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M. Karamoddin, F. Varaminian



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M. Karamoddin, F. Varaminian

School of Chemical, Gas and Petroleum Engineering, Semnan University

Email: fvaraminian@semnan.ac.ir

Tel: ++982313354280

Fax: ++982313354120

## Abstract

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## 1. Introduction

There is a wide variety of refrigerants used in air conditioning equipment. In general the most common refrigerants used in the industry belong to the three categories of CFC, HCFC and HFC. The group of CFC is chloro fluoro carbon refrigerants such as R11 that were found as the most harmful to ozone layer. HCFC are hydro chloro fluoro carbon refrigerants, such as R22 that were identified as slightly harmful to the ozone layer, and HFC

are the hydro fluorocarbon refrigerants, such as R134a. The last group is the new refrigerants that do not harm the ozone layer, and are being used to replace the CFC and HCFC.

The chloro fluoro carbons have been widely used as refrigerants, solvents, propellants and foaming agents. These refrigerants have increased the greenhouse effect and a strong ozone depletion potential [1]. Development of alternatives to replace CFCs is necessary to protect the world's environment. Then hydro fluoro carbons group (HFCs) that contain no chlorine, are selected as good candidates [2].

In other way another application of refrigerants is using them for gas hydrate formation. Clathrate hydrates are ice-like crystalline solid compounds. This structure has hydrogen-bonded water molecules as host molecules, and some other species molecules as guest molecules. Water molecules create lattices are in a cage-like structure and guest components such as hydrocarbon and refrigerants are trapped in the cage at which engender to stabilization of the structure under suitable temperature and pressure condition (commonly high pressure and low temperature) [3]. Most components (gas or liquid) can be formed hydrate crystal at a temperature above the freezing point of water under low pressures. Refrigerant gas hydrates are formed at low pressure above 273.15K, and can be considered for the variety of applications such as promising materials for energy storage and desalination of water, and they are especially suitable for air conditioning and cool storage systems [4]. Because of the application of refrigerants as gas hydrate formation, it is necessary to know urgent to determine their solubility in water.

Around the industry related chemistry and chemical engineering, the solubility determination of components in water seems important. For case the solubility of hydrocarbon is a key concern in engineering that Nasrifar and Moshfeghian [5] calculated easily the solubility of water in hydrocarbons from cubic equations of state (EOS). The cubic equations of state play an important role in chemical engineering and they are applied in the study of the phase

equilibrium of fluid mixtures. Most phase equilibrium calculations are carried out using the classic equation of state such as SRK and PR EOSs. However the CPA equation of state is very successful in describing for systems containing reservoir fluids and polar compounds (such as water) [6]. The thermodynamic modeling for solubility of water and reservoir fluid is also performed using the CPA EoS by Kontogeorgis and Stenby [6].

Whereas of the increasing need for information on the properties of refrigerant gases, in this study authors calculate the solubility of some refrigerants like  $\text{CHClF}_2$  (R22),  $\text{CHF}_3$  (R23),  $\text{CH}_2\text{F}_2$  (R32),  $\text{C}_2\text{H}_2\text{F}_4$  (R134a),  $\text{C}_2\text{H}_4\text{F}_2$  (R152a),  $\text{C}_2\text{HF}_5$  (R125) and  $\text{CO}_2$  (R744) in the different temperatures and pressures. In this work, the (fugacity coefficient – fugacity coefficient) approach has been used to evaluate the applicability of the classic equation of state (VPT) by a modified mixing rule and the associated equation of state (CPA) by a simple mixing rule to predict the solubility data.

## 2. Thermodynamic Modeling

At phase equilibrium, the fugacities or chemical potentials of species in the various phases must be equal. For two-phase liquid water–vapor ( $VL_w$ ) equilibrium, the basic equations for the equilibrium condition are:

$$f_i^V = f_i^L \quad (1)$$

In this research, the equilibrium calculations in two-phase vapor and liquid are based on fugacity coefficients. In this method, the fugacity of a component is calculated using Valderrama–Patel–Teja (VPT) equation of state [7] with modified mixing rule and Cubic-Plus-Association (CPA) equation of state [8] using Van der Waals classical mixing rule. The CPA equation of state combines the simple cubic SRK equation of state [9] and an association term [8]. Then generalized cubic equation of state is generally:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + Uv + W} \quad (2)$$

$$\begin{aligned}
 a &= \Omega_a \frac{R^2 T_c^2}{P_c} \alpha(T_r) = a_0 \alpha(T_r) \\
 b &= \Omega_b \frac{RT_c}{P_c} \\
 c &= \Omega_c \frac{RT_c}{P_c}
 \end{aligned} \quad (3)$$

Table (1) shows the classical EOSs which is used in this work and their parameters.

