

# High Pressure Phase Equilibrium of (Solvent + Salt + CO<sub>2</sub>) Systems by the Extended Peng-Robinson Equation of State

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**ABSTRACT:** An extended Peng-Robinson equation of state (EPR-EOS) is used to model the vapor-liquid equilibrium (VLE) in systems containing (water + NaCl + CO<sub>2</sub>), (water + methanol + NaCl + CO<sub>2</sub>), (water + Na<sub>2</sub>SO<sub>4</sub> + CO<sub>2</sub>) and (water + NH<sub>4</sub>Cl + CO<sub>2</sub>). The binary and ternary interaction parameters between salt and solvent are adjusted to experimental mean solvent activity of salts (NaCl and Na<sub>2</sub>SO<sub>4</sub>). For the system containing (water + Na<sub>2</sub>SO<sub>4</sub> + CO<sub>2</sub>), the EPR-EOS is used to predict the P-T diagram when the moles of Na<sub>2</sub>SO<sub>4</sub> in 1 kg water are 0.25, 0.5 and 1. The calculated results for the (water + Na<sub>2</sub>SO<sub>4</sub> + CO<sub>2</sub>) system by the extended PR-EOS are compared with the correlation results by Anderko-Pitzer EOS. The average absolute deviation of ( $\Delta P/P_{exp}$ ) % between the correlation results by Anderko-Pitzer EOS and experimental data is 8.4 % while this value for extended PR-EOS is 6 %. The P-x diagram for (water + NH<sub>4</sub>Cl + supercritical-CO<sub>2</sub>) system at temperatures (333 and 353 K) are also obtained and compared with the calculation results by VTPRLIFAC model. The average absolute deviation between calculation results by VTPRLIFAC model and experimental data is 7.8 % but this value for our calculations is 6.2 %.

**KEY WORDS:** Vapor-liquid equilibrium (VLE), Peng-Robinson equation of state (PR-EOS), CO<sub>2</sub>, Salt.

## INTRODUCTION

The modeling of salt containing systems and more specifically mixed solvent-electrolyte systems containing inorganic salts is important because these type of mixtures are found in many processes such as systems including regeneration of solvents, liquid-liquid extraction for mixtures containing salts, and supercritical water oxidation that comprises the oxidation of organic salts in an aqueous medium.

One of the most important systems used in industries is systems containing supercritical carbon dioxide, solvent and solutes.

Several data series of the systems with CO<sub>2</sub>-water and CO<sub>2</sub>-water-inorganic salts are found in literature. To mention only a few, *Nighs Wander et al.* [1] measured the CO<sub>2</sub> solubility in pure water and in a 1wt % aqueous NaCl solution at pressure up to 10 MPa and temperature ranges from 353 K up to 473 K.

*Bamberger et al.* measured and reported data of the system CO<sub>2</sub>-water from 313 K up to 353 K and pressure up to 14 MPa. Many other researchers measured the solubility of CO<sub>2</sub> in water [2-5]. *Prupton and Savage* published the data of solubility of CO<sub>2</sub> in water and effect

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of salt  $\text{CaCl}_2$  on the concentration of phases at 348, 373 and 393 K and pressure up to 70 MPa [6].

An experimental determination of phase equilibria over the whole temperature, pressure and concentration range for these systems can normally not be performed because of costs and time. Therefore it is necessary to use thermodynamic models for correlation and prediction of phase concentration in such kind of systems.

One of the most conventional methods to calculate the high pressure phase equilibrium of systems with supercritical components is to use an equation of state. *Donohue and coworkers* [7,8] developed the extended perturbed-anisotropic-chain-theory [9] that consisted of 10 contributions to the Helmholtz free energy. Seven contributions of their proposed EOS were needed to describe the nonionic interactions and the remaining terms were needed to consider the ionic interactions.

*Raatschen et al.* [10] developed an equation of state to describe the phase equilibrium of the water + methanol + lithium bromide system. They applied the hard-sphere equation of *Boublik and Mansoori et al.* in combination with a Lennard-Jones potential to describe nonionic systems. For ionic systems the equation was extended using by the Born equation, a Debye-Hückel term, and a modified Pitzer equation. *Liu et al.* [11] combined an electrolyte perturbation theory with the mean spherical approximation theory and the statistical associating fluid theory to derive an equation of state for aqueous electrolyte systems. *Zuo and Guo* [12] applied the three-parameter cubic equation of state by *Patel and Teja* combining with an excess Gibbs energy term to find a new mixing rule for some model parameters. They used a Debye-Hückel term for electrostatic interactions.

*Fürst and Renon* [13] combined the cubic equation of *Schwartzentruber et al.* and the mean-spherical approximation (MSA) model to consider the interactions between charge species. They applied this equation to consider interactions between charged species.

*Thomsen and Iliuta* [14] used extended UNIQUAC model for correlation of vapor-liquid-solid equilibria in aqueous salt systems containing alcohols-water-salt systems. They calculated the fugacities of gas-phase component for vapor-liquid equilibrium calculations with the Soave-Redlich-Kwong equation of state. *Sun and Bullock* [15] used a modification of the salvation model of *Ohe* to calculate vapor-liquid equilibria (VLE) in

alcohol-water-salt system, covering a temperature range from 298 to 375 K and salt concentration up to about 8 molality. *Bermejo and coworkers* [16] modeled the system of  $\text{CO}_2\text{-H}_2\text{O-Na}_2\text{SO}_4$  by using the Anderko-Pitzer EOS at high temperatures and pressures.

