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Published in:
Industrial and Engineering Chemistry Research

Link to article, DOI:
[10.1021/acs.iecr.9b03335](https://doi.org/10.1021/acs.iecr.9b03335)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Sun, L., Kontogeorgis, G. M., von Solms, N., & Liang, X. (2019). Modeling of Gas Solubility Using the Electrolyte Cubic Plus Association Equation of State. *Industrial and Engineering Chemistry Research*, 58(37), 17555-17567. <https://doi.org/10.1021/acs.iecr.9b03335>

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Thermodynamics, Transport, and Fluid Mechanics

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Ind. Eng. Chem. Res., **Just Accepted Manuscript** • DOI: 10.1021/acs.iecr.9b03335 • Publication Date (Web): 21 Aug 2019

Downloaded from pubs.acs.org on August 24, 2019

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**Modeling of Gas Solubility using the Electrolyte Cubic
Plus Association Equation of State**

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Keywords: Gas Solubility; Inorganic Salts; Electrolyte Solution; e-CPA; Multi-salt
solution

Abstract

The prediction of the solubilities of carbon dioxide and methane in aqueous solutions of inorganic salts is important for geological carbon storage, enhanced oil recovery, gas hydrate formation and seawater desalination. Few electrolyte equations of state can be used for accurate gas solubility calculations over wide ranges of temperature, pressure and salt molality. This work presents a thermodynamic modeling study on the solubilities of carbon dioxide and methane in aqueous solutions of several inorganic salts with the electrolyte Cubic-Plus-Association equation of state. The binary interaction parameters between ion and gas are obtained by fitting the experimental data of gas solubility in single-salt solutions. It is shown that the equation of state can satisfactorily correlate the gas solubility over a wide range of conditions, with deviation less than the reported experimental uncertainties (7%) for most systems. The equation of state is then used to predict the gas solubility in multi-salt solutions, and a satisfactory performance is achieved. The salting-out effects resulting from ion size, charge density, and salt concentration are also extensively discussed.

1. Introduction

One important way of reducing carbon dioxide (CO_2) emissions is to capture and inject it into deep saline formations. The injected CO_2 dissolves into the saline pore water and forms an aqueous solution. That is why some inorganic salts, such as sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl_2), magnesium chloride (MgCl_2), and sodium sulfate (Na_2SO_4), water (H_2O), and CO_2 are the most common species in geological fluids¹. Methane (CH_4), another important greenhouse gas, has also been found in many geological fluids². Some inorganic salts (such as NaCl and KCl) are common thermodynamic inhibitors for gas hydrate formation, because these salts can significantly shift the phase equilibria of hydrate and aqueous solution³. Accurate calculations of gas solubility over a wide range of conditions (temperature, pressure and salt concentration) is important for the analysis of fluid inclusion data⁴, geological carbon storage⁵, the prediction of gas hydrate formation, as well as in the applications, such as enhanced oil recovery, seawater desalination and designing certain separation equipment in the chemical industries⁶.

Thermodynamic modeling is an attractive approach for calculating gas solubility. Extensive thermodynamic modeling studies have been made for calculating the solubilities of CO_2 and CH_4 in aqueous solutions of inorganic salts. The so-called $\varphi - \gamma$ approach has played a vital role in these studies⁶⁻²⁴. The equations of state (EOS) of Peng-Robinson (PR)²⁵, Soave-Redlich-Kwong (SRK)²⁶, Redlich-Kwong (RK)²⁷, Virial truncated after the second term^{16,18}, Patel and Teja (PT)²⁸ and Perturbed-Chain statistical associating fluid

theory (PC-SAFT)^{29,30} have been used for modeling the fugacity coefficient (ϕ), while LIFAC³¹, extended UNIQUAC³², Non-Random Two-Liquid (NRTL)³³, Pitzer's equation³⁴, electrolyte NRTL^{35,36} and empirical correlations⁷ are typical choices for the activity coefficient (γ). This $\phi - \gamma$ approach usually requires many adjustable parameters (even up to 20 for a single-salt solution²³), and it has not been used for modeling gas solubility in multi-salt solutions.

An electrolyte EOS for all the phases provides a more consistent framework, as well as the possibility to calculate other properties, e.g. density and surface tension. Some practices have also been done for modeling the solubilities of CO₂ and CH₄ in aqueous salt solutions³⁷⁻⁴⁹. Unfortunately, on one hand, a few electrolyte EOS can predict gas solubility over wide ranges of temperature, pressure and salt concentration with accuracy close to the experimental one, and fewer studies made systematic investigations. On the other hand, if the electrolyte EOS is set up for ions, it shall in principle be working for multi-salt solutions. To the best of our knowledge, however, no research on modeling gas solubility in aqueous multi-salt solutions has been reported for electrolyte EOS. More discussion is presented in Section 4.

The electrolyte cubic plus association (CPA) EOS developed by Maribo-Mogensen et al.⁴⁹ is investigated in this work for modeling the gas solubilities of CO₂ and CH₄ in single-salt and multi-salt solutions. In the rest of the paper, the model is firstly presented, and then the data and parameter estimation are discussed. And then the results are presented and discussed followed by a summary discussion. Finally, the conclusion is given.

2. Thermodynamic Model

2.1 The Electrolyte CPA EOS

The electrolyte CPA EOS (e-CPA)⁴⁹ is an extension of the CPA EOS⁵⁰

$$A^r = A^{SRK} + A^{ASSOC} + A^{DH} + A^{Born} \quad (1)$$

where A^{SRK} and A^{ASSOC} are the two contributions from the original CPA, A^{DH} is from the Debye-Hückel (DH) theory⁵¹, and A^{Born} is from the Born equation⁵².

