



Modeling of Gas Solubility Using the Electrolyte Cubic Plus Association Equation of State

Sun, Li; Kontogeorgis, Georgios M.; von Solms, Nicolas; Liang, Xiaodong

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>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

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

Li Sun, Georgios M. Kontogeorgis, Nicolas von Solms, and Xiaodong Liang

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

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

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

Li Sun, Georgios M. Kontogeorgis, Nicolas von Solms, Xiaodong Liang*

Center for Energy Resources Engineering

Department of Chemical and Biochemical Engineering

Technical University of Denmark

2800-Kongens Lyngby, Denmark

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 (CO₂) emissions is to capture and inject it into deep saline formations. The injected CO₂ 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 (CaCl₂), magnesium chloride (MgCl₂), and sodium sulfate (Na₂SO₄), water (H₂O), and CO₂ are the most common species in geological fluids¹. Methane (CH₄), 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 CO₂ and CH₄ 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

1
2
3
4 theory (PC-SAFT)^{29,30} have been used for modeling the fugacity coefficient (φ), while
5
6 LIFAC³¹, extended UNIQUAC³², Non-Random Two-Liquid (NRTL)³³, Pitzer's equation³⁴,
7
8 electrolyte NRTL^{35,36} and empirical correlations⁷ are typical choices for the activity
9
10 coefficient (γ). This $\varphi - \gamma$ approach usually requires many adjustable parameters (even
11
12 up to 20 for a single-salt solution²³), and it has not been used for modeling gas solubility
13
14 in multi-salt solutions.
15
16
17

18
19 An electrolyte EOS for all the phases provides a more consistent framework, as well as the
20
21 possibility to calculate other properties, e.g. density and surface tension. Some practices
22
23 have also been done for modeling the solubilities of CO₂ and CH₄ in aqueous salt
24
25 solutions³⁷⁻⁴⁹. Unfortunately, on one hand, a few electrolyte EOS can predict gas solubility
26
27 over wide ranges of temperature, pressure and salt concentration with accuracy close to the
28
29 experimental one, and fewer studies made systematic investigations. On the other hand, if
30
31 the electrolyte EOS is set up for ions, it shall in principle be working for multi-salt solutions.
32
33 To the best of our knowledge, however, no research on modeling gas solubility in aqueous
34
35 multi-salt solutions has been reported for electrolyte EOS. More discussion is presented in
36
37 Section 4.
38
39
40
41
42
43

44
45 The electrolyte cubic plus association (CPA) EOS developed by Maribo-Mogensen et al.⁴⁹
46
47 is investigated in this work for modeling the gas solubilities of CO₂ and CH₄ in single-salt
48
49 and multi-salt solutions. In the rest of the paper, the model is firstly presented, and then the
50
51 data and parameter estimation are discussed. And then the results are presented and
52
53 discussed followed by a summary discussion. Finally, the conclusion is given.
54
55
56
57

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 combing 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.

1
2
3
4 Duan et al.² reviewed the experimental data of the solubility of CH₄ in aqueous CaCl₂
5
6 solution from Blanco and Smith⁶⁶, and determined the valid range, i.e. from 25 to 125 °C
7
8 and from 100 to 600 bar. Duan et al.² pointed out that the most comprehensive data reported
9
10 for the solubility of CH₄ in aqueous NaCl solution were from Blount et al.⁶⁷, while Price et
11
12 al.⁶⁸ pointed out an experimental error in Blount et al.'s work⁶⁷, and they concluded that
13
14 about 70% of the solubility data points for pressure below 300 bar had a high deviation
15
16 (10-35%). Duan et al.² pointed out that the data from Duffy et al.⁶⁹ and Michels et al.⁷⁰
17
18 showed large uncertainties. Moreover, Duan et al.² suggested not using the solubility data
19
20 of CH₄ in aqueous NaCl solution from Barta and Bradley⁷¹ and Drummond⁶³. In a later
21
22 work, Duan et al.⁷² pointed out that experimental data for the solubility of CH₄ in aqueous
23
24 CaCl₂ solution from Duffy et al.⁶⁹ and Michels et al.⁷⁰ were unreliable, as were those in
25
26 NaCl solutions, due to adopting an inaccurate pressure decline technique. Pérez-