*Evans and Powell* [17] constructed a method for activity calculation in saline, mixed solvent, supercritical aqueous solutions at conditions of pressure between 0.2 and 1.4 GPa and temperatures between 500 and 200 °C and  $x_{\text{H}_2\text{O}}$  from 0.1 to 1. They calculated the activity coefficients with expressions that take the configuration of the ions solution into account. They applied a limited Debye-Hückel term to mixed solvents and concentrated solutions combining with a multi-component Van Laar formulation to calculate activity coefficients.

In this paper the extended PR-EOS of *Maurer et al.* [18] is developed to calculate the phase equilibrium in aqueous salt containing systems with supercritical component. Systems studied here contain (water + methanol +  $\text{NaCl}$  + SC- $\text{CO}_2$ ), (water +  $\text{Na}_2\text{SO}_4$  + SC- $\text{CO}_2$ ), (water +  $\text{NaCl}$  + SC- $\text{CO}_2$ ) and (water +  $\text{NH}_4\text{Cl}$  + SC- $\text{CO}_2$ ).

## MODELING

For a mixture of several components, the extended PR-EOS is defined in terms of Helmholtz free energy,  $A$ . For aqueous salt containing mixtures, the Helmholtz free energy at temperature  $T$  and volume  $V$  consists of four terms [18]:

$$A = A^0 + \Delta A^{\text{IG}} + \delta A_{\text{nonionic}} + \delta A_{\text{ionic}} \quad (1)$$

where  $A^0$  is the Helmholtz energy of pure component in the ideal gas state at  $(T, P^0)$ ,  $\Delta A^{\text{IG}}$  is the change of the Helmholtz energy due to mixing the ideal gases and changing of the Helmholtz energy to end up at volume  $V$ ,  $\delta A_{\text{nonionic}}$  is the incremental Helmholtz energy due to nonionic intermolecular forces and  $\delta A_{\text{ionic}}$  is the incremental Helmholtz energy due to ionic intermolecular forces.

The nonionic contribution of Helmholtz energy,  $\delta A_{\text{nonionic}}$ , is given by:

$$\delta A_{\text{nonionic}} = \Delta A^{\text{rep}} + \Delta A^{\text{att}} \quad (2)$$

where  $\Delta A^{\text{rep}}$  and  $\Delta A^{\text{att}}$  are repulsive and attractive contributions of Helmholtz energy, respectively.

In this work the repulsive and attractive terms are calculated according to Melhem modification of PR-EOS [19]:

$$\Delta A^{\text{rep}}(T, V, \vec{n}) = RT \sum_{i=1}^{N_c} n_i \ln \frac{V}{V - b n_T} \quad (3)$$

$$\Delta A^{\text{att}}(T, V, \vec{n}) = \frac{a(T)n_T}{2\sqrt{2}b} \ln \frac{V + b n_T (1 - \sqrt{2})}{V + b n_T (1 + \sqrt{2})} \quad (4)$$

where  $n_i$  and  $n_T$  are the mole number of component  $i$  and the total number of moles in the mixture, respectively.  $b$  is a covolume parameter and  $a$  is an energy parameter.

The ionic contribution of Helmholtz energy is separated into two terms including the modified Dedye-Hückel term,  $\Delta A^{\text{DH}}$ , and the short range electrostatic interaction between ions and solvent,  $\Delta A^{\text{ia}}$ , as follows:

$$\delta A_{\text{ionic}} = \Delta A^{\text{DH}} + \Delta A^{\text{ia}} \quad (5)$$

The modified Debye-Hückel term,  $\Delta A^{\text{DH}}$ , is calculated based on the  $G^E$ -model of Pitzer [20]:

$$\Delta A^{\text{DH}}(T, \vec{n}) = -n_T RT \frac{4A_x I_x}{X} \ln(1 + X\sqrt{I_x}) \quad (6)$$

$I_x$  is the ionic strength on mole fraction scale:

$$I_x = \frac{1}{2} \sum_{i=1}^{N_c} x_i z_i^2 \quad (7)$$

where  $z_i$  is the charge on ion  $i$  and  $x_i$  is its mole fraction. The summation extends over all ionic species in the solution.  $X$  is calculated by following equation [20]:

$$X = \frac{2}{\sqrt{M^*}} \quad (8)$$

$M^*$  is an average molecular mass:

$$M^* = \frac{1}{1000} \sum_{i=1}^{N_c} x_i^* M_i \quad (9)$$

$M_i$  is molecular weight of solvent component  $i$  and  $x_i^*$  is the mole fraction of solvent component  $i$  in the salt-free solvent mixture.

$A_x$  is given by [20]:

$$A_x = \frac{1}{3} \left( \frac{2\pi N_A}{v_{\text{mix}}^*} \right)^{1/2} \left( \frac{e^2}{4\pi\epsilon_0\epsilon_{\text{mix}}kT} \right)^{3/2} \quad (10)$$

$N_A$  is Avogadro's number,  $v_{\text{mix}}^*$  is the molar volume of the salt-free solvent mixture,  $e$  is the charge of an

electron,  $\epsilon^0$  is the permittivity of vacuum,  $\epsilon_{\text{mix}}$  is the relative dielectric constant of the salt-free solvent mixture and  $k$  is the Boltzmann's constant.