In terms of residual Helmholtz energy, the cubic Soave-Redlich-Kwong EOS²⁶ can be written

$$A^{SRK} = nRT \left[-\ln \left(1 - \frac{b}{v} \right) - \frac{a(T)}{bRT} \ln \left(1 + \frac{b}{v} \right) \right] \quad (2)$$

where R is the gas constant, T is the temperature, v is the molar volume, n is the total number of moles, and b is the co-volume parameter of the mixture

$$b = \sum_i x_i b_i \quad (3)$$

where x_i and b_i are respectively the mole fraction and the pure co-volume parameter of component i (solvent, gas, cation, anion).

For the binary of water and gas, the classical one-fluid mixing rule is used for the temperature dependent energy parameter of the mixture $a(T)$

$$a(T) = \sum_i \sum_j x_i x_j \sqrt{a_i(T) a_j(T)} (1 - k_{ij}) \quad (4)$$

with

$$a_i(T) = a_{0i} \left(1 + c_{1i} (1 - \sqrt{T_{ri}}) \right)^2 \quad (5)$$

where T_{ri} is the reduced temperature of component i , defined as $T_{ri} = T/T_{ci}$, and T_{ci} is the critical temperature of component i .

For the binary involving an ion, the Huron-Vidal/NRTL (HV-NRTL) mixing rule is used, due to its additional flexibility for electrolyte systems^{49,53}

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{g^{E,\infty}}{\ln 2} \quad (6)$$

$$\frac{g^{E,\infty}}{RT} = \sum_i x_i \frac{\sum_j x_j b_j \exp\left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT}\right) \frac{\Delta U_{ji}}{RT}}{\sum_j x_j b_j \exp\left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT}\right)} \quad (7)$$

where $g^{E,\infty}$ is the excess Gibbs energy at infinite pressure, α_{ji} is the non-randomness parameter, and ΔU_{ji} is the change in interaction energy between the unlike and the like interactions ($\Delta U_{ji} = \Delta U_{ij} - \Delta U_{jj}$), for which a quadratic temperature dependence is used

$$\frac{\Delta U_{ij}}{R} = \frac{\Delta U_{ij}^{ref}}{R} + \omega_{\Delta U_{ij}} \left[\left(1 - \frac{T}{T_{\Delta U_{ij}}}\right)^2 - \left(1 - \frac{T_{ref}}{T_{\Delta U_{ij}}}\right)^2 \right] \quad (8)$$

where ΔU_{ij}^{ref} is a binary interaction parameter between ion and solvent or gas at the reference temperature, $\omega_{\Delta U_{ij}}$ is an adjustable parameter for the linear dependency, and $T_{\Delta U_{ij}}$ is a parameter of the temperature dependency. T_{ref} is the reference temperature at which ΔU_{ij}^{ref} is valid, and it is set to 298.15 K in this work.

It is worth pointing out that the HV-NRTL mixing rule has the flexibility to reduce to the classical one-fluid mixing rule, i.e. equation (4) can be integrated into equations (6) and (7). More details can be found in the book⁵⁴.

The residual Helmholtz energy for association A^{ASSOC} is obtained from^{55,56, 57,58}

$$A^{assoc} = RT \left[\sum_i n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \right] \quad (9)$$

$$\frac{1}{X_{A_i}} = 1 + \sum_j \rho_j \sum_{B_i} X_{B_j} \Delta_{A_i B_j} \quad (10)$$

where n_i is the number of moles of component i , X_{A_i} is the fraction of site A on component i that is not bonded to any other site, ρ_j is the density of component j , and $\Delta_{A_i B_j}$ is the association strength

$$\Delta_{A_i B_j} = g(\rho) \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{k_B T} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (11)$$

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and the association volume, respectively. b_{ij} follows the combining rule $b_{ij} = (b_i + b_j)/2$, and $g(\rho)$ is the simplified radial distribution function given by $g(\rho) = (1 - 1.9\eta)^{-1}$, where η is the packing fraction equal to $b/4v$.

The residual Helmholtz energy from the long-range ionic interactions is calculated from the DH theory⁵¹, as shown in the following equation,

$$A^{DH} = - \frac{k_B T V}{4\pi N_A \sum_i n_i Z_i^2} \sum_i n_i Z_i^2 \chi_i \quad (12)$$

where k_B and N_A are respectively the Boltzmann constant and the Avogadro constant, V is the total volume, Z_i is the charge of component i , and χ_i is merely an auxiliary function

$$\chi_i = \frac{1}{d_i^3} \left[\ln(1 + \kappa d_i) - \kappa d_i + \frac{1}{2}(\kappa d_i)^2 \right] \quad (13)$$

where κ is the inverse Debye screening length, and d_i is the distance of closest approach of ion i .

The residual Helmholtz energy from the ion solvation is described by the Born equation^{52,59}

$$A^{Born} = \frac{N_A e^2}{8\pi\epsilon_0} \sum_i \frac{n_i Z_i^2}{r_{Born,i}} \left(\frac{1}{\epsilon_r} - 1 \right) \quad (14)$$

where e is the elementary charge and $r_{Born,i}$ is the Born radius.

The relative static permittivity (also called dielectric constant) ϵ_r plays a central role in the thermodynamics of electrolyte solutions⁶⁰. In e-CPA, the theory proposed by Maribo-Mogensen et al.⁶¹ for predicting the relative static permittivity is used. For more details, the reader is referred to the work of Maribo-Mogensen et al.⁴⁹.