(Table 1)

The coefficients  $a$ ,  $b$  of equations of state (VPT) are obtained for the mixtures using the modified mixing rule. In this mixing rule, the attraction parameter  $a$  has been separated into two parts, the Van der Waals classical mixing rule part  $a^c$  and the asymmetric contribution part  $a^A$ , as follows [10]:

$$\begin{aligned}
 a &= a^c + a^A \quad (4) \\
 a^c &= \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i x_j a_{ij} (1 - k_{ij}) \\
 b_{mix} &= \sum_{i=1}^{NC} x_i b
 \end{aligned} \quad (5)$$

Where  $k_{ij}$  is the binary interaction parameter and  $a_{ij} = (a_i a_j)^{0.5}$ .

$$a^A = \sum_{p=1}^{NPOLAR} x_p^2 \sum_{i=1}^{NC} x_i a_{pi} l_{pi} \quad (6)$$

Where  $p$  stands for polar component and  $l_{pi}$  is the binary interaction parameter between the polar component and the other components, which is a function of temperature, calculated by the following expression [10]:

$$l_{pi} = l_{pi}^0 - l_{pi}^1 (T - T_0) \quad (7)$$

## 2.1. CPA Equation of State

The Cubic-Plus-Association model is an equation of state. This model combines the simple cubic equation of state (SRK) and an association powerful (chemical) term [8,11]. The

chemical term is concluded from Wertheim theory [12-14]. In terms of the compressibility factor  $Z$  can be given as [8]:

$$Z^{CPA} = Z^{SRK} + Z^{assoc} \quad (8)$$

The compressibility factor contribution from the SRK equation of state has been described above via equations (2) and (3), and the energy parameter  $\alpha$ , can be calculated as a function of temperature presented in Table (1).

The association term in equation (8) is written by [8,11,14]:

$$Z^{assoc} = \sum_i X_i \sum_i \rho_i \sum_{A_j} \left[ \left( \frac{1}{X_{Ai}} - \frac{1}{2} \right) \right] \frac{\partial X_{Ai}}{\partial \rho_i} \quad (9)$$

In equation (9),  $\rho_i$  is the molar density of component  $i$ ,  $X_{Ai}$  is the mole fraction of the molecule  $i$  not bonded at site  $A$ , and  $x_i$  is the superficial mole fraction of component  $i$  [8]. The site fractions in equation (9),  $X_{Ai}$ , is related to the association strength between site  $A$  on molecule  $i$  and site  $B$  on molecule  $j$ ,  $\Delta^{A,B_j}$ , and the fractions  $X_B$  of all other kind of association sites  $B$  given by [6,8]:

$$X_{Ai} = \frac{1}{1 + \rho \sum_j n_j \sum_{B_j} X_{B_j} \Delta^{A,B_j}} \quad (10)$$

In equation (10)  $n_j$  is mole fraction of substance  $j$ . Also the association strength  $\Delta^{A,B_j}$ , between site  $A$  on molecule  $i$  and site  $B$  on molecule  $j$  is presented by equation (11). Values  $\epsilon^{A,B_j}$  and  $\beta^{A,B_j}$  indicate the association energy and volume of interaction between site  $A$  of molecule  $i$  and site  $B$  of molecule  $j$ , respectively, and  $g(\rho)^{ref}$  is the radial distribution function for the reference fluid [6,8]:

$$\Delta^{A,B_j} = g(\rho)^{ref} \left[ \exp\left(\frac{\epsilon^{A,B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A,B_j} \quad (11)$$

Huang and Radosz (1990) applied eight different association schemes that the site-4C association scheme is used for water molecule in CPA model according to Figure (1) [14].

(Figure 1)

Kontogeorgis et al.(1999) presented easily the hard-sphere radial distribution as equation

$$g(\rho) = \frac{1}{1-1.9\eta}, \quad (\eta = \frac{B\rho}{4}),$$

and a much simpler general expression for the association term was given by Yakoumis et al. (2001) [6,8].