$v_{\text{mix}}^*$  and  $\epsilon_{\text{mix}}$  are approximated by the following expressions:

$$v_{\text{mix}}^* = \sum_{i=1}^{N_c} x_i^* b_i \quad (11)$$

$$\epsilon_{\text{mix}} = \frac{1}{v_{\text{mix}}^*} \sum_{i=1}^{N_c} x_i^* b_i \epsilon_i \quad (12)$$

where  $b_i$  and  $\epsilon_i$  are the covolume and relative dielectric constant of the pure solvent  $i$ , respectively.

Short range electrostatic interactions between ions and solvents are calculated according to Margules term with binary,  $B_{ij}$ , and ternary,  $C_{ijk}$ , interaction parameters.

$$\Delta A^{\text{ia}}(T, \vec{n}) = \frac{RT}{n_T} \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} n_i n_j B_{ij} + \quad (13)$$

$$\frac{RT}{n_T^2} \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} \sum_{k=1}^{N_c} n_i n_j n_k C_{ijk}$$

To reduce the number of interaction parameters, it is assumed that all binary ( $B_{ij}$ ) and ternary ( $C_{ijk}$ ) interaction parameters are symmetric and all interaction parameters between the same species are negligible ( $B_{ii}=C_{iii}=0$ ). Then, only parameters for interaction between ionic and neutral species are important. With these assumptions, there are only one binary ( $B_{\text{sol,salt}}$ ) and two ternary ( $C_{\text{sol,sol,salt}}$  and  $C_{\text{sol,salt,salt}}$ ) interaction parameters.

In this work the Helmholtz free energy expressed in equation (1) is used to calculate pressure,  $P$ , chemical potential of component  $i$ ,  $\mu_i$ , and the fugacity coefficient of component  $i$ ,  $\phi_i$  by following general thermodynamic equations [21]:

$$P(T, V, \vec{n}) = - \left( \frac{\partial A(T, V, \vec{n})}{\partial V} \right)_{T, \vec{n}} \quad (14)$$

$$\mu_i(T, P, \vec{x}) = \left( \frac{\partial A(T, V, \vec{n})}{\partial n_i} \right)_{T, V, n_i \neq n_j} \quad (15)$$

$$RT \ln \phi_i = \left( \frac{\partial A_{\text{nonionic}}}{\partial n_i} \right)_{T, V, n_i \neq j} + \quad (16)$$

$$\left( \frac{\partial \delta A_{\text{ionic}}}{\partial n_i} \right)_{T, V, n_i \neq j} - RT \ln Z$$

Table 1: The relative dielectric constant of pure components [18].

Component	Equation
CO <sub>2</sub>	$\epsilon_{\text{CO}_2} = 1.6$
H <sub>2</sub> O	$\epsilon_{\text{H}_2\text{O}} = -19.29 + 29814.5 / T - 0.019678 T + 0.013189 \times 10^{-2} \times (T^2) - 0.031144 \times 10^{-5} (T^3)$
MeOH	$\epsilon_{\text{MeOH}} = 134.183 + 9993.4 / T - 23.6914 \ln(T)$

Table 2: Ionic interaction parameters for the extended Peng-Robinson EOS for salt-containing systems.

Component		T (K)	P (atm)	m <sub>salt</sub> (mol/kg)	B <sub>1,2</sub>	C <sub>1,1,2</sub>	C <sub>1,2,2</sub>
H <sub>2</sub> O	NaCl	300-390	5 - 110	0-4	-3.46	0	-0.9776
H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub>	290-370	10 - 110	0-1	-3.7042	-4.0840	-0.8987
H <sub>2</sub> O	NH <sub>4</sub> Cl	300-360	10-100	3-4	-0.3149	-0.31	-0.07
CO <sub>2</sub>	NaCl	300-390	5 - 110	0-4	1.4359	0	0
CO <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	290-370	10 - 110	0-1	1.3518	0	0
CO <sub>2</sub>	NH <sub>4</sub> Cl	300-360	10-100	3-4	0.15	0	0
MeOH	NaCl	300-390	5 - 110	0-4	0.41018	0	0

