

Equation of state for the systems containing aqueous salt: Prediction of high pressure vapor-liquid equilibrium

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(Received 12 March 2008 • accepted 15 July 2008)

Abstract—An equation of state (EOS), which is based upon contributions to the Helmholtz energy, is presented for systems containing aqueous electrolyte solutions at high pressure. The Peng-Robinson equation of state is used to provide the Helmholtz energy of a reference system. The electrolyte terms consist three terms containing a modified Debye-Hückel term for long-range electrostatic interactions, the Born energy contribution for electrostatic works and a Margules term for short-range electrostatic interactions between ions and solvents. The binary and ternary interaction parameters of the equation of state are obtained by experimental osmotic coefficient data. Systems that were studied here are (water+NaCl+SC-CO₂), (water+NH₄Cl+SC-CO₂), (water+Na₂SO₄+SC-CO₂) and (water+methanol+NaCl+SC-CO₂). It is found that the proposed equation of state is able to accurately represent the experimental data over a wide range of pressure, temperature and salt concentration.

Key words: Equation of State, Electrolyte Solution, Vapor-liquid Equilibrium

INTRODUCTION

Salt containing and more specifically aqueous electrolyte solutions are involved in many industrial processes, such as extractive distillation, solution crystallization, ion exchange, waste water treatment, liquid-liquid extraction and many other processes. Supercritical carbon dioxide is also used in systems containing (supercritical carbon dioxide, solvent and salt). Several data series of these systems have been found in the literature. To mention only a few, Wander and coworkers (1989) measured the CO₂ solubility in pure water and in a 1% wt aqueous NaCl solution at pressures up to 10 MPa and temperature range from 353 K up to 473 K. Koschel et al. [1] studied the dissolution of carbon dioxide in water and in aqueous solution of sodium chloride by measuring the heat of mixing, ΔH_{mix} , of a supercritical gas with the liquid phase. Prutton and Savage [2] published the data of solubility of CO₂ in water and effect of salts CaCl₂ on the concentration of phases at 348, 373 and 393 K and pressures up to 70 MPa.

For ambient pressure conditions, several activity coefficient models have been developed to represent the vapor liquid equilibrium (VLE) in mixed solvent-electrolyte systems [3-7]. But these models are not suitable for systems containing supercritical components. An alternate description of high-pressure phase equilibria is provided by a single equation of state to calculate the fugacity of each species in each phase. Such equations of state do not have any problem to select a truly useful standard state for the supercritical components. However, the widely used equations for high-pressure phase equilibrium calculations, such as the cubic equations of state, have to be developed with systems containing electrolytes. Efforts along these lines were reported in several works (Donohue et al., 1991; [8-11]).

Donohue and coworkers [13] developed the extended perturbed-

anisotropic-chain-theory. Their theory consists of ten contributions to the Helmholtz energy. Seven contributions of their proposed EOS are needed to describe the nonionic interactions, and the remaining three are needed to consider the ionic interactions. Clarke [8] used an equation of state based on contributions to the Helmholtz energy from a non-electrolyte term and three electrolyte terms. The non-electrolyte term comes from the Trebble-Bishnoi equation of state, and the electrolyte terms consist of a Born energy term, a mean spherical approximation term and a newly developed hydration term.

Raatschen and coworkers [9] 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 in combination with a Lennard-Jones potential to describe nonionic systems. They used the Born equation, a Debye-Hückel term, and a modified Pitzer equation to describe the ionic interactions. Harvey and Prausnitz [10] presented a procedure for superimposing ionic effects on a conventional equation of state for non-electrolytes. They used a modification of Born's equation to describe charging the ions, in combination with mean spherical approximation to describe ion-ion interactions. They calculated an adjustable salt/solvent parameter from osmotic-coefficient data and obtained good results for phase equilibria in a natural-gas/brine system at high pressure. Liu et al. [12] 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 [13] applied a three-parameter cubic equation of state by Patel and Teja [14] combined 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.

