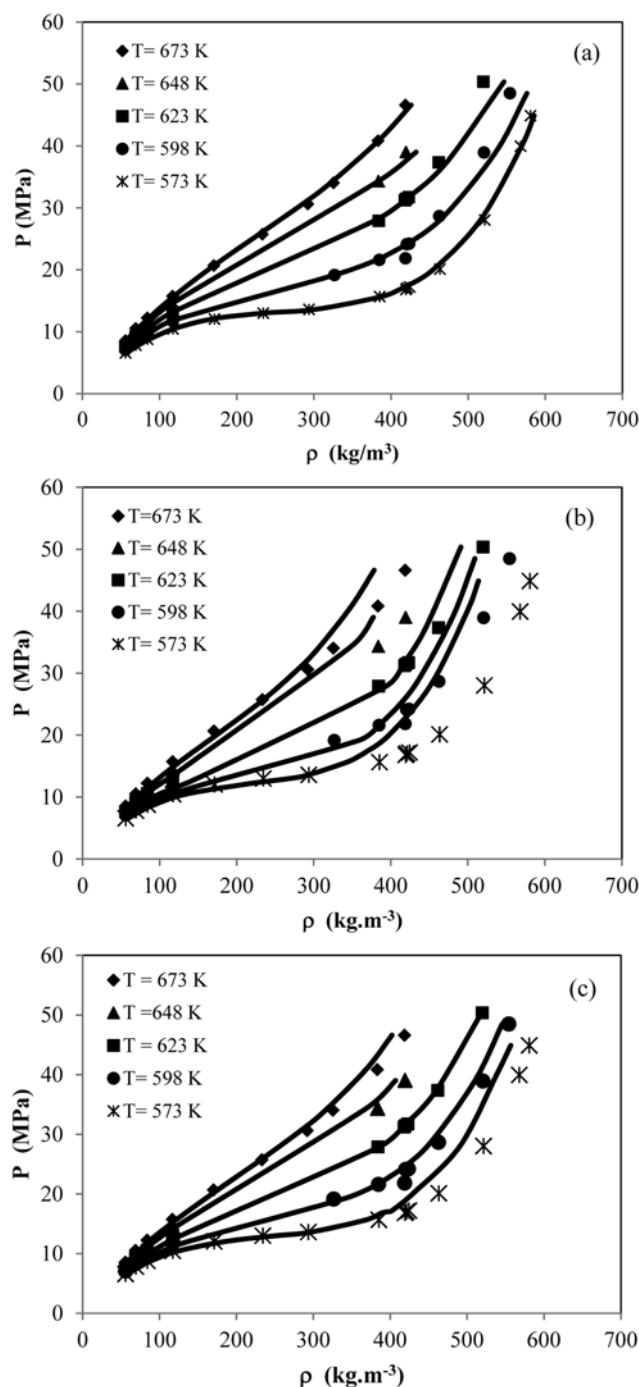

Fig. 1. Diagrams for pressure (P) of a supercritical ($0.5H_2O+0.5$ C_2H_5OH) mixture against density (ρ) along various isotherms. Solid lines correspond to the results obtained from (a) PR/WS/UNIQUAC, (b) PR/LCVM/UNIQUAC and (c) CPA models, and symbols correspond to the experimental data.
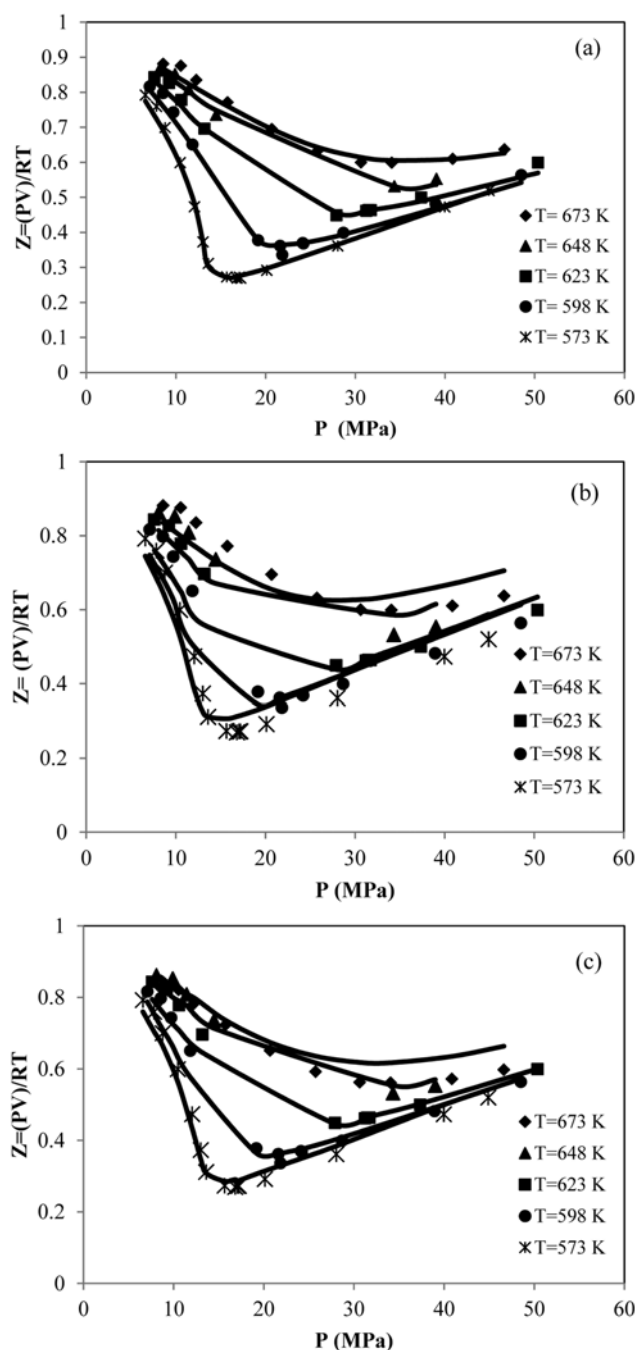
Fig. 2. Diagrams for compressibility factor (Z) of a supercritical (0.5H$_2$O+0.5C$_2$H$_5$OH) mixture against pressure (P) along various isotherms. Solid lines correspond to the results obtained from (a) PR/WS/UNIQUAC, (b) PR/LCVM/UNIQUAC and (c) CPA models, and symbols correspond to the experimental data.

Fig. 3. Diagrams for pressure (P) of a supercritical (0.2H$_2$O+0.8 C$_2$H$_5$OH) mixture against density (ρ) along various isotherms. Solid lines correspond to the results obtained from (a) PR/WS/UNIQUAC, (b) PR/LCVM/UNIQUAC and (c) CPA models, and symbols correspond to the experimental data.