3. Data and Parameter Estimation

3.1 Data Analysis

Sometimes experimental data may represent large uncertainties because of the experimental apparatus, measurement methods and/or operations. In order to obtain accurate binary interaction parameters between ion and gas, and ensure that the model describes the actual phase behavior, experimental data have been analyzed and filtered prior to modeling.

Duan and Sun¹⁷ collected and analysed the solubility data of CO₂ in aqueous NaCl solution, and concluded that most experimental data sets were consistent within errors of about 7%.

Yan et al.⁶² made an extensive review for the solubility data of CO₂ in aqueous NaCl solution, and concluded that the solubility data measured by Kiepe et al.¹⁰ and Drummond⁶³ were doubtful. Yan et al.⁶² pointed out further that most solubility data of CO₂ in aqueous NaCl solution at high pressure were from three data sources: Takenouchi and Kennedy⁶⁴, Rumpf et al.¹⁶, and Koschel et al.⁶⁵.

Duan et al.² reviewed the experimental data of the solubility of CH₄ in aqueous CaCl₂ solution from Blanco and Smith⁶⁶, and determined the valid range, i.e. from 25 to 125 °C and from 100 to 600 bar. Duan et al.² pointed out that the most comprehensive data reported for the solubility of CH₄ in aqueous NaCl solution were from Blount et al.⁶⁷, while Price et al.⁶⁸ pointed out an experimental error in Blount et al.'s work⁶⁷, and they concluded that about 70% of the solubility data points for pressure below 300 bar had a high deviation (10-35%). Duan et al.² pointed out that the data from Duffy et al.⁶⁹ and Michels et al.⁷⁰ showed large uncertainties. Moreover, Duan et al.² suggested not using the solubility data of CH₄ in aqueous NaCl solution from Barta and Bradley⁷¹ and Drummond⁶³. In a later work, Duan et al.⁷² pointed out that experimental data for the solubility of CH₄ in aqueous CaCl₂ solution from Duffy et al.⁶⁹ and Michels et al.⁷⁰ were unreliable, as were those in NaCl solutions, due to adopting an inaccurate pressure decline technique. Pérez-Salado et al.²¹ stated that the data from Kiepe et al.¹⁰ had low credibility.

It is known from Takenouchi and Kennedy⁷³ and Tödheide and Franck⁷⁴ that the change of the solubility of CO₂ with pressure at temperatures above 538 K differs sharply from that at temperatures below 538 K. In this work, therefore, the modelling temperature is set to lower than 538 K. Moreover, the range of salt molality of most collected data follows the work of Maribo-Mogensen et al.⁴⁹ i.e. NaCl: 6 mol/kg water, KCl: 6 mol/kg water, CaCl₂: 3 mol/kg water, MgCl₂: 2 mol/kg water, and Na₂SO₄: 2 mol/kg water.

The solubility data of CO₂ in aqueous solutions of salts other than NaCl and CaCl₂, and the solubility data of CH₄ in aqueous solutions of salts other than NaCl, KCl and CaCl₂ are

limited. Moreover, the overlapping space is very small, and a clear conclusion cannot be reached regarding the reliability of these data sets. For the gas solubility in aqueous multi-salt solutions, the experimental data are limited and scattered. Therefore, all these collected data of aqueous multi-salt solutions are considered reliable.

3.2 Parameter Estimation

As presented above, e-CPA is set up for ions, i.e. the model parameters are by nature ion specific. The pure component e-CPA parameters of an ion are: b_i , Γ_i ($= a_{0i}/Rb_i$), c_{1i} , $\epsilon^{A_iB_i}$, $\beta^{A_iB_i}$, d_i and $r_{Born,i}$. The binary interaction parameters of ion and another species are: α_{ij} , ΔU_{ij}^{ref} , $\omega_{\Delta U_{ij}}$ and $T_{\Delta U_{ij}}$. In order to minimize the number of parameters, the following assumptions have been made⁴⁹: the CPA reduced energy parameter (Γ_i) and the temperature dependence parameter (c_{1i} in Eq. (5)) of ions are both set to zero; the ions are assumed to be non-associating, thus eliminating the two association parameters; the three size parameters b_i , d_i and $r_{Born,i}$ are connected with only one adjustable parameter left⁷⁵. the NRTL non-randomness factor and the ion-ion interaction parameters are set to zero. In this work, ion-solvent and ion-gas interaction parameters are transformed to cation/anion-solvent, and cation/anion-gas interaction parameters, which means that the interaction parameter $\Delta U_{cation-solvent}$ is equal to $\Delta U_{anion-solvent}$, and $U_{cation-gas}$ is equal to $\Delta U_{anion-gas}$.

The objective function used for the regression is

$$F = \sum \left[\frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}} \right]^2 \quad (15)$$

where x_i^{cal} represents the calculated solubility (mole fraction), and x_i^{exp} represents the experimental solubility (mole fraction of gas in liquid phase).

The results are typically listed as absolute average deviation (AAD) defined by

$$AAD\% = \frac{1}{Np} \sum_i \left| \frac{y_i^{cal} - y_i^{exp}}{y_i^{exp}} \right| \times 100\% \quad (16)$$

where Np is the number of data points, y_i^{cal} and y_i^{exp} respectively represent the calculated results and experimental value of any property, e.g. solubility, osmotic coefficient, or water activity.

The gas solubility in aqueous solutions is calculated by a two-phase PT-flash with the successive substitution method^{54,76}. The physical properties and pure component e-CPA parameters are taken from literature and summarized in Tables S1-S2 of Supporting Information.