Lu and coworkers [15] used a model for electrolyte solutions. Their model consists of the cluster equation theory, with which the osmotic coefficient and activity coefficient in the dilute concentration range, can be predicted by using the Pauling ionic diameter.

Collinet and Gmehling [16] proposed the volume translated Peng-

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Robinson (VTPR) group contribution equation of state, which is commonly used for the prediction of phase equilibria with subcritical as well as supercritical compounds. They extended the EOS for electrolyte systems by linking it with the group contribution model LIFAC.

Fürst and Renon [17] combined the cubic equation of Schwarzen-truber and the mean-spherical approximation (MSA) model to consider the interactions between charge species.

Sun and Bullock [18] used a modification of the salvation model of Ohe to calculate vapor-liquid equilibria (VLE) in alcohol-water-salt systems. Bermejo and coworkers [19] 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 [20] constructed a method for activity calculation in saline, mixed solvent, supercritical aqueous solutions. They applied the Debye-Hückel term to mixed solvents and concentrated solutions combining with a multi-component van Laar formulation to calculate activity coefficients.

Sieder and Maurer [11] proposed an extended Peng-Robinson equation of state to describe the high-pressure vapor-liquid phase equilibrium of the aqueous salt containing systems with supercritical components. They applied the Debye-Hückel and Margules terms to extend the Peng-Robinson EOS for ionic systems.

In this work the extended PR-EOS by Sieder and Maurer is developed. The proposed EOS is used to calculate the phase equilibrium in aqueous salt containing systems with supercritical component. The electrolyte terms of the proposed equation of state consist of a modified Debye-Hückel term for long-range electrostatic interactions, the Born term that gives the change in the Helmholtz energy in charging neutral particles against its own electrostatic field, and a Margules term for short-range electrostatic interactions between ions and solvents. Systems studied here contain (water+NaCl+SC- CO_2), (water+ NH_4Cl +SC- CO_2), (water+ Na_2SO_4 +SC- CO_2), (water+methanol+NaCl+SC- CO_2).

2. Modeling

For a mixture of several components, the extended PR-EOS is proposed in terms of Helmholtz energy, A . For aqueous salt-containing mixtures, the Helmholtz energy at temperature T and volume V consists of four terms [11]:

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

where A^0 is the Helmholtz energy of pure component in the ideal gas state at (T, P^0) , ΔA^{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 contribution of Helmholtz energy due to nonionic intermolecular forces and δA_{ionic} is the contribution of 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 ΔA^{rep} and ΔA^{att} are repulsive and attractive contributions of Helmholtz energy, respectively.

The repulsive and attractive terms are calculated according to Melhem modification of PR-EOS [21]:

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

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

where n_i and n_T are the mole number of component i and the total number of moles in the mixture. a and b are covolume and energy parameters, respectively. In this work the influence of temperature on the energy parameter is calculated by the modification of Melhem et al. [21]. a and b for a mixture are calculated based on the van der Waals mixing rule. Binary interaction parameters are given according to model of Panagiotopoulos and Reid [22].

The ionic contribution of Helmholtz energy is separated into three terms, including the Born energy contribution, ΔA^{Born} , a modified Debye-Hückel term for long-range electrostatic interactions, ΔA^{DH} , and a Margules term for short-range electrostatic interactions between ions and solvent, ΔA^{ia} , as follows:

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

The change in the Helmholtz energy that is required to charge uncharged ions, in a medium of dielectric constant D_m , is given by the Born term [8]:

$$\Delta A^{\text{Born}} = RT \sum_{i=1}^{N_i} \frac{(z_i e)^2 N_A n_i}{4 \pi \epsilon_0 D_m \sigma_i} \quad (6)$$

In this equation N_i is the number of ionic species and D_m is dielectric constant of mixture (salt containing solution) that depends on the total volume of the solution. Therefore, the Born energy contribution is implicitly dependent upon the total volume of the solution. In this paper, the dielectric constant of the solution is calculated by the expression of Fürst and Renon [17]. Eq. (6) can be differentiated with respect to the total volume, at a constant temperature and number of moles, to give the pressure contribution from the Born energy term [8]:

$$P^{\text{Born}} = -RT \sum_{i=1}^{N_i} \frac{(z_i e)^2 N_A n_i}{4 \pi \epsilon_0 D_m^2 \sigma_i} \left(\frac{\partial D_m}{\partial V} \right)_{T, n_i} \quad (7)$$

The Born energy term does not contribute to the chemical potential of non-ionic species, such as water and carbon dioxide, because the summation is only carried out for the charged species.