demonstrated similar trends and their figures are not presented for the sake of brevity. As can be seen from Figs. 1-4, at higher pressures, there is a significant difference between prediction capability of the PR/WS/UNIQUAC and CPA compared to that of PR/LCVM/ UNIQUAC. Out of the first two models, the PR/WS/UNIQUAC also leads to more accurate predictions almost for all temperatures and pressures. This is while PR/LCVM/UNIQUAC predictions are
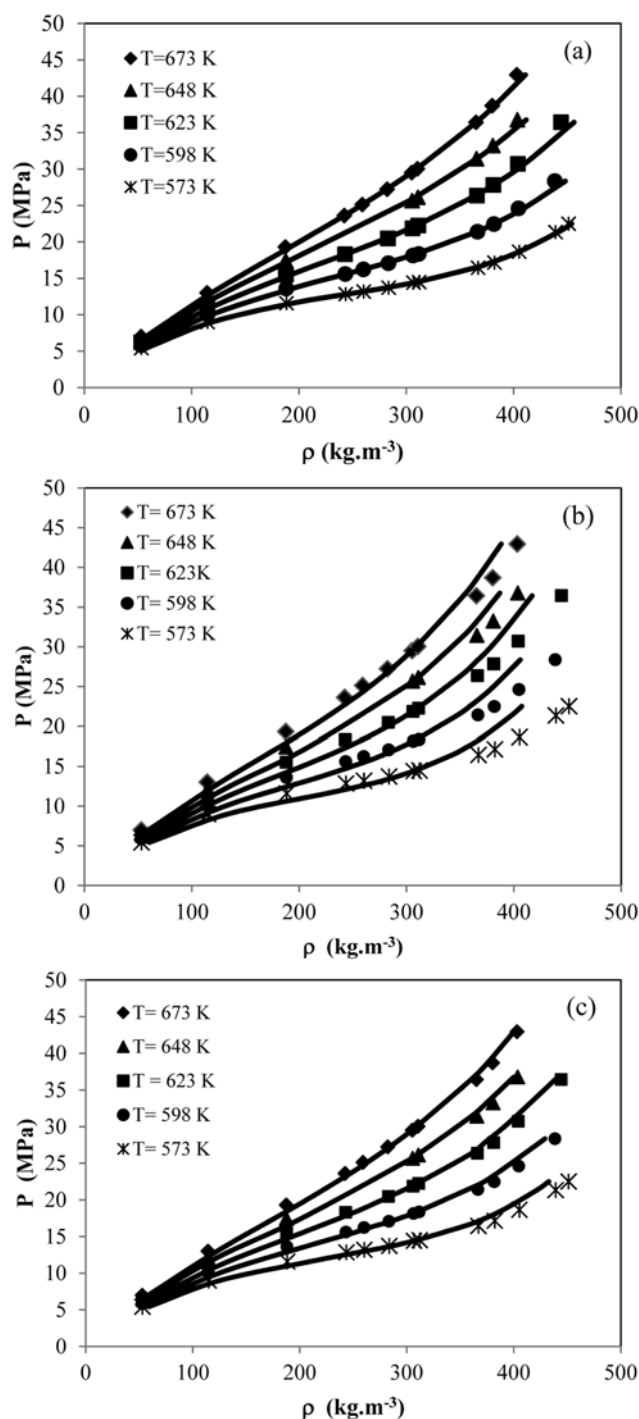
increasingly inaccurate at higher pressures. Therefore, it appears that temperature-dependent parameters might be needed in the LCVM mixing rule to produce results of comparable accuracy to the WS mixing rule and CPA, both of which contain temperature-independent parameters.
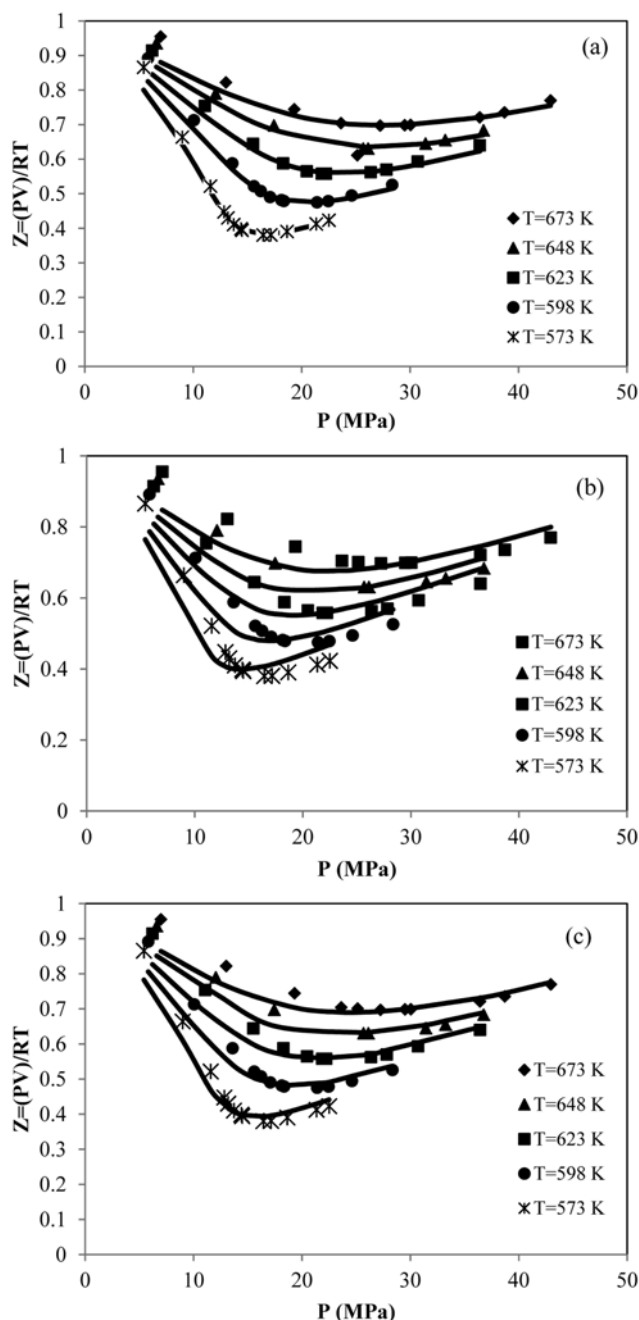
Fig. 4. Diagrams for compressibility factor (Z) of a supercritical ($0.2H_2O+0.8C_2H_5OH$) mixture against pressure (P) along various isotherms. Solid lines correspond to the results obtained from (a) PR/WS/UNIQUAC, (b) PR/LCVM/UNIQUAC and (c) CPA models, and symbols correspond to the experimental data.