The extension of the CPA model to mixtures requires mixing rules only for the parameters of the SRK equation of state. The mixing rules and combining rules for (a) and (b) parameters are as classical van der Waals equation (5).

The main objective of this work is to investigate the applicability of the EOS-approach for describing the solubility data of several refrigerants namely R22, R23, R32, R134a, R152a, R125 and R744 in water based on measured experimental data from other works.

CPA equation of state has five parameters, three for non-associating compounds ( $a_0$ ,  $b$ ,  $c_1$ ) that were obtained by critical temperature, pressure and acentric factor and using SRK equation of state; and two additional parameters for associating compounds ( $\epsilon$ ,  $\beta$ ) for polar water component [6,8,11]. Obtained parameters for non-associating compounds and associating values for water were given in Table (2). Also Table (3) presented the critical properties for pure components.

(Table 2)

(Table 3)

### 3. Results and Discussion

For calculation of pressure or determination of solubility in equilibrium conditions using the fugacity coefficient model, first we must determine interaction parameters in each equation of state and mixing rule. The experimental data used for the optimizing calculation to evaluate the interaction parameters is the two-phase equilibrium data ( $VL_w$ ) [2,15,16].

The binary interaction parameters in the modified mixing rule are three parameters including  $k_{12}$ ,  $l_{21}^0$ , and  $l_{21}^1$  and about the classical van der Waals rule is  $k_{12}$ . These parameters are



determined for each mixture by minimizing the following objective function by using Nelder mead method:

$$O.F = w_1 \sum_{i=1}^{NP} \frac{|y_i^{cal} - y_i^{exp}|}{y_i^{exp}} + w_2 \sum_{i=1}^{NP} \frac{|x_i^{cal} - x_i^{exp}|}{x_i^{exp}} \quad (12)$$

In equation (12),  $x$  and  $y$  are the mole fraction of liquid and vapor phases respectively. Also  $w_1$  and  $w_2$  are weight fraction in each term and in this work, ( $w_1=0$ ,  $w_2=1$ ).

However optimized interactions parameters in various EOSs and mixing rules are evaluated in the systems containing hydrocarbons, H<sub>2</sub>S and N<sub>2</sub> in previous works [17-18]. Unlike to hydrocarbons, the refrigerants are asymmetric molecules due to replacement hydrogen atoms by chlorine (Cl) and fluor (F). Obtained parameters in VPT equation of state for modified mixing rule, and  $k_{12}$  obtained in CPA equation of state for van der Waals mixing rule are presented in Tables (4) and (5) respectively for R22-H<sub>2</sub>O, R23-H<sub>2</sub>O, R32- H<sub>2</sub>O, R134a-H<sub>2</sub>O, R152a-H<sub>2</sub>O, R-125- H<sub>2</sub>O and R744- H<sub>2</sub>O systems.

(Table 4)

(Table 5)

By using obtained coefficients for mixing rule in Tables (4) and (5), the two-phase flash equilibrium calculation ( $VL_w$ ) is used, and the solubility of refrigerants in water with equations of state is calculated. Obtained results and comparison with experimental data are given in Table (6) – (12) for R22, R23, R32, R134a, R152a, R125 and R744 solubility in water respectively.

(Table 6)

(Table 7)

(Table 8)

(Table 9)

(Table 10)

(Table 11)

(Table 12)

Generally the solubility of gas refrigerants in water is low. According to the results of the two-phase flash calculation presented in Tables (6) to (12), it is apparently good agreement between obtained solubility and the experimental data. The summary of models error for determine of solubility has been given in Table (13). The VPT equation of state can be well predicted the experimental data using adjustable parameters  $k_{12}$ ,  $l_{21}^0$  and  $l_{21}^1$  in the modified mixing rule. Therefore the error of the VPT model is 1.90, 0.83, 2.12, 0.40, 0.90, 3.60 and 0.36 % for R22, R23, R32, R134a, R152a, R125 and R744 respectively. The errors of CPA equation of state with optimized parameter  $k_{12}$  for determination of solubility data are 6.30, 1.55, 4.17, 4.66, 0.78, 2.00 and 4.79% for R22, R23, R32, R134a, R152a, R125 and R744 respectively. Generally the average errors of VPT and CPA models are obtained about 1.5% and 3.5% respectively. In VPT model, the effects of asymmetric and polarity of water component are calculated through modified mixing rule and related optimized parameters, while in CPA model, associating parameters for water ( $\epsilon, \beta$ ) are effective.