Based on the results of Gao and coworkers [23], the anion diameters are kept constant and their values are listed in Table 1.

But the cations diameter may be regressed because there are no specific diameter values for these ions in the literature. In this work we contend that the diameter of the anions is equal to the Pauling diameters, but we use the cavity diameter for Na^+ calculated with Harvey and Prausnitz [10]. For NH_4^+ the effective diameter of cations is calculated with method that Gao and coworkers [23] developed and then this cation diameter is a function of salt molality.

The Debye-Hückel term, ΔA^{DH} , is calculated based on the G^E -model of Pitzer [24]:

Table 1. Ions diameter

Ion	Ion diameter (10^{-10} m)	Reference
Cl^-	3.62	[10]
SO_4^{2-}	3.87	[8]
Na^+	3.14	[10]
NH_4^+	variable	[23]

$$\Delta A^{DH}(T, \vec{n}) = -n_T RT \frac{4A_x I_x}{\chi} \ln(1 + \chi \sqrt{I_x}) \quad (8)$$

I_x is the ionic strength on mole fraction scale:

$$I_x = \frac{1}{2} \sum_{i=1}^{N_c} x_i z_i^2 \quad (9)$$

where z_i is the charge of ion i and x_i is its mole fraction. The summation extends over all ionic species in the solution. χ is calculated by following equation [24]:

$$\chi = \frac{2}{\sqrt{M^*}} \quad (10)$$

M^* is an average molecular mass:

$$M^* = \frac{1}{1000} \sum_{i=1}^{N_c} x_i^* M_i \quad (11)$$

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 [24]:

$$A_x = \frac{1}{3} \left(\frac{2\pi N_A}{v_{mix}^*} \right)^{1/2} \left(\frac{e^2}{4\pi\epsilon_0 D_s kT} \right)^{3/2} \quad (12)$$

N_A is Avogadro's number, v_{mix}^* is the molar volume of the salt-free solvent mixture, e is the charge of an electron, ϵ_0 is the permittivity of vacuum, D_s is the relative dielectric constant of the salt-free solvent mixture and k is the Boltzmann's constant. v_{mix}^* and D_s are approximated by following expressions:

$$v_{mix}^* = \sum_{i=1}^{N_c} x_i^* b_i \quad (13)$$

$$D_s = \frac{1}{v_{mix}^*} \sum_{i=1}^{N_c} x_i^* b_i \epsilon_i \quad (14)$$

where b_i and ϵ_i are the covolume and relative dielectric constant of the pure solvent i (H_2O , methanol and CO_2), respectively.

Short-range electrostatic interaction between ions and solvents is

calculated according to the Margules term with binary, B_{ij} , and ternary, C_{ijk} , interaction parameters:

$$\Delta A^{ia}(T, \vec{n}) = \frac{RT}{n_T} \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} n_i n_j B_{ij} + \frac{RT}{n_T} \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} \sum_{k=1}^{N_c} n_i n_j n_k C_{ijk} \quad (15)$$

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

Debye-Hückel and Margules terms of Helmholtz energy make no contribution to the pressure, P , because their derivatives with respect to the volume are zero. In our proposed EOS, the Born term is added to consider the total electrostatic work done to charge each ion from the natural state against its own electrostatic field. This term is implicitly dependent upon the total volume of the solution. The pressure contribution of the Born term is obtained by Eq. (7).