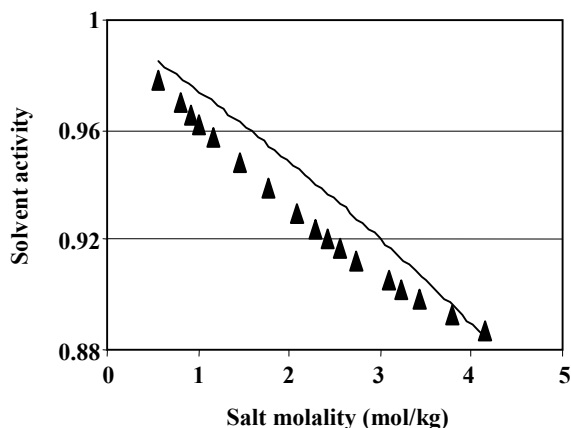
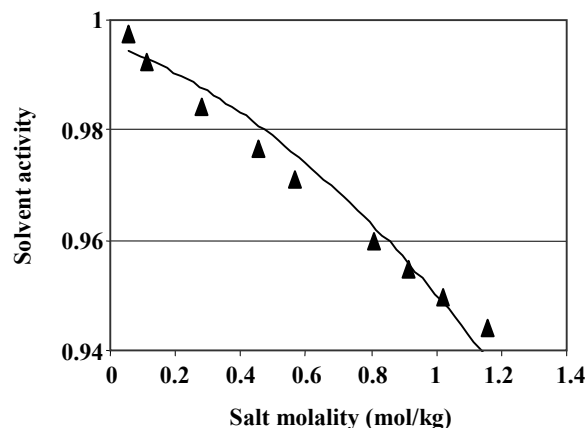


Fig. 1: Solvent activity of system (water + NaCl) at P=1 atm and T=298 K. Experimental data: (▲) [24]. Calculation results (-).

Fig. 2: Solvent activity of system (water + Na<sub>2</sub>SO<sub>4</sub>) at P=1 atm and T=298 K. Experimental data: (▲) [24]. Calculation results (-).

Substituting Eqs. (2) and (5) in Eq. (16), the following equation for the fugacity coefficient is derived.

$$\ln \varphi_i = \left( \frac{\partial \delta A}{\partial n_i} \right)_{T, V, n_{i \neq j}} / RT - \ln Z \quad (17)$$

$$\left( \frac{\partial \delta A}{\partial n_i} \right)_{T, V, n_{i \neq j}} = \left( \frac{\partial (\Delta A^{\text{IG}} + \Delta A^{\text{rep}} + \Delta A^{\text{att}})}{\partial n_i} \right)_{T, V, n_{i \neq j}} +$$

$$\left( \frac{\partial \Delta A^{\text{DH}}}{\partial n_i} \right)_{T, V, n_{i \neq j}} + \left( \frac{\partial \Delta A^{\text{iaa}}}{\partial n_i} \right)_{T, V, n_{i \neq j}}$$

$$\left( \frac{\partial (\Delta A^{\text{IG}} + \Delta A^{\text{rep}} + \Delta A^{\text{att}})}{\partial n_i} \right)_{T, V, n_{i \neq j}} =$$

$$\frac{RT}{b_{\text{mix}}} \left[ \frac{\partial (nb_{\text{mix}})}{\partial n_i} \right]_{T, n_i} (Z-1) - RT \ln \left[ \frac{(V - b_{\text{mix}})Z}{V} \right] +$$

$$\frac{a_{\text{mix}}}{b_{\text{mix}}} RT \left( \frac{1}{a_{\text{mix}}} \left[ \frac{1}{n} \left[ \frac{\partial (n^2 a_{\text{mix}})}{\partial n_i} \right]_{T, n_j} \right] \right) -$$

$$\frac{1}{b_{\text{mix}}} \left[ \frac{1}{n} \left[ \frac{\partial (nb_{\text{mix}})}{\partial n_i} \right]_{T, n_j} \right] RT \ln \left( \frac{V + ub_{\text{mix}}}{V + wb_{\text{mix}}} \right) + RT \ln Z$$