According to Figure (1), the 4C association scheme is used for water in CPA EOS while no association scheme is introduced for refrigerant components despite of their high polarity. So CPA model error is generally more than VPT model. It is expected that if the type of scheme and the parameters ( $\epsilon, \beta$ ) is evaluated for refrigerants in the associated equation of state, CPA model can be more effective than VPT model. For determine of the polarity extent, dipole moment of components is extracted from papers and is compared together.

Table (13) gives the dipole moment of refrigerants in liquid. Apparent and effective dipole in the liquid is predicted by Kirkwood and Kirkwood – Frolich theory respectively. Some studies illustrate dimer structures and n-molecule clusters in liquid phase for HFC refrigerants [19,20]. Cabral and Castro (2001) have determined the dimer structures and dimerization

energies for the HFC compounds. The dimer structures are stabilized by double and triple F...H hydrogen bonds that these interactions have a main role for HFCs dipole moment in liquid state. Their results indicate that the orientation order in the liquid phase may involve not only correlations between the dipoles of monomeric units but also interactions between dimers stabilized by hydrogen bonds [19]. The apparent dipole is calculated from relative permittivity measurements. Cabral and Castro explain the relationship between the apparent dipole and the effective dipole moment in the liquid by statistical-mechanical theories [19,20]. Considering to the formation of dimer structures based on Kirkwood theory, apparent dipole moment for HFCs refrigerants are high therefore the interactions between refrigerants and water molecules increase and the CPA error is subsequently raised. (These interactions in VPT equation are considered in modified mixing rule). For example the error of CPA model is further for R32 and R134a systems that have high dipole moment (3.6 and 3.54 D). Also for CO<sub>2</sub> molecule, although its dipole moment is zero, but CO<sub>2</sub> and water both have polar bonds, and negative and positive poles of two molecules is strongly linked together. Hence the binary interactions in (CO<sub>2</sub>-H<sub>2</sub>O) mixture increase and the dipole moment of CO<sub>2</sub> in water is not zero. Anyway the reason of high error in CPA model (about 5%) can be know the above justification.

The deviation between the calculated and experimental solubility for R125 and R152a) by using CPA model is lower than what seen in VPT model. Reported Values in Table 13 for the apparent dipole moment of HFCs based on the Kirkwood theory are as: ***R125<R134a<R32***. Also effective dipole moments predicted by Kirkwood – Frolich theory show order: ***R125<R152a<R32<R134a***. Since R125 and R152a have the lower moment than other refrigerants, their interactions with water are decreased and CPA EOS can be powerful for determine of their solubility.

(Table 13)

#### 4. Conclusion

In this work, two-phase flash calculation ( $VL_w$ ) to the determination of the solubility for R22, R23, R32, R134a, R152a, R125 and R744 refrigerants in water are carried out. For purpose, VPT (by modified mixing rule) and CPA (by Van der Waals classical mixing rule) equation of state are applied to the liquid and vapor phases. The correlation results are satisfactory and indicate that the EOS approach is capable of describing the solubility values with good accuracy. Based on the dipole moment of refrigerants and the error of models, it seems that, the using of classic equation of state (VPT) with suitable modified mixing rule can be more effective than the using of associated equation of state (CPA) for the determination of the refrigerants solubility in water. In CPA EOS the 4C association scheme is used for water while no association scheme is introduced for refrigerant components despite of their high polarity. HFC refrigerants can create dimer structures in liquid phase that these structures are stabilized by double and triple F...H hydrogen bonds. Therefore apparent dipole moment for HFCs refrigerants are high and the interactions between refrigerants and water molecules increase and the CPA error is subsequently raised (such as R32 molecule). We must stress that the CPA model is powerful for R125 and R152a refrigerants because the comparison of dipole moments predicted by Kirkwood – Frolich theory shows that R125 and R152a have the lower moment than other refrigerants,  $R125 < R152a < R32 < R134a$ .