4. Results and Discussion

4.1 Binary Systems

Before modelling the H₂O-salt-gas ternary systems, the performance of e-CPA on H₂O-gas, and H₂O-salt binary systems has been evaluated. Gas solubility is the maximum quantity of gaseous solutes that can dissolve in a certain quantity of solvent at a specified temperature and pressure⁷⁷. CO₂ and CH₄ are not very soluble in H₂O. The dissolution of CO₂ in H₂O contains an additional equilibrium of two acids, which can increase the solubility of CO₂ in H₂O⁷⁸. The evaluation results are presented in Table 1 together with temperature-dependent binary interaction parameters, and CO₂ is considered as a non-associating fluid in this work. On one hand, e-CPA can satisfactorily correlate the solubility

of CO₂ in water with the binary interaction parameter from literature, and large deviations are only found at low pressure and high temperature. On the other hand, with the published interaction parameters⁷⁹, e-CPA cannot describe the solubility of CH₄ in H₂O accurately for the experimental data collected in this work. This might be because the temperature range and data used in correlation are different, and it leads to a new correlation as given in Table 1. It needs to be pointed out that the existence of two liquid phases has not been taken into account in this work, and the same strategy is applied for the modelling of ternary systems below.

Table 1. Modelling performance of gas solubility in pure H₂O with e-CPA *.

Gas	k_{ij}	T [K]	Evaluation results			
			T [K]	P [MPa]	Np	AAD [%]
CO ₂	$-0.15508+0.000877 T^{80}$	298.15-	273.75-	0.095-	328	8.3
		477.6	473.15	82.88		
CH ₄	$0.6769-213.5/T^{79}$	274.0-	274.19-	0.101-	206	12.2
		473.0	444.26	100.0		
CH ₄	$0.8243-245.33/T$	274.19-	274.19-	0.101-	206	4.5
		444.26	444.26	100.0		

* The first T [K] is the temperature range used in the binary interaction parameter regression.

Np is the number of data points. The data of H₂O-CO₂ and H₂O-CH₄ are taken from

literature ^{7,10,62,73,81-87} and literature ⁸⁸⁻⁹⁴, respectively.

The binary systems of H₂O-NaCl, H₂O-KCl, H₂O-CaCl₂, H₂O-MgCl₂, and H₂O-Na₂SO₄ have been investigated previously. The modelling performance of e-CPA on mean ionic activity coefficients and osmotic coefficients of these systems are shown in Figure 1, and more details can be found in Table S3 of Supporting Information. It is readily seen that e-CPA with the binary interaction parameters from literature⁴⁹ can correlate the mean ionic activity coefficients and osmotic coefficients of H₂O-salt binary systems very well.

It is worth mentioning that the mean ionic activity coefficients and osmotic coefficients of aqueous solutions of NaCl, KCl, CaCl₂, MgCl₂ and Na₂SO₄ exhibit different trends. The activity coefficients for aqueous solutions of CaCl₂ and MgCl₂ decrease first and then increase sharply as the salt concentration increases. These properties of the aqueous Na₂SO₄ solutions are smaller than those of other systems.

Figure 1. Experimental and calculated mean ionic activity coefficients and osmotic coefficients for binary systems at 298.15 K: $\text{H}_2\text{O}-\text{NaCl}$ ^{95,96}; $\text{H}_2\text{O}-\text{KCl}$ ⁹⁷; $\text{H}_2\text{O}-\text{CaCl}_2$ ⁹⁸; $\text{H}_2\text{O}-\text{MgCl}_2$ ⁹⁹; $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4$ ¹⁰⁰. Dash lines are for mean ionic activity coefficients and solid lines are for osmotic coefficients. $\gamma_{\pm}^m$ and Φ represent mean ionic activity coefficients and osmotic coefficients, respectively.

4.2 H_2O -salt-gas Ternary Systems

The temperature dependency $T_{\Delta U_{ij}}$ was respectively set to 340 K and 300 K for chloride salts and sulfate salts in the work of Maribo-Mogensen et al.⁴⁹. In this work, three fitting approaches have been investigated for the regression of the ion-gas binary interaction parameters, as listed in Table 2. Approach A has 3 adjustable parameters (including 2 temperature-dependent parameters), Approach B has 2 adjustable parameters (including 1

temperature-dependent parameter), and Approach C has 1 adjustable parameter (no temperature-dependent parameters).

Table 2. Fitting approaches of ion-gas interaction parameters used in this work.

Approaches	$\Delta U_{ij}^{ref}/R$ [K]	$T_{\Delta U_{ij}}$ [K]	$\omega_{\Delta U_{ij}}$ [K]
A	adjustable	adjustable	adjustable
B	adjustable	340 K (for chloride salts) 300 K (for sulfate salts)	adjustable
C	adjustable	-	-

Table 3 summarizes the ion-gas binary interaction parameters and the performance of e-CPA on correlating the gas solubility with Approach A. It can be seen, on one hand, that the energy interaction parameters $\Delta U_{ij}^{ref}/R$ of ion-CO₂ and ion-CH₄ follow the same order: NaCl>KCl>CaCl₂>MgCl₂, and $\Delta U_{ij}^{ref}/R$ of Na₂SO₄-CO₂ has the highest value: 1449.66 K. On the other hand, the deviations (AAD%) are very satisfactory, less than the aforementioned experimental uncertainty 7% for most of the investigated systems. For the results of H₂O-NaCl-CH₄ system, the larger deviations of the solubility of CH₄⁶⁷ might be from high temperatures (up to 513.15 K), as the binary interaction parameters between CH₄ and H₂O are obtained by fitting the data up to 444.26 K, in a combination of the doubtful data⁶⁷ as discussed above.