where:  $w = (1 + \sqrt{2})$ ,  $u = (1 - \sqrt{2})$

$$\begin{aligned}
\left(\frac{\partial \Delta A^{DH}}{\partial n_i}\right)_{T,V,n_{j \neq i}} = & \left[ \left( RT \sqrt{8} \left( \frac{e^2 \sum x_i b_i}{\pi \epsilon_0 k T \sum x_i b_i \epsilon_i} \right)^{(3/2)} * x_i * \left( \frac{1}{1000} \sum x_i M_i \right)^{0.5} * \ln \left[ 1 + \frac{3.464 x_i^{0.5}}{\left( \frac{1}{1000} \sum x_i M_i \right)^{0.5}} * \pi * N_a * (b_i - \sum x_i b_i) \right] \right) \right. \\
& \left. / \left[ 16 \sqrt{\frac{\pi N_a}{\sum x_i b_i}} * (\sum x_i b_i)^2 \right] - \left( \frac{3}{16} \right) RT \sqrt{2} \left[ \sqrt{\frac{\pi N_a}{\sum x_i b_i}} * \sqrt{4} * \sqrt{\frac{e^2 \sum x_i b_i}{\pi \epsilon_0 k T (\sum x_i b_i \epsilon_i)}} * x_i \right] * \left( \frac{1}{1000} \sum x_i M_i \right)^{0.5} \right. \\
& \left. \ln \left[ 1 + \frac{3.464 x_i^{0.5}}{\left( \frac{1}{1000} \sum M_i x_i \right)^{0.5}} * \left( \frac{-1}{\pi \epsilon_0 k T (\sum x_i b_i \epsilon_i)^2} \right) * (e^2 (\sum x_i b_i) * (b_i \epsilon_i - \sum x_i b_i \epsilon_i)) \right] \right. \\
& \left. + \frac{e^2 * (b_i - \sum x_i b_i)}{\pi \epsilon_0 (\sum x_i b_i \epsilon_i)} \right] - 1 / \left( \frac{1}{1000} \sum x_i M_i \right)^{0.5} * \left[ 0.0625 RT \sqrt{2} \sqrt{\frac{\pi N_a}{\sum x_i b_i}} * 2 * \left[ \frac{e^2 \sum x_i b_i}{\pi \epsilon_0 k T \sum x_i b_i \epsilon_i} \right]^{(3/2)} \right] * \\
& x_i \ln \left[ 1 + \frac{3.464 (x_i^{0.5})}{\left( \frac{1}{1000} \sum x_i M_i \right)^{0.5}} * \left( \frac{1}{1000} (M_1 - \sum x_i M_i) \right) \right] - 1/8 / \left[ 1 + \frac{3.464 (x_i)^{0.5}}{\left( \frac{1}{1000} * \sum x_i M_i \right)^{0.5}} \right] \\
& * \left[ RT 2 \sqrt{2} \sqrt{\frac{\pi N_a}{\sum x_i b_i}} \left[ \frac{e^2 (\sum x_i b_i)}{\pi \epsilon_0 k T (\sum x_i b_i \epsilon_i)} \right]^{(3/2)} \right] * x_i * \left( \frac{1}{1000} \sum x_i M_i \right)^{0.5} * \\
& \left[ \frac{-1}{\left( \frac{1}{1000} \sum x_i M_i \right)^{1.5}} * (1.73205 (x_i^{0.5}) * \left( \frac{1}{1000} * (M_1 - \sum M_i x_i) \right)) \right] - (1.73205 x_i / \left( \left( \frac{1}{1000} \sum x_i M_i \right)^{0.5} * x_i^{0.5} \right)) \\
\left(\frac{\partial \Delta A^{ia}}{\partial n_i}\right)_{T,V,n_{j \neq i}} = & 2RT \sum_j x_j B_{ij} + 3RT \sum_k \sum_j x_j x_k C_{ijk}
\end{aligned}$$

If one mol of salt MX dissociates in to  $v$  ions the osmotic coefficient and activity of solution are obtained by these equations [21]:

$$\phi = - \left[ \frac{1000}{v m_{MX} M_s} \right] \ln a_s \quad (18)$$

$$\ln(a_s) = \frac{-M_s}{1000} m_i - \frac{-M_s}{1000} \int_0^{m_i} m_i \left( \frac{\partial \ln \gamma_i}{\partial m_i} \right)_{T,P} dm_i \quad (19)$$

where  $M_s$  is molar mass of solvent and  $m_{MX}$  is molality of salt.

## RESULTS AND DISCUSSION

The relative dielectric constants for CO<sub>2</sub>, water and methanol, are given in table 1 [18].

Sieder and Maurer presented the extended Peng-Robinson EOS in terms of Helmholtz free energy. Starting point for the using of the EOS was derivation of fugacity coefficient expression based on the extended PR-EOS. In order to check the calculation, one of the systems applied in Sieder and Maurer's work is selected.

The calculated results for (water + methanol + NaCl + CO<sub>2</sub>) system showed that the obtained expression for the

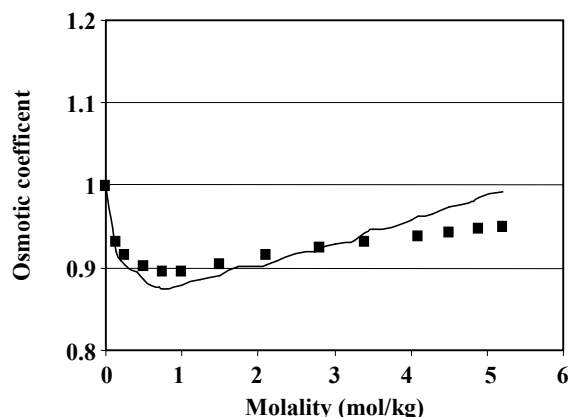


Fig. 3: Osmotic coefficient of  $(\text{NH}_4\text{Cl}+\text{H}_2\text{O})$  system. ■: Experimental data [23]. (—): calculation results.

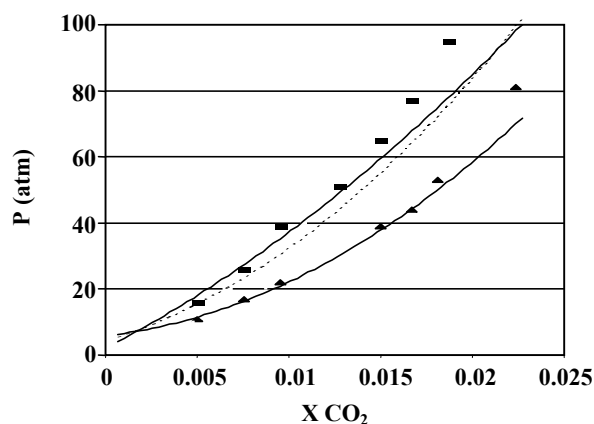


Fig. 4: VLE of the system (carbon dioxide + water + methanol + sodium chloride) for  $T=313$  K with 5 mol % methanol. Experimental data: ( $\blacktriangle$ ) salt-free; ( $\blacksquare$ ) with NaCl and  $m_{\text{NaCl}} = 1.7$  mol/kg [18]. Prediction results of: (---) Sieder & Maurer [18] for the solution with NaCl; (—) our predictions for both solutions, salt free and with NaCl.