#### 5. References

- [1] Fialho, P.S., Nieto de Castro, C.A., 1996. Prediction of Halocarbon Liquid Densities by a Modified Hard Sphere–De Santis Equation of state. *Fluid Phase Equilibria*, 118, 103–114.
- [2] Miguel, A.F., Ferreira, G.M., Fonseca, M.A., 2000. Solubilities of Some New Refrigerants in Water. *Fluid Phase Equilibria*, 173, 97–107.
- [3] Sloan, E.D., 1998. *Clathrate Hydrates of Natural Gases*. Marcel and Dekker, New York.

- [4] Li, J., Guo K., Fan Sh., Wang R., 2006. Formation and Dissociation of HFC134a Gas Hydrate in Nano\_Copper Suspension. *Energy Conversion and Management*, 47, 201- 210.
- [5] Nasrifar, Kh., Moshfeghian, M., 2002. Liquid–Liquid Equilibria of Water–Hydrocarbon Systems from Cubic Equations of State. *Fluid Phase Equilibria*, 193, 261–275.
- [6] Kontogeorgis, G., Stenby, E., 2011. Mutual Solubility of MEG, Water and Reservoir Fluid: Experimental Measurements and Modeling Using the CPA Equation of State. *Fluid Phase Equilibria*, 300, 172-181.
- [7] Valderrama, J.O., 1990. Generalized Patel-Teja Equation of Four Polar and Nonpolar Fluids and Their Mixtures. *J. Chem. Eng. Jpn*, 23(87).
- [8] Hartono, A., Kim, I., 2004. Calculation of Vapor-Liquid Equilibria for Methanol-Water Mixture using Cubic-Plus-Association Equation of State. Project work in the subject KP8108, Advanced Thermodynamics.
- [9] Soave, G., 1972. Equilibria Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci*, 27, 1197-1203.
- [10] Avlonnitis, d., Danesh, A., Todd, A.C., 1994. Prediction of VL & VLL Equilibria of Mixtures Containing Petroleum Reservoir Fluids & Methanol with a Cubic EOS. *Fluid phase Equilibria*, vol. 94, 181-216.
- [11] Folas, G., 2006. Modeling of Complex Mixtures Containing Hydrogen Bonding Molecules. Technical University of Denmark, Ph.D. Thesis.
- [12] Wertheim, M.S., 1986. Fluids with Highly Directional Attractive Forces III. Multiple attraction sites, *J. Statist. Phys*, 42- 459.
- [13] Wertheim, M.S., 1986. Fluids with Highly Directional Attractive Forces IV. Equilibrium polymerization, *J. Statist. Phys*, 42- 477.
- [14] Nikbakht, F., Izadpanh, A., Varaminian, F., Mohammadi, A., 2012. Thermodynamic Modeling of Hydrate Dissociation Conditions for Refrigerants R134a, R141b and R152a. *International Journal of Refrigeration*, Article in Press.
- [15] Guo T., Zheng D., Knapp H., 1997. Experimental and Modeling Studies on the Solubility of CO<sub>2</sub>, CHClF<sub>2</sub>, CHF<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>F<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>F<sub>2</sub> in Water and Aqueous NaCl Solutions under Low Pressures. *Fluid Phase Equilibria*, 129, 197-209.
- [16] Duan, Zh., Zhu, Ch., 2006. An Improved Model for the Calculation of CO<sub>2</sub> Solubility in Aqueous Solutions. *Marine Chemistry* 98, 131–139.
- [17] Karamoddin, M., Varaminian, F., 2011. Prediction of Gas Hydrate Forming Conditions by Using PR Equation of State and Different Mixing Rules. *Iranian Journal of Chemical Engineering*, 8, 46-55.
- [18] Karamoddin, M., Varaminian, F., 2011. Prediction of Equilibrium Pressure for CH<sub>4</sub> and N<sub>2</sub> Gas Hydrate by Different Equation of State. the 7<sup>th</sup> International Chemical Engineering Congress, Kish Island.
- [19] Cabral, B.J.C., Guedes, R.C., Panandike, R.S., Nieto de Castro, C.A., 2001. Hydrogen bonding and the dipole moment of hydrofluorocarbons by density functional theory. *Phys. Chem. Chem. Phys*, 3, 4200-4207.
- [20] Ribeiro, A.P.C., Nieto de Castro, C.A., 2011. Dielectric properties of liquid refrigerants. *International Journal of Refrigeration*, 34, 391-401.