Table S4 of Supporting Information lists the details of the modelling results for all three approaches. Approach A shows an overall better performance than Approaches B and C, which is to be expected as there are more adjustable parameters. It needs to be pointed out that Approach A, from a mathematical point of view, is in general more sensitive to the data used in the parameter fitting than the two other approaches. Approach A and Approach B can be recommended when there are enough data over a wide range of temperature available, while Approach C is recommended if limited data are available and extrapolations are required. With Approach C, the binary interaction parameters of Na⁺/Cl⁻-CO₂ and that of Na⁺/Cl⁻-CH₄ are not the same but close to what were reported by Maribo-Mogensen et al.⁴⁹ ($\Delta U_{ij}^{ref}/R = 816.4\text{K}$ versus 724.8 K for Na⁺/Cl⁻-CO₂, and $\Delta U_{ij}^{ref}/R = 1329\text{ K}$ versus 1128 K for Na⁺/Cl⁻-CH₄). The small differences are due to the different binary interaction parameters between H₂O and gas, as well as the different experimental data. It is a good indication that Approach C is not so sensitive to the data, and with this approach Maribo-Mogensen et al.⁴⁹ showed the predictive capability of e-CPA for the solubility of CO₂ and CH₄ in NaCl containing systems. In the following part of this work, Approach A is used except for the H₂O-MgCl₂-CH₄ system which is modeled with Approach C because of the limited number of data points.

Table 3. Ion-gas interaction parameters and model performance of e-CPA on correlating the gas solubility.

Gas	T [K]	P [MPa]	m [mol/kg water]	Np ^a	Interaction Parameters			
					$\Delta U_{ij}^{ref}/R$ [K]	$T_{\Delta U_{ij}}$ [K]	$\omega_{\Delta U_{ij}}$ [K]	AAD ^b [%]
H ₂ O-NaCl-gas								
CO ₂	273.15-523.15	0.101-141.855	0.1-6.0	435 ^{16,62,64,65,101-105}	644.84	251.07	596.44	6.6
CH ₄	298.15-513.15	2.413-89.632	0.349-5.71	137 ^{67,106,107}	1107.70	282.46	2963.99	12.0
CH ₄ ^c	298.15-398.15	2.413-61.606	0.5-4.0	57 ^{106,107}	1110.46	276.18	2499.19	3.4
CH ₄ ^c	373.15-513.15	48.26-89.632	0.349-5.71	80 ⁶⁷	849.42	305.29	1018.36	7.9
H ₂ O-KCl-gas								
CO ₂	273.35-433.1	0.101-15.81	0.1-4.5	140 ^{21,101,103,108}	510.80	449.22	-3787.54	3.9
CH ₄	298.15-373.21	0.419-9.791	0.5-4.0	98 ^{107,109}	1060.34	338.89	24562.08	8.4
H ₂ O-CaCl ₂ -gas								
CO ₂	309.28-424.43	1.53-71.21	0.117-3.0	154 ^{101,108,110-112}	199.49	703.17	-912.99	5.7
CH ₄	298.15-398.15	2.413-60.795	0.50-2.0	39 ^{66,107}	612.76	714.10	15.00	4.9

H₂O-MgCl₂-gas

CO ₂	309.58-424.63	1.25-34.93	0.333-2.0	31 ^{108,110}	96.71	378.86	4588.76	5.7
CH ₄ ^d	298.15	2.413-5.171	0.5-2.16	9 ¹⁰⁷	239.13	-	-	4.5

H₂O-Na₂SO₄-gas

CO ₂	313.11-433.16	0.422-15.0	0.333-2.01	120 ^{18,108}	1449.66	82.56	17.63	4.8
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a. N_p is the number of data points; b. AAD of gas solubility (molality of gas, [mol/kg water]); c. separate regression with different data sets as indicated by the references; d. Approach C.

Figure 2. Comparison of the model results against the experimental data of the solubility of (a) CO₂ in aqueous NaCl solution at 323.15 K^{62,65,102}; (b) CH₄ in aqueous NaCl solution at 298.15 K¹⁰⁷.

Figure 2 presents the solubilities of CO_2 and CH_4 in aqueous NaCl solution as a function of pressure at different salinity and a constant temperature. Figure 2 (a) shows that the solubility of CO_2 decreases as the NaCl concentration increases, which is a typical ‘salting-out’ effect, defined as the reduction of the solubility of a gas due to the presence of ionic species in a solvent¹¹³. Carvalho et al.¹¹⁴ and Wiebe et al.⁸² found that the increase of the brine’s salinity led to a reduction of CO_2 dissolution, regardless of the system pressure and temperature. They explained the reduction of the solubility of CO_2 in a brine solution on ‘solvation’ terms: involvement of H_2O molecules in ions solvation made the dissolved CO_2 out of the interstice of water molecules. They also pointed out that the salting-out effect was not that pronounced at low salinities, and the pressure dependency of the solubility reduced as the pressure increases^{82,114}.

Similar with CO_2 , it can be seen from Figure 2 (b) that e-CPA can correlate very well the solubility of CH_4 in aqueous NaCl solution, and the solubility of CH_4 decreases as the NaCl concentration increases. Combining with Figure S1, which presents the solubility of CH_4 in aqueous NaCl solution at different salinity and temperatures, it is also observed that the solubility of CH_4 decreases as temperature increases and pressure decreases, which is consistent with the literature^{106,107}.

Figure S2 in the Support Information show the calculated gas solubility in aqueous KCl solution as a function of pressure at different salinity and temperatures. It can be seen, similar to the aqueous NaCl solution, that gas solubility in aqueous KCl solution decreases as temperature increases and as pressure decreases. As the molality of KCl increases, the

gas solubility decreases significantly, which means that KCl has a salting-out effect on the gas solubilities of CO₂ and CH₄ in H₂O.