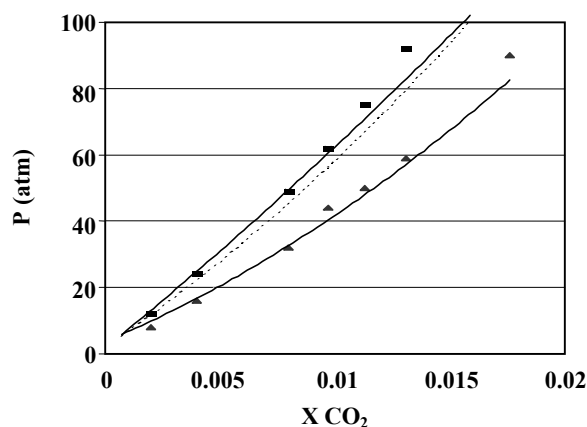


Fig. 5: The same as Fig. 4 but for  $T=353$  K.

fugacity coefficient (Eq. (17)) is valid. Since experimental VLE data for (water +  $\text{Na}_2\text{SO}_4$  +  $\text{CO}_2$ ), (water +  $\text{NaCl}$  +  $\text{CO}_2$ ) and (water +  $\text{NH}_4\text{Cl}$  +  $\text{CO}_2$ ) systems are available in the literature, the extended PR-EOS is then used to predict the phase equilibrium of these systems.

Extension of the model to systems with ionic species requires a Debye-Hückel term,  $\Delta A^{\text{DH}}$  and a Margules term,  $\Delta A^{\text{ia}}$ . No additional parameter has to be fitted for the Debye-Hückel term as the relative dielectric constants of the molecular components are known. However,  $\Delta A^{\text{ia}}$  contains binary interaction parameter ( $B_{ij}$ ) and ternary interaction parameters ( $C_{\text{sol, sol, salt}}$ ,  $C_{\text{sol, salt, salt}}$ ) between ionic and natural species that have to be adjusted to experimental mean solvent activity of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  solutions (table 2).

Figs. 1 and 2 demonstrate the solvent activity of  $\text{NaCl}$ -water and  $\text{Na}_2\text{SO}_4$ -water systems at 298 K and 1atm and salt molality between 0.001 and 5 for  $\text{NaCl}$  and salt molality between 0.1 and 1.6 for  $\text{Na}_2\text{SO}_4$ . For (water (1) + sodium chloride (2)) system,  $B_{1,2}$  and  $C_{1,2,2}$  are sufficient to reach the proper deviation. The average absolute deviation of solvent activity for the (water + sodium chloride) system is 2.13 %.

For (water (1) + sodium sulfate (2)) system  $B_{1,2}$ ,  $C_{1,1,2}$  and  $C_{1,2,2}$  are used. The average absolute deviation between the calculated results and experimental data for the solvent activity of this system is 0.87 %.

For water-ammonium chloride system experimental osmotic coefficient data [23] are used to calculate the binary and ternary interaction parameters. Fig. 3 shows the results of this system and that the absolute average deviation of osmotic coefficient is 6 %. The ionic interaction parameters between carbon dioxide (1) and salt (2) ( $B_{1,2}$ ) are adjusted to vapor-liquid experimental data for carbon dioxide-water-salt system [18].

Figs. 4 to 6 show vapor - liquid equilibrium of the system (carbon dioxide + water + methanol + sodium chloride) at 313 K, 353 K and 393 K. These figures demonstrate the predictive capability of the extended PR-EOS by new parameters obtained in this work and the predicted results by Sieder and Maurer obtained by their adjusted parameters. The average absolute deviation of our calculated results and the experimental data is 5.7 % while this value for Maurer's results is 6.4 %.

These figures show the effect of carbon dioxide composition on the pressure of system with sodium

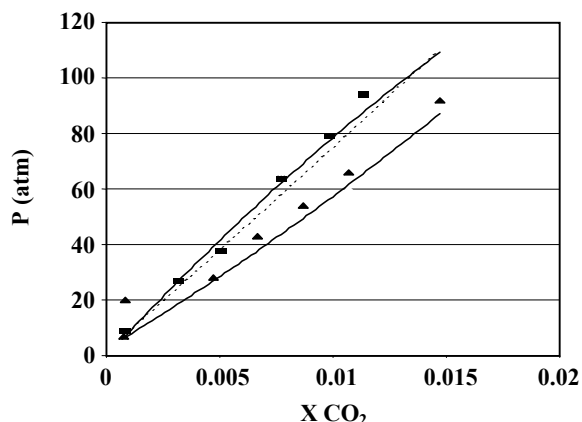


Fig. 6: The same as Fig. 4 but for  $T=393$  K.