In this work, the Helmholtz energy expressed in Eq. (1) is used to calculate pressure, P , chemical potential of component i , μ_i , and the fugacity coefficient of component i , ϕ_i by the following general thermodynamic equations [25]:

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T, \vec{n}} \quad (16)$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j \neq n_i} \quad (17)$$

$$RT \ln \phi_i = \left(\frac{\partial \Delta A}{\partial n_i} \right)_{T, V, n_{ij}} - RT \ln Z \quad (18)$$

Table 2. Pure component parameters [11]

Component	T_c (K)	P_c (MPa)	m	n
CO_2	304.2	7.38	0.6877	0.3813
H_2O	647.3	22.05	0.8795	0.0565
MeOH	512.6	7.98	1.1954	-0.7215

Table 3. Binary interaction parameters for the Peng-Robinson EOS and the mixing rule of Panagiotopoulos and Reid [11]

Interaction parameters			
Carbon dioxide (1)+water (2)	$k_{12} = -0.4271 + 1.0337 \cdot 10^{-3} (T/K)$	$k_{21} = -0.4516 + 1.9813 \cdot 10^{-3} (T/K)$	
Carbon dioxide (1)+methanol (2)	$k_{12} = -0.2907 + 1.1068 \cdot 10^{-3} (T/K)$	$k_{21} = 0.0298 + 0.1587 \cdot 10^{-3} (T/K)$	
Water (1)+methanol (2)	$k_{12} = -0.1933 + 0.3579 \cdot 10^{-3} (T/K)$	$k_{21} = -0.1410 + 0.1413 \cdot 10^{-3} (T/K)$	

Table 4. Binary and ternary interaction parameters between salt and solvent

Component		T (K)	P (atm)	m_{salt} (mol/Kg)	$B_{1,2}$	$C_{1,1,2}$	$C_{1,2,2}$
(1)	(2)						
H ₂ O	NaCl	300-390	5-110	0-4	−6.3506	0	0.9866
H ₂ O	Na ₂ SO ₄	290-370	10-110	0-1	−4.1482	−6.5177	−0.8572
H ₂ O	NH ₄ Cl	333-393	5-120	0-4	−0.2778	−1.3652	−0.0461
CO ₂	NaCl	300-390	5-110	0-4	3.0063	-	-
CO ₂	Na ₂ SO ₄	290-370	10-110	0-1	1.1455	-	-
CO ₂	NH ₄ Cl	333-393	5-120	0-4	0.3177	-	-
MeOH	NaCl	300-390	5-110	0-4	0.2936	-	-

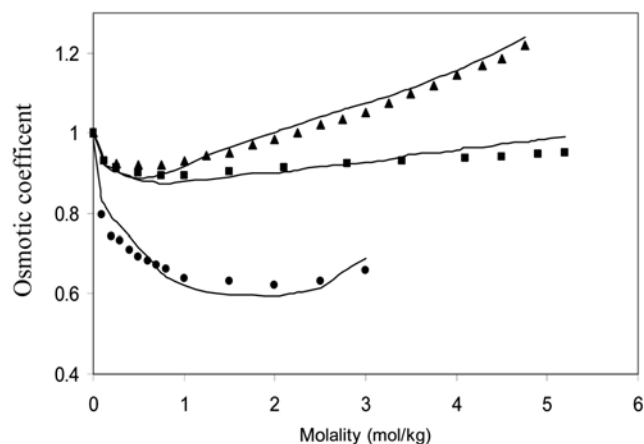


Fig. 1. Osmotic coefficient of systems: \blacktriangle Experimental data of system (water+sodium chloride) [15]. \blacksquare : (water+ammonium chloride) [26]. \bullet : (water+sodium sulfate) [27]. (—): Calculation results.

where $\delta A = \delta A_{\text{nonionic}} + \delta A_{\text{ionic}}$.

RESULTS AND DISCUSSION

The ion diameters, the model pure component parameters and the binary interaction parameters of the mixing rule of Panagiotopoulos and Reid [22] are given in Tables 1 to 3, respectively [11].

Experimental osmotic coefficients of NaCl, Na₂SO₄ and NH₄Cl are used to determine the binary interaction ($B_{\text{sol,salt}}$) and ternary interaction parameters ($C_{\text{sol,sol,salt}}$, $C_{\text{sol,salt,salt}}$) between salt and solvent (Table 4).