Figures 3 (a) and (b) present the modeling results of the solubilities of CO₂ and CH₄ in the aqueous CaCl₂ solution, respectively. More modeling results of this system are presented in the Figures S3 in the Support Information. It can be seen that CaCl₂ also has a significant salting-out effect on the solubilities of CO₂ and CH₄ in H₂O. The solubilities of both gases again increase as pressure increases. It is surprising that e-CPA can accurately capture the intersection of the solubility of CO₂ in aqueous CaCl₂ solution at 349.15K and 374.15K. This indicates that the temperature dependence of the salt-outing effect will depend on the pressure, which can also be deduced from Figure 3 (a). The solubility of CH₄ in aqueous CaCl₂ solution decreases as temperature increases.

Figures 4 (a) and (b) show the comparison of the modeling results and experimental data of the solubilities of CO₂ and CH₄ in aqueous MgCl₂ solution. Figure 4 (a) clearly shows that the solubility of CO₂ decreases as temperature increases at a constant pressure and salinity, and the solubility of CH₄ increases as pressure increases. A significant salting-out effect is also observed. It can be seen that e-CPA can accurately correlate the solubilities of CO₂ and CH₄ in aqueous MgCl₂ solution. It is worth pointing out that the molality of CaCl₂ and MgCl₂ is smaller than that of NaCl and KCl, and a more detailed comparison is given below.

(a)

(b)

Figure 3. Comparison of the modelling results against the experimental data of the solubility of (a) CO_2 in aqueous CaCl_2 solution at 349.15 K and 374.15 K¹¹²; (b) CH_4 in aqueous CaCl_2 solution at 298.15 K^{66,107}.

(a) Solubility of CO₂ at 15MPa

(b) Solubility of CH₄ at 298.15 K

Figure 4. Comparison of the modelling results against the experimental gas solubility in aqueous MgCl₂ solution: (a) CO₂ at 15 MPa¹⁰⁸; (b) CH₄ at 298.15 K¹⁰⁷.

It can be seen from Figure 5 that e-CPA can satisfactorily correlate the solubility of CO₂ in aqueous Na₂SO₄ solution, and a similar behavior of the intersection of different temperatures occurring at higher pressures might be suspected, as seen from Figure 3 (a).

Figure 5. Comparison of the modelling results against the experimental solubility of CO₂¹⁸ in aqueous Na₂SO₄ solution.

4.3 Extension to Multi-salt Systems

In this work, within the e-CPA framework, there are no binary interaction parameters between ions, and the parameters for single H₂O-salt and salt-gas can be applied to multi-salt solutions without new adjustable parameters, provided that the anion and cations are compatible, i.e. having the same cation or same anion. Maribo-Mogensen et al.⁴⁹ used the binary interaction parameters of from aqueous single-salt solutions to calculate the osmotic coefficients of aqueous multi-salt solutions (KCl+NaCl, Na₂SO₄+NaCl,

NaCl+KCl+MgCl₂) and reasonably good predictions were obtained in all cases. Table 4 lists the predictions of the osmotic coefficients and water activity for aqueous multi-salt solutions. It can be seen from Table 4 that e-CPA can give good agreement with water activity and osmotic coefficients of aqueous multi-salt solutions, except for the system H₂O-CaCl₂-MgCl₂. The large deviation of this system is because the salt molality goes far beyond the correlation range, or saying the maximum effective molality range, and the ion-pairing effect may have become an important contribution, which is not considered in e-CPA. It can be concluded that the model with single-salt (cation/anion)-H₂O interaction parameters can be used for aqueous multi-salt solutions.

Table 4. e-CPA performance for osmotic coefficients and water activity of aqueous multi-salt solutions.

Salt	T [K]	I _{max} ^a [mol/kg water]	Np	AAD [%]	
				Φ	a _w ^b
NaCl+KCl	298.15	12 ^{115,116}	57	2.3	-
		14.6 ¹¹⁷	1	-	0.3
KCl+CaCl ₂	298.15	5 ¹¹⁸	30	3.4	-
CaCl ₂ +MgCl ₂	298.15-323.15	17.0 ¹¹⁹	71	9.1	-
NaCl+KCl+MgCl ₂	298.15	14.01 ¹¹⁷	2	-	2.7

a. I_{max} is the maximum ionic strength; b. a_w is the water activity.

Compared to the solubility data of CO₂ in aqueous single-salt solutions, the sources of the solubility data in aqueous multi-salt solutions are much limited, and the predictions are presented in Table 5 and Figures 6-8. There are only few scatter data¹²⁰ of the solubility CH₄ in aqueous multi-salt solutions, Table S5 of Supporting Information lists the results of these scatter data (AAD=5.9%). It can be seen from Tables 5 and S5 and Figures 6-8 that e-CPA can very reasonably predict the gas solubility in aqueous solutions over a wide range of salt mixtures. It needs to be pointed out that Liu et al.¹⁰¹ did not clearly state which scale they used to report the solubility data, which are assumed to be salt-free in our modeling.

Table 5. Modelling performance of e-CPA for the solubility of CO₂ in aqueous multi-salt solutions with the binary interaction parameters from Table 3.