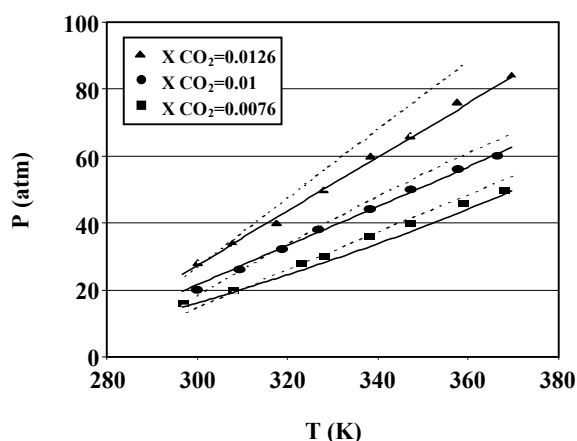


Fig. 7:  $P$ - $T$  diagram for the system (water + carbon dioxide). (▲ ● ■): Experimental data [16]. (...): correlation results of Bermejo et al. [16]. (—): our predictions.

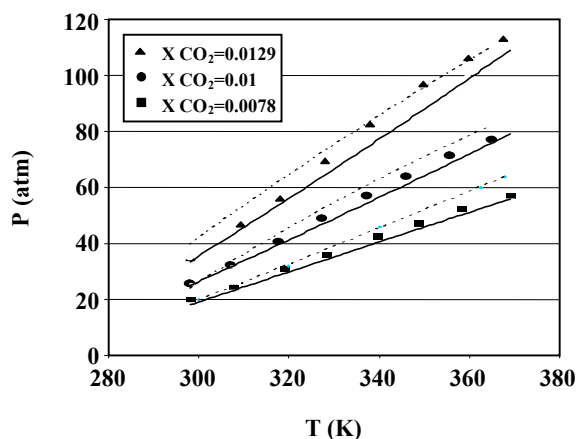


Fig. 8:  $P$ - $T$  diagram for the system (water + carbon dioxide + sodium sulfate) for  $m_{Na_2SO_4}=0.25$ . (▲ ● ■): Experimental data [16]. (...): correlation results of Bermejo et al. [16]. (—): our predictions.

chloride. Sodium chloride molality equals 1.7 (mol/kg).

These figures also demonstrate that the pressure of system increases when sodium chloride is added.

Fig. 7 shows the  $P$ - $T$  diagram for the system of (water + carbon dioxide) which contains 0.76, 1 and 1.26 mol % of carbon dioxide without a salt.

In this figure, our calculation results are compared with both experimental data and the calculation results of Bermejo et al. [16] by Anderko-Pitzer EOS. Figs. 8 to 10 demonstrate the predictive capability of the extended PR-EOS for (water +  $Na_2SO_4$  +  $CO_2$ ) system which contains 0.25, 0.5 and 1 moles of sodium sulfate in 1 kg water. These figures show that the total pressure decreases when the  $Na_2SO_4$  concentration goes up.

The average absolute deviation of  $(\Delta P/P_{exp})$  % between correlation results of Bermejo et al. and experimental data is 8.4 % while this value for our predictions is 6 %. The maximum deviation of  $(\Delta P/P_{exp})$  % of Bermejo results is 14.2 % while this value for our predictions is 10 %.

Fig. 11 shows the vapor liquid equilibrium of system containing ( $CO_2$  +  $H_2O$  +  $NaCl$ ) at 323 and 373 K. Concentration of salt in Fig. (11, A) is 1 (mol/ kg) and this value for Fig. (11, B) is 3 (mol/ kg). The average absolute deviation between our prediction results and experimental data for this system is 6.3 %.

Fig. 12 shows the  $P$ - $x$  diagram for (water +  $CO_2$  +  $NH_4Cl$ ) system at temperatures (333 and 353 K). In this figure our calculation results by extended PR-EOS are compared with the calculation results of Colinet and Gmehling [25] by VTPRLIFAC model. Concentration of salt in the system is 4 (mol/kg solvent). The average absolute deviation between calculation results by VTPRLIFAC model and experimental data [25] is 7.8 % but this value for our calculations is 6.2 %. Considering these values show that the extended PR-EOS is more precise with respect to the other mentioned models.