- [21] Kriebel, C., Mecke, M., Winkelmann, J., Vrabec, J., Fischer, J., 1998. An equation of state for dipolar two-center Lennard-Jones molecules and its application to refrigerants. *Fluid Phase Equilibria*, 142, 15-32.

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- VPT and CPA equations of state were used.
- The binary interaction parameters were optimized by two phase equilibrium data.
- The accuracy of VPT EOS- modified mixing rule model was obtained about 1.5%.
- The accuracy of CPA EOS-Van der Waals mixing rule model was obtained about 3.5%.
- The effect of dipole moment of components in error of CPA model was investigated.

## (Tables)

Table 1: Equations of state and their parameters

EOS	U	W	$\Omega_b$	$\Omega_c$	$\Omega_a$	$\alpha(T_r)$	$C_1$	Ref
SRK	b	0	0.08664	-	0.42748	$1+c_1(1-\sqrt{T_r})^2$	$0.48+1.547\omega-0.176\omega^2$	[9]
VPT	b+c	-bc	0.02207 +0.2086 $z_c$	0.57765 -1.8708 $z_c$	0.66121 -0.76105 $z_c$	$1+c_1(1-\sqrt{T_r})^2$	$0.46283+3.5823(\alpha z_c)+8.1941(\alpha z_c)^2$	[7]

Table 2: CPA parameters for the nominated components for this work

Component	$a_0$ ( $J*m^3/mol^2$ )	$b*10^5$ ( $m^3/mol$ )	$c_1$	$\varepsilon$ ( $J/mol$ )	$\beta$	Ref
R22	0.81619	5.38	0.816	--	--	--
R23	0.54452	4.44	0.818	--	--	--
R32	0.62992	4.37	0.831	--	--	--
R134a	1.01905	6.64	0.973	--	--	--
R152a	0.99502	6.27	0.868	--	--	--
R125	0.93833	6.74	0.833	--	--	--
R744	0.37040	2.96	0.890	--	--	--
water	0.12277	1.45	0.673	16655	0.0692	[8]

Table 3: Critical properties for pure component

Refrigerant	$T_C$ (K)	$P_C$ (bar)	Acentric factor
R22	369.3	49.36	0.22082
R23	298.6	48.37	0.22183
R32	351.2	57.84	0.23023
R134a	374.2	40.59	0.32680
R152a	386.9	44.44	0.25560
R125	339.1	36.20	0.23141
R744	304.2	73.80	0.22500
water	647.3	220.50	0.34400



Table (4): Optimized parameters of the modified mixing rule in VPT equation of state for several refrigerants in water

<i>Component</i>	$k_{21}$	$l_{21}^0$	$l_{21}^1$
R22	0.54869	1.61698	0.002566
R23	0.10461	0.94594	0.002862
R32	0.26100	0.97980	0.00289
R134a	0.53131	1.75024	0.002321
R152a	0.51262	1.67671	0.002208
R125	0.09190	1.24380	0.003410
R744	0.35324	1.08269	0.002673

Table (5): Optimized parameter of the classical van der Waals mixing rule in CPA equation of state for several refrigerants in water

<i>Component</i>	<i>R22</i>	<i>R23</i>	<i>R32</i>	<i>R134a</i>	<i>R152a</i>	<i>R125</i>	<i>R744</i>
$k_{21}$	-0.130	-0.173	-0.094	-0.072	-0.192	-0.346	-0.075

Table (6): R22 solubility in water

<i>T (K)</i>	<i>P (bar)</i>	<i>X (exp)[15]</i>	<i>VPT</i>		<i>CPA</i>	
			<i>X(cal)</i>	<i>Error %</i>	<i>X(cal)</i>	<i>Error %</i>
278.24	0.4574	0.000589	0.000575	2.3	0.000528	10.3
278.24	0.4630	0.000595	0.000581	2.3	0.000533	10.4
308.06	0.6913	0.000284	0.000276	2.8	0.000279	1.7
308.06	0.7159	0.000290	0.000286	1.3	0.000290	0.0
338.11	0.8694	0.000141	0.000141	0.0	0.000149	5.6
338.11	0.8852	0.000148	0.000144	2.7	0.000163	10.1
				<i>Error = 1.9%</i>	<i>Error = 6.3%</i>	