Salts	T [K]	P [MPa]	I ^a	N _p	AAD ^b [%]
NaCl+KCl	308.9-424.67	1.07-17.16	1.053, 1.69	22 ^{101,110}	4.8
NaCl+CaCl ₂	318.15	2.46-16.02	2.45	8 ¹⁰¹	4.2
KCl+CaCl ₂	318.15	2.09-15.87	2.25	8 ¹⁰¹	5.0
NaCl+KCl+CaCl ₂	308.15-328.15	1.34-15.85	1.00-3.20	75 ¹⁰¹	6.1
NaCl+KCl+CaCl ₂ + MgCl ₂	297	0.52-14.12	1.70, 2.65	84 ¹²¹	15.7

a. ionic strength [mol/kg water]; b. for gas solubility in molality.

Figure 6. Comparison of the modelling results against the experimental solubility of CO_2^{101} in aqueous solutions of two salts at $T=318.15\text{ K}$. The weight percentage of the two salts are given in the Figure legend.

Figure 7. Comparison of the modelling results against the experimental solubility of CO_2^{101} in the aqueous solutions of three salts at $T=308.15\text{ K}$ and different mass fraction of salts. The weight ratio of NaCl , KCl and CaCl_2 is 1:1:1.

Figure 8. Comparison of the modelling results against the experimental solubility of CO_2 ¹²¹ in two aqueous salt solutions: Brines A ($m\text{NaCl}=1.001$, $m\text{KCl}=0.101$, $m\text{CaCl}_2=0.100$, $m\text{MgCl}_2=0.100$, all in mol/kg water), Brines B ($m\text{NaCl}=1.396$, $m\text{KCl}=0.047$, $m\text{CaCl}_2=0.339$, $m\text{MgCl}_2=0.061$, all in mol/kg water) at 297 K.

4.4 Discussion

4.4.1 Salting Effects of Different Salts

It is known that different salts have different salting-out effects, and the ion concentration and ion charge are believed the two main factors. The studies of the ion hydration and ion- H_2O molecule interactions^{122,123} demonstrated that ions with smaller size and higher charge density bind H_2O molecules stronger, which weakens the capacity of helping solvent trap dissolved gas molecules. Anions usually have larger ionic radii than cations, so the hydration of cations is usually much stronger than that of anions¹²⁴. In order to analyze the

salting-out effect of different salts in detail, the solubilities of CO₂ and CH₄ in different aqueous salt solutions are compared in Figures 9 and 10.

(a) different salts with same molality (1.0 mol/kg water)

(b) different salts with same ionic strength (1.0 mol/kg water)

Figure 9. Comparison of the solubility of CO₂ in aqueous solutions of different salts at 323.15 K^{62,65,108,111}.

It can be seen from Figure 9 (a) that different salts exhibit different salting-out effects, and the salting-out effects on CO₂ follow a sequence of KCl<NaCl<CaCl₂ ≈ MgCl₂<Na₂SO₄ with the same molality. This is consistent with the findings from Jacob and Saylor¹²¹. Na₂SO₄ shows the strongest salting-out effect on the solubility of CO₂ mainly because 1 mol Na₂SO₄ has 2 mol Na⁺, and this is similar to the salting-out effect on the solubility of amino acids in water¹²⁵.

For KCl, NaCl, CaCl₂ and MgCl₂, the salting-out effect is significantly greater with divalent cations, because the ion charge is more important than ion size in relation to the salting-out effect in these aqueous solutions with the same salt molality.

KCl shows the weakest salting-out effect, mainly because K⁺ has a low charge density and it binds H₂O weakly, and there are more intervals to accommodate gas molecules^{101,108,122,123}. The low charge density of K⁺ comes from that K⁺, with charge of '+1', has a relatively bigger size than Na⁺, Mg²⁺ and Ca²⁺ (Pauling Radius: K⁺-1.33 Å; Na⁺-0.95 Å; Ca²⁺-0.99 Å; Mg²⁺-0.65 Å). Kiepe et al.¹⁰ observed that the salting-out effect of KCl is smaller than that of NaCl on the solubility of CO₂.

Figure 9 (b) shows that the salting-out effects on CO₂ follow a sequence of KCl<CaCl₂<MgCl₂<NaCl with the same ionic strength, and this is consistent with the work of Zhao et al.¹⁰⁸.

It can also be observed from both Figures 9 (a) and (b) that MgCl₂ and CaCl₂ have similar salting-out effects. Portier et al.⁸ pointed out that the salting-out effect of CaCl₂ or MgCl₂ on the solubility of CO₂ in aqueous solutions is lower than that of NaCl of equivalent ionic

strength, because Ca^{2+} and Mg^{2+} tended to form ion pairs easier.

Figure 10 shows that the salting-out effects on-the solubility of CH_4 follow a sequence of $\text{KCl} < \text{NaCl} < \text{MgCl}_2 \approx \text{CaCl}_2$ with the same molality, and MgCl_2 and CaCl_2 have similar salting-out effects.

Figure 10. Comparison of the solubility of CH_4 in different electrolyte aqueous solutions with the same molality (1.0 mol/kg water) at 298.15 K and $P=2.41 \text{ MPa}^{107}$.