## CONCLUSIONS

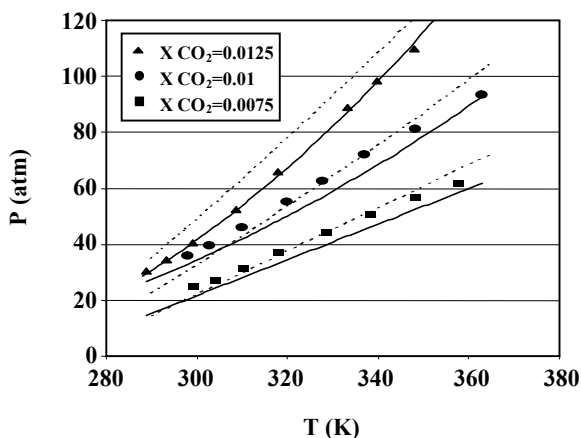
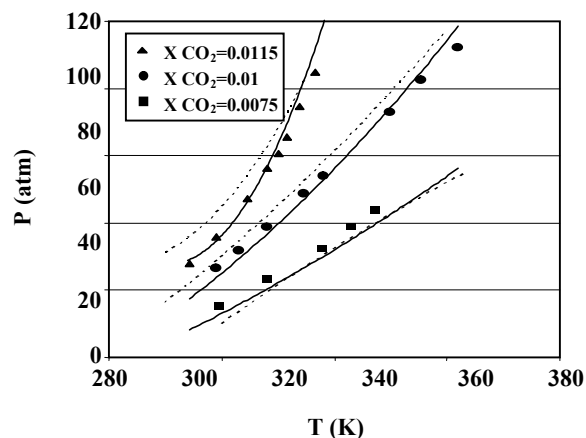
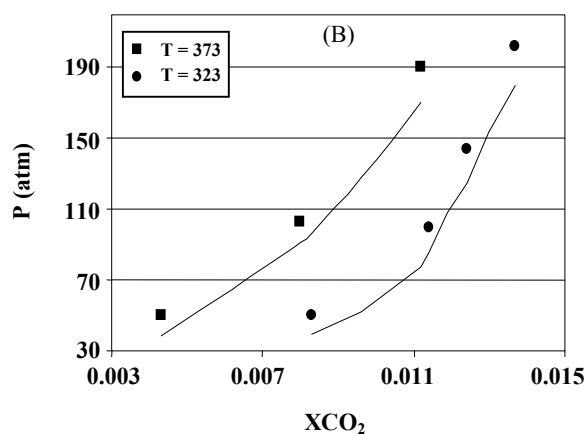
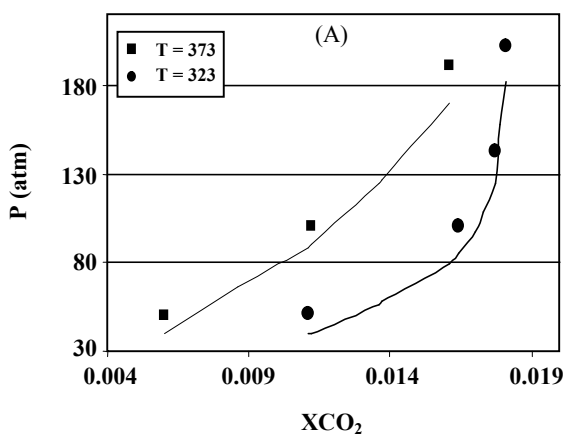
It is concluded that the extended Peng-Robinson EOS can be used to obtain the phase diagram over a wide range of temperatures, pressures for the ternary and quaternary aqueous solutions.

The average absolute deviations between calculated results and experimental data show that the extended Peng-Robinson model is better than Anderko-Pitzer

Table 3: Comparison between experimental data and calculation results from various models.

System	Type of model	AAD %	References
(CO <sub>2</sub> + H <sub>2</sub> O + NaCl + MeOH)	Extended PR-EOS	6.4 %	[18]
	Extended PR-EOS	5.7 %	This work
(CO <sub>2</sub> + H <sub>2</sub> O + Na <sub>2</sub> SO <sub>4</sub> )	Anderko-Pitzer -EOS	8.4 %	[16]
	Extended PR-EOS	6.0 %	This work
(CO <sub>2</sub> + H <sub>2</sub> O + NaCl)	Extended PR-EOS	6.3 %	This work
(CO <sub>2</sub> + H <sub>2</sub> O + NH <sub>4</sub> Cl)	VTPRLIFAC	7.8 %	[25]
	Extended PR-EOS	6.2 %	This work

$$\text{AAD \%} = \left( \sum_{i=1}^n \left| \frac{\Delta P}{P^{\text{Exp}}} \right|_i \right) / n \times 100$$

Fig. 9: The same as Fig. 7 but for  $m_{\text{Na}_2\text{SO}_4} = 0.5$ .Fig. 10: The same as Fig. 7 but for  $m_{\text{Na}_2\text{SO}_4} = 1$ .Fig. 11: P-x diagram for system (water + CO<sub>2</sub> + NaCl) at temperatures 323 and 373 K. The salt molality equals to (A: 1 and B: 3 mol/kg). (■, ●): experimental data [26]. (—): calculation results.



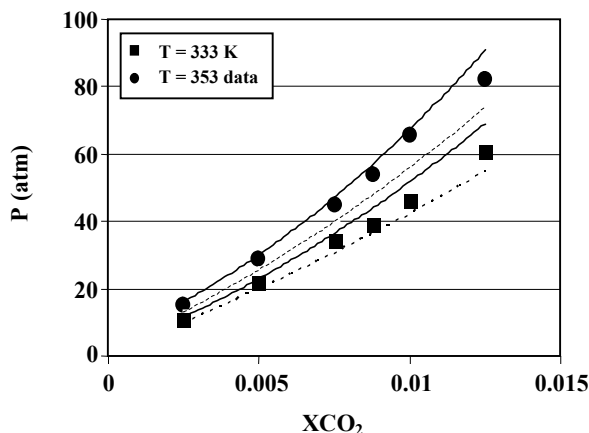


Fig. 12: P-x diagram for (water + CO<sub>2</sub> + NH<sub>4</sub>Cl) system at temperatures 333 and 353 K. The salt molality equals to 4 mol/ kg. (■, ●): experimental data [25]. (—): calculation results by extended Peng Robinson equation of state. (---): calculation results by VTPR-LIFAC [25].

model for water-carbon dioxide-sodium sulfate ternary system. Table 3 shows the average absolute deviation between the experimental data and the correlation results of pressure for various models.

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