Table (7): R23 solubility in water

$T(K)$	$P(bar)$	$X$ ( <i>exp</i> )[15]	VPT		CPA	
			$X(cal)$	Error %	$X(cal)$	Error %
278.20	0.6875	0.000287	0.000286	0.3	0.000286	0.3
278.20	0.6916	0.000290	0.000288	0.6	0.000288	0.6
308.15	0.8133	0.000134	0.000136	1.4	0.000140	4.4
308.15	0.8248	0.000136	0.000138	1.4	0.000135	0.7
338.21	0.9005	0.000705	0.000697	1.1	-	-
338.21	0.9147	0.000712	0.000714	0.2	-	-
				$\overline{Error} = 0.8\%$	$\overline{Error} = 1.5\%$	

Table (8): R32 solubility in water

$T(K)$	$P(bar)$	$X$ ( <i>exp</i> )[2]	VPT		CPA	
			$X(cal)$	Error %	$X(cal)$	Error %
289.16	1.013	0.000758	0.000765	0.9	0.000713	5.9
290.50	1.013	0.000730	0.000730	0.0	0.000689	5.6
291.29	1.013	0.000710	0.000709	0.2	0.000675	4.9
292.35	1.013	0.000689	0.000682	1.0	0.000657	4.6
293.14	1.013	0.000674	0.000666	1.5	0.000644	4.4
294.20	1.013	0.000640	0.000639	0.1	0.000627	2.0
294.99	1.013	0.000623	0.000622	0.1	0.000615	1.2
296.04	1.013	0.000599	0.000599	0.0	0.000599	0.0
297.08	1.013	0.000568	0.000579	1.9	0.000584	2.8
298.12	1.013	0.000545	0.000559	2.5	0.000570	4.5
298.90	1.013	0.000535	0.000544	1.6	0.000559	4.4
299.94	1.013	0.000504	0.000526	4.1	0.000525	4.1
301.23	1.013	0.000474	0.000504	6.3	0.000509	7.3
302.26	1.013	0.000446	0.000487	9.1	0.000416	6.7
				$\overline{Error} = 2.1\%$	$\overline{Error} = 4.2\%$	

Table (9): R134a solubility in water

$T$ (K)	$P$ (bar)	$X$ ( <i>exp</i> )[15]	VPT		CPA	
			$X$ ( <i>cal</i> )	<i>Error</i> %	$X$ ( <i>cal</i> )	<i>Error</i> %
275.16	0.6377	0.0004080	0.0003990	2.2	0.000407	0.2
278.16	0.6093	0.0003830	0.0003820	0.2	0.000347	9.3
308.08	0.7976	0.0001610	0.0001610	0.0	0.000173	7.4
308.08	0.8302	0.0001680	0.0001680	0.0	0.000171	1.7
338.12	0.9025	0.0007820	0.0007820	0.0	-	-
338.12	0.9306	0.0008010	0.0008010	0.0	-	-
				$\overline{\text{Error}} = 0.4\%$	$\overline{\text{Error}} = 4.7\%$	

Table (10): R152a solubility in water

$T$ (K)	$P$ (bar)	$X$ ( <i>exp</i> )[15]	VPT		CPA	
			$X$ ( <i>cal</i> )	<i>Error</i> %	$X$ ( <i>cal</i> )	<i>Error</i> %
278.19	0.3667	0.000660	0.000660	0.0	0.000660	0.0
278.19	0.3724	0.000674	0.000670	0.5	0.000671	0.4
308.13	0.6161	0.000371	0.000378	1.8	0.000373	0.5
308.13	0.6236	0.000375	0.000383	2.1	0.000380	1.3
338.19	0.7926	0.000196	0.000194	1.0	0.000192	2.0
338.19	0.7992	0.000197	0.000197	0.0	0.000198	0.5
				$\overline{\text{Error}} = 0.9\%$	$\overline{\text{Error}} = 0.8\%$	