CONCLUSIONS

EoS/G^E model and CPA EoS were employed to correlate PVTx for water/methanol, water/ethanol, water/benzene, water/toluene, water/methane, water/n-butane, water/n-pentane, water/n-hexane, water/heptane, and water/octane single-phase systems, in near-critical and supercritical conditions (temperatures of 573-698 K and pressures of 7.0-276.0 MPa). Here, PR EoS, LCVM and WS mixing

rules in conjunction with UNIQUAC activity coefficient model are used. The results indicate that PR/WS model from EoS/G^E is satisfactorily capable of correlating thermodynamic behavior of such nonideal and highly polar systems. However, considering the three adjusting parameters and more CPU time consuming calculations for the above, CPA EoS with only one adjustable parameter and simpler EoS structure over the other similar EoS like SAFT could adequately describe molecular interactions. As far as the accuracy of the models used is concerned, their AARD% indicate the order of superior compatibility with experimental data as being PR/WS/UNIQUAC followed by CPA and PR/LCVM/UNIQUAC with AARD% being 2.99, 5.14 and 11.11, respectively.

NOMENCLATURE

Abbreviations
AARD : average absolute relative deviation
APACT : associated perturbed anisotopic chain theory
CPA : cubic plus association equation of state
CR   : combining rules
ECR   : elliott combining rules
EoS   : equation of state
EoS/G : equation of state-excess gibbs free energy model
GA   : genetic algorithms
LCVM : linear combination Vidal-Michelsen
MHV2 : second-order modified Huron-Vidal mixing rules
NP   : number of data points
PR   : Peng-Robinson
PSRK : predictive Soave-Redlich-Kwong
SAFT : statistical associating fluid theory
SRK : Soave-Rendlich-Kwong equation of state
UNIQUAC : universal quasichemical model
VdW : van der Waals
VLE : vapor-liquid equilibria
WS   : Wong-Sandler

List of Symbols
a   : energy term in the SRK/PR equations of state [bar·dm^6/mol^2]
b   : co-volume parameter of cubic equations of state [dm^3/mol]
g   : radial distribution function
k_{ij} : binary interaction parameter (in equations of state)
M   : molecular weight [kg/kg·mol]
P   : pressure [bar]
q   : van der Waals area
R   : gas constant [J/mol·K]
r   : van derWaals volume
T   : temperatur [K]
X   : monomer fraction
x   : mole fraction
Z   : compressibility factor

Greek Letters
β : association volume
Δ : association strength
ε : association energy [bar·dm^3/mol]
η : reduced fluid density
θ : average area fraction

v   : molar volume [m^3/mol]
ρ : density [kg/m^3]
τ : binary interaction parameter (UNIQUAC model)
φ : average segment fraction
ω : acentric factor

Superscripts/Subscripts
A_i : site A in molecule i
ave   : average
B_j : site B in molecule j
c   : critical property
calc   : calculated value
E   : excess
exp   : experimental value
i, j   : component index
r   : reduced property

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