Fig. 1 shows the osmotic coefficient of NaCl-water, Na₂SO₄-water and NH₄Cl-water systems at 298.15 K and 1 atm and salt molality between 0.001 and 5 for NaCl and salt molality between 0.1 to 3 for Na₂SO₄ and 0.125 to 4.5 (mol/kg) for NH₄Cl. For (water (1)+sodium chloride (2)) system, $B_{1,2}$ and $C_{1,2,2}$ are sufficient to reach the proper relative deviation. The average relative deviation for osmotic coefficient, $([\phi^{\text{exp}} - \phi^{\text{cal}}]/\phi^{\text{exp}}) \%$, of the (water+sodium chloride) system is 6.8%. For (water (1)+sodium sulfate (2)) and (water (1)+ammonium chloride (2)) systems, $B_{1,2}$, $C_{1,1,2}$ and $C_{1,2,2}$ are used. The average relative deviation between the calculated results and experimental data for the osmotic coefficient of (H₂O+Na₂SO₄) system is 7%, and this value for (H₂O+NH₄Cl) system is about 6.2%. 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 systems.

In Fig. 2 the vapor-liquid equilibrium of the system (carbon dioxide+water+sodium chloride) from our proposed EOS and the EOS of Sieder and Maurer [11] are compared with experimental data [1]. For T=323 K and 373 K, this figure shows that the system pressure increases when the carbon dioxide composition increases. We can see that when the salt concentration is increased from a molality of 1 to 3, at a constant temperature and pressure, the solubility of carbon dioxide decreases.

In Fig. 3, predictions of the P-T diagram from our EOS are made for the system water-carbon dioxide, which contains 0.76, 1 and 1.26 mol% of carbon dioxide without a salt. In this figure, the predic-

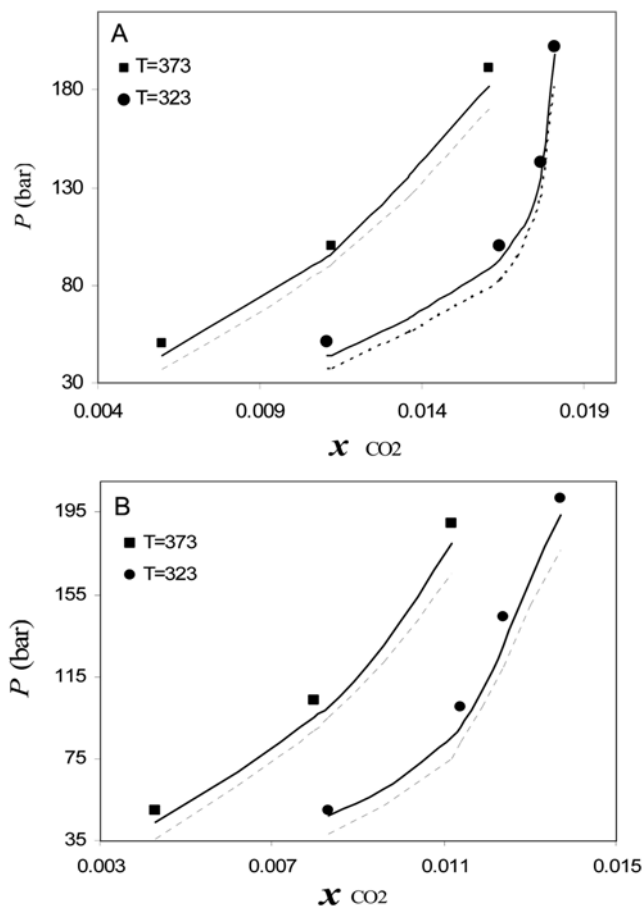


Fig. 2. VLE of the system (carbon dioxide+water+sodium chloride) at 373 and 323 K and for salt molality of A: 1 (mol/kg) and B: 3 (mol/kg). (\blacksquare , \bullet): Experimental data [1]. (—): Calculation results by our proposed EOS. (---): Calculation results by Sieder and Maurer EOS.