Table (11): R125 solubility in water

$T(K)$	$P(bar)$	$X$ ( <i>exp</i> )[2]	VPT		CPA	
			$X(cal)$	<i>Error %</i>	$X(cal)$	<i>Error %</i>
289.16	1.013	0.000769	0.000853	10.9	0.000784	1.9
290.13	1.013	0.000763	0.000814	6.6	0.000758	0.6
291.03	1.013	0.000753	0.000779	3.4	0.000734	2.5
292.09	1.013	0.000715	0.000739	3.3	0.000707	1.1
293.14	1.013	0.000694	0.000703	1.2	0.000682	1.7
294.20	1.013	0.000668	0.000668	0.0	0.000658	1.4
294.99	1.013	0.000643	0.000644	0.1	0.000641	0.3
296.15	1.013	0.000630	0.000609	3.3	0.000616	2.2
297.34	1.013	0.000583	0.000577	1.0	0.000592	1.5
299.16	1.013	0.000557	0.000531	4.6	0.000558	0.1
299.94	1.013	0.000534	0.000513	3.9	0.000544	1.8
301.23	1.013	0.000504	0.000484	3.9	0.000522	3.5
302.01	1.013	0.000485	0.000468	3.5	0.000509	4.9
303.03	1.013	0.000470	0.000448	4.6	0.000492	4.6
			$\overline{Error} = 3.6\%$		$\overline{Error} = 2.0\%$	

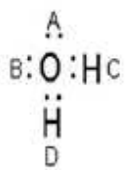
Table (12): R744 solubility in water

$T(K)$	$P(bar)$	$X$ ( <i>exp</i> )[15]	VPT		CPA	
			$X(cal)$	<i>Error %</i>	$X(cal)$	<i>Error %</i>
278.15	0.4906	0.000551	0.000548	0.5	0.000514	6.7
278.15	0.5088	0.000569	0.000568	0.1	0.000561	1.4
303.12	0.6419	0.000327	0.000327	0.0	0.000319	2.4
303.12	0.6583	0.000334	0.000335	0.2	0.000328	1.7
308.08	0.6834	0.000305	0.000304	0.3	0.000304	0.3
308.08	0.7017	0.000311	0.000312	0.3	0.000313	0.6
333.15	0.7844	0.000177	0.000177	0.0	0.000192	8.4
333.15	0.7937	0.000181	0.000179	1.1	0.000195	7.7
338.15	0.8330	0.000163	0.000163	0.0	0.000180	10.4
338.15	0.8417	0.000168	0.000166	1.1	0.000182	8.3
			$\overline{Error} = 0.3\%$		$\overline{Error} = 4.8\%$	

Table (13): The summary of models error and dipole moment of components

<i>Group</i>	<i>Refrigerant</i>	<i>Formula</i>	<i>Dipole</i>	<i>Dipole</i>	<i>VPT</i>	<i>CPA</i>
			<i>moment</i>	<i>moment</i>	<i>Error %</i>	<i>Error %</i>
			<i>K (D)</i>	<i>KF (D)</i>		
HCFC	R22	CHF <sub>2</sub> Cl	NA*	1.35 [21]	1.9	6.3
HFC	R23	CHF <sub>3</sub>	NA	NA	0.8	1.5
HFC	R32	CH <sub>2</sub> F <sub>2</sub>	3.60 [19]	2.61 [19]	2.1	4.2
HFC	R134a	CH <sub>2</sub> FCF <sub>3</sub>	3.54 [19]	2.67 [19]	0.4	4.7
HFC	R152a	CHF <sub>2</sub> CH <sub>3</sub>	-	2.55 [19]	0.9	0.8
HFC	R125	CHF <sub>2</sub> CF <sub>3</sub>	2.48 [19]	1.84 [19]	3.6	2.0
-	R744	CO <sub>2</sub>	0.00	0.00	0.3	4.8

\*: Not Available



$$X_A = X_B = X_C = X_D$$

Figure 1: Association schemes for water [14]

- VPT and CPA equations of state were used.
- The interaction parameters for mixing rules in each mixture were optimized by using two-phase equilibrium data ( $VL_w$ ).
- The predicted solubility of the selected refrigerants in water agreed with the experimentally data with accuracy about 1.5% and 3.5% by VPT equation of state - modified mixing rule and CPA equation of state – Van der Waals classic mixing rule respectively.
- Relation between the dipole moment of components and CPA error were investigated.

- VPT and CPA equations of state were used.
- The binary interaction parameters were optimized by two phase equilibrium data.
- The accuracy of VPT EOS- modified mixing rule model was obtained about 1.5%.
- The accuracy of CPA EOS-Van der Waals mixing rule model was obtained about 3.5%.
- The effect of dipole moment of components in error of CPA model was investigated.