4.4.2 Comparison with Literature Electrolyte EOS

Table 6 shows a comparison of different electrolyte EOS for gas solubility calculations in aqueous solutions of inorganic salts. In these electrolyte EOS, Zuo and Guo⁴⁰, Sun and Dubessy⁴⁵, Tan et al.⁴², and Ji et al.⁴⁸ assumed that the dielectric constant of electrolyte solution is equal to that of the solvent. Other models^{37-39,41,43,46,47} take the effect of salt presence on dielectric constant into account. e-CPA uses a theoretical model for dielectric constant calculation, which eliminates the kinetic depolarization. Søreide and Whitson³⁷, Aasberg-Petersen et al.³⁹, Haghighi et al.⁴¹, and Sun and Dubessy^{44,45} did not explicitly take the ion solvation contribution into account, while other models included the ion solvation contribution via the Born term, which is believed important for salting-out effects and thermodynamic modeling of other properties and behavior. Temperature dependency of ion-gas interactions is used in some works, and the most studied system is H₂O-NaCl-CO₂. Both Harvey and Prausnitz³⁸ and Rozmus et al.⁴⁶ stated that their models can be applied to multi-salt solutions flexibly. To the best of our knowledge, however, no electrolyte EOS has been really applied for calculating the gas solubility in aqueous multi-salt solutions. In this work, e-CPA has been extended to multi-salt systems without new adjustable parameters.

Table 6. Summary of modelling of gas solubility in aqueous solutions with electrolyte EOS.

Ref	EOS	Elect. Terms	Ion-Gas IPs	Salts
			N ₂ : 4 (T-dep ^a)	
37	PR	None	CO ₂ : 6 (T-dep)	NaCl
			H ₂ S: 2 (T-dep)	
38	P-LJ ^b	MSA+Born	1 (T-ind ^c)	NaCl, CaCl ₂
39	ALS	DH	1 (T-ind)	NaCl, CaCl ₂
40	PT	DH	1 (T-ind)	NaCl, CaCl ₂
[TW, ⁴⁹] ^d	CPA	DH+Born	3 (T-dep)	NaCl, CaCl ₂ , KCl, MgCl ₂ , Na ₂ SO ₄ , multi-salt
41	CPA	DH	5 (T-dep)	NaCl, CaCl ₂ , KCl, MgCl ₂
42	CPA	PMSA+Born	3 (T-dep)	NaCl
43	CPA	MSA+Born	3 (T-dep)	NaCl
42	PC-SAFT	PMSA	3 (T-dep)	NaCl
45	SAFT-LJ	MSA	3 (T-dep)	NaCl
46	PPC-SAFT	MSA+Born	Neglected	NaCl
47	SAFT-VR	MSA+Born	3 (T-dep)	NaCl
48	SAFT1	RPM	1 (T-ind)	NaCl

a. T-dep: Temperature-dependent; b. Short-range perturbed term with Lennard-Jones potential; c. T-ind: Temperature-independent; d. TW: This work;

Most of the electrolyte EOS listed in Table 6 perform satisfactorily at low salt molality. Harvey-Prausnitz model³⁸ overestimates CO₂ solubility (AAD $\approx$ 10-20%) at high salt molality. The model (ALS+DH) proposed by Aasberg-Petersen et al.³⁹ slightly overpredicts gas solubility at high salt molality, and the deviation between calculated and experimental values may in certain cases be 10-15%, while the deviations are somewhat larger for the aqueous CaCl₂ solution. The MPT EOS⁴⁰ shows inaccurate results for the CO₂ solubility in aqueous NaCl solution, and it can only be applied over narrow temperature ranges, probably because the temperature-dependent parameters have not been used. Although the Søreide-Whitson model³⁷ is relatively simple, it uses two different sets of interaction parameters. Thus, it is essentially an inconsistent thermodynamic model, and it cannot satisfactorily describe the solubility of CO₂ in aqueous solutions with high salt molality (by more than 20% at 50 °C in NaCl solution with molality=2 mol/kg water, and at pressures=100 bar). Tan et al.'s model⁴² (CPA+PMSA) performs poorly at high molality and pressure. Courtial et al.⁴³ used some unreliable experimental data for modelling, and the deviations of solubility are large. Sun and Dubessy^{44, 45} applied their model (SAFT-LJ+MSA) to calculate the solubility of CO₂ in aqueous NaCl solution (range from 273 to 573 K, from 0 to 1000 bar, and from 0 to 6 mol/kg NaCl). The deviation for the solubility of CO₂ with NaCl molality lower than 4 mol/kg is 3%. Schreckenberget al.⁴⁷ stated that

the performance of their model for calculating the solubility of CO_2 is not good at high salt molality. It is easy to notice that the solubility of CO_2 is higher than that of CH_4 in the same system under the same condition, which as mentioned above is probably because of the CO_2 dissociation. The chemical equilibria have not been taken into account in this work. For modelling the solubility of CO_2 with an electrolyte EOS considering chemical equilibria, readers might be referred to^{126,127}. It would be interesting to make a fair and systematic comparison for these two approaches in term of easiness of parameterization, predictive capability and flexibility of extension to multi-salt solutions.

5. Conclusion

The solubilities of CO_2 and CH_4 in several aqueous solutions of inorganic salts have been studied systematically with the e-CPA EOS. In this work. It can be concluded that e-CPA gives accurate agreements with the experimental solubility data of H_2O -gas and H_2O -salt binary systems. With temperature-dependent ion-gas interaction parameters, e-CPA gives excellent agreement with the experimental gas solubility data over wide ranges of temperature, pressure and salt molality. e-CPA also predicts satisfactory agreements with the experimental gas solubility data in aqueous multi-salt solutions, without new adjustable parameters. Moreover, e-CPA shows a good performance on the salting-out effects from temperature and pressure as well as from ion size, charge density and salt concentration.

Acknowledgments

This work is supported by the Department of Chemical and Biochemical Engineering, Technical University of Denmark and China Scholarship Council (No. 201608320224).

Supporting Information

Support Information consists of three parts: Properties and pure component parameters for e-CPA; Modelling performance of mean ionic activity coefficients and osmotic coefficients for water-salt binary systems; Modelling performance for gas solubility in aqueous single-salt and multi-salt solutions.

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