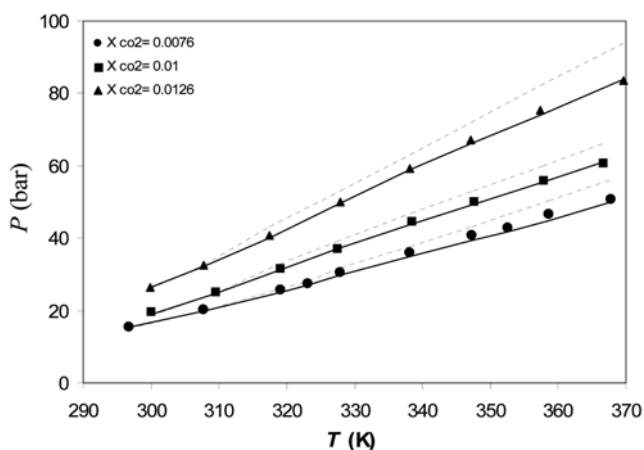


Fig. 3. P-T diagram for the system (water+carbon dioxide). (\blacktriangle , \bullet , \blacksquare): Experimental data [19]. (---) Calculation results of Bermejo and coworkers [19] by Anderko-Pitzer EOS; (—) Calculation results by our proposed EOS.

tions using our proposed EOS are compared with both experimental data and the calculation results of Bermejo and coworkers [19]

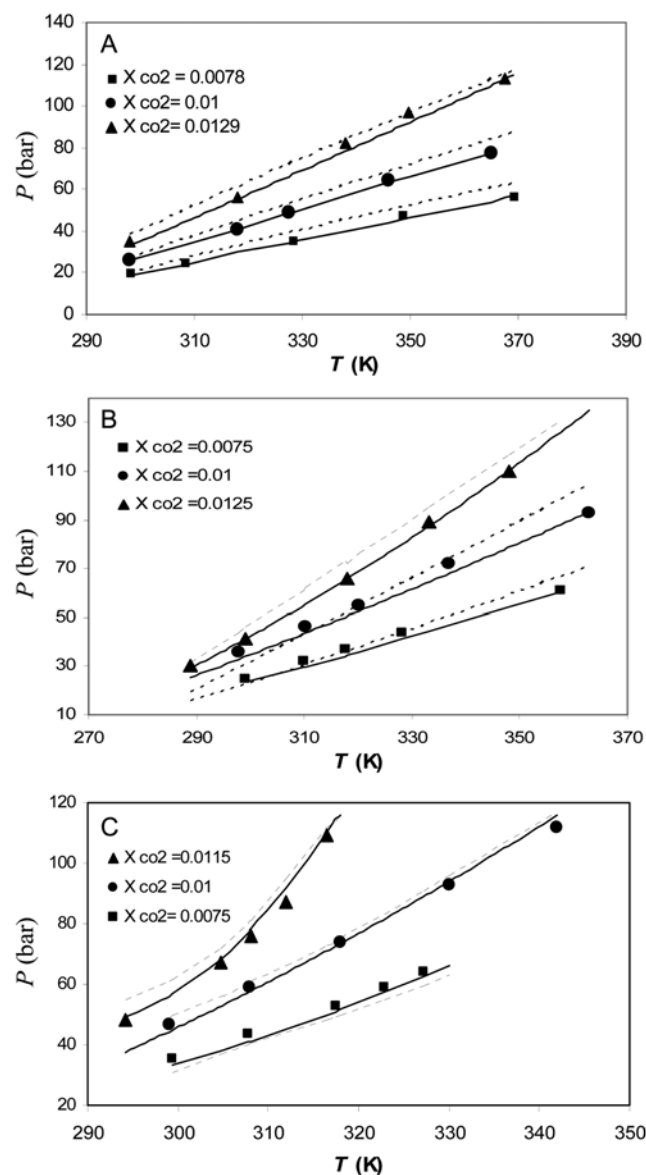


Fig. 4. P-T diagram for the system (water+carbon dioxide+sodium sulfate) for $m_{Na_2SO_4}$ =A: 0.25, B: 0.5 and C: 1 (mol/kg). (▲ ● ■): Experimental data [19]. (...) Calculation results of Bermejo and coworkers [19] by Anderko-Pitzer EOS; (—) Calculation results by our proposed EOS.

by Anderko-Pitzer EOS.

Fig. 4 demonstrates the predictive capability of the proposed EOS for (water+carbon dioxide+sodium sulfate) system, which contains 0.25, 0.5 and 1 moles of sodium sulfate in 1 kg water. The predictive results by Bermejo and coworkers' EOS are also shown in this figure. The average relative deviation of pressure between calculated results of Bermejo et al. by Anderko-Pitzer EOS and experimental data, $(\Delta P/P^{exp})$ %, is 8.6%, while this value for our calculations is 5.6%.

Fig. 5 shows the P-x diagram for the ternary system of (water+ NH_4Cl +SC- CO_2) for various temperatures (333, 353, 373 and 393 K). The average relative deviation between our results and experimental data is about 9.2%.

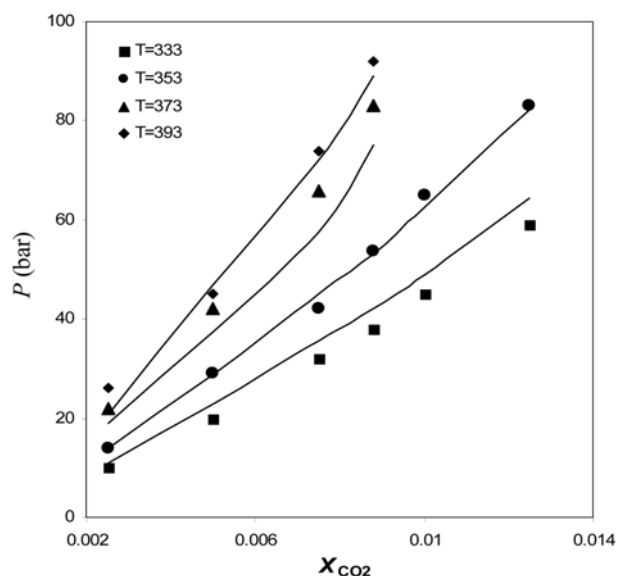


Fig. 5. P-x diagram for system (water+carbon dioxide+ammonium chloride) for $m_{NH_4Cl}=4$ (mol/kg) and various temperatures. (■, ●, ▲, ◆): Experimental data [16]. (—): Calculation results by our proposed EOS.

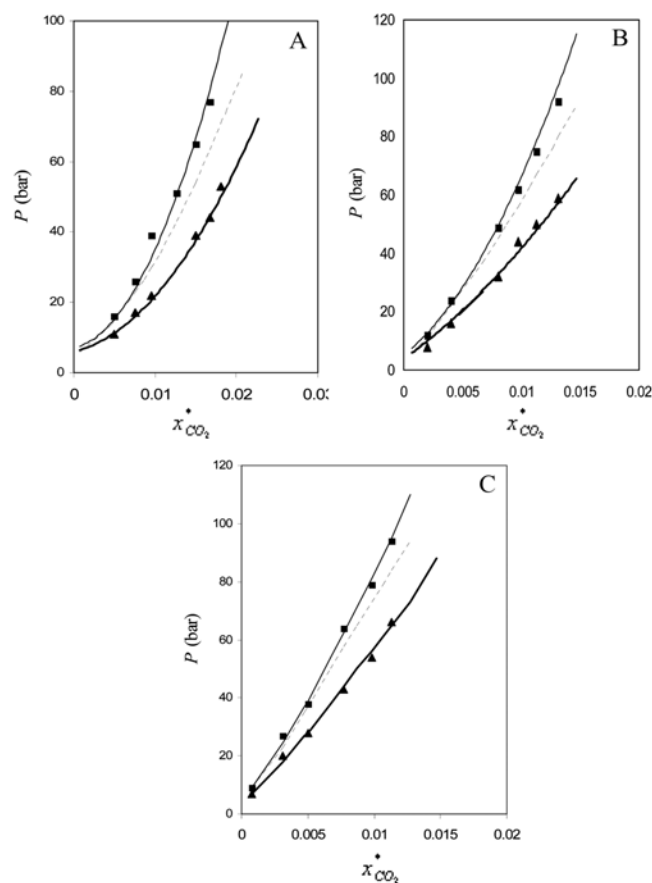


Fig. 6. VLE of the system (carbon dioxide+water+methanol+sodium chloride) for A: T=313 K, B: T=353 K, C: T=373 K with 5 mol% methanol. Experimental data: (▲) salt-free; (■) with NaCl and $m_{NaCl}=1.7$ mol/kg [11]. Calculation results by: (—) Our proposed EOS; (...) Sieder and Maurer EOS.

Table 5. Comparison between experimental data and calculation results from various modes

System	Type of model	($\Delta P/P_{exp}$)%	References
(CO ₂ +H ₂ O+NaCl+MeOH)	extended PR-EOS	6.4%	[11]
	this work	5.0%	
(CO ₂ +H ₂ O+Na ₂ SO ₄)	Anderko-Pitzer-EOS	8.6%	[19]
	this work	5.6%	
(CO ₂ +H ₂ O+NH ₄ Cl)	this work	9.2%	[11]
(CO ₂ +H ₂ O+NaCl)	extended PR-EOS	7.8%	
	this work	5.1%	

Fig. 6 shows the vapor-liquid equilibrium for quaternary system of (water+methanol+NaCl+SC-CO₂) from our proposed EOS and Sieder and Maurer [11] EOS. In this figure the results of both EOS are compared with experimental data [11] for various temperatures (313, 353 and 373 K), and for salt free and salt concentration about 1.7 mol/(kg solvent).

CONCLUSION

The Peng-Robinson equation of state has been used here to provide the Helmholtz energy of a reference system. The additional ionic terms of proposed equation of state consist of three terms containing a modified Debye-Hückel term for long-range electrostatic interaction, the Born energy contribution for electrostatic work and a Margules term for short-range electrostatic interactions. The binary and ternary interaction parameters have been determined by reported experimental osmotic coefficient data. In order to check the predictive capability of the proposed EOS, the VLE calculated results by the proposed EOS have been compared with the reported experimental data for four aqueous salt-containing systems. It is found that the proposed equation of state is able to accurately represent the experimental data over a wide range of pressure, temperature and salt concentration. Table 5 shows the average relative deviation between the experimental data and correlation results for the pressure for various models.

NOMENCLATURE

a	: Peng-Robinson EOS interaction energy parameter
a _s	: activity of solvent
A	: Helmholtz energy
b	: Peng-Robinson EOS volume parameter
B _{ij}	: binary ionic interaction parameter
C _{ijk}	: ternary ionic interaction parameter
D _m	: dielectric constant of mixture (salt containing solution)
D _S	: relative dielectric constant of the salt-free solvent mixture
e	: charge of an electron
I _x	: ionic strength on mole fraction scale
k	: Boltzmann's constant
k _{ij} , K _{ij}	: nonionic binary interaction parameter
m	: molality
M*	: average molecular mass
n _i	: number of moles of component i
N _A	: Avogadro's number
N _C	: number of components

N _i	: number of ionic species
P	: pressure
R	: universal gas constant
T	: thermodynamic temperature
n	: molar volume
V	: volume
x _i [*]	: mole percent of component i in the salt free solvent mixture
z _i	: number of electrical charges on species i

Greek Letters

α	: temperature-dependent parameter for calculation of a(T)
δ	: residual part
Δ	: difference
ε	: relative dielectric constant of pure solvent
ε ₀	: permittivity of free space
μ _i	: chemical potential of component i
σ	: ion diameter
φ	: fugacity coefficient
φ	: osmotic coefficient
χ	: empirical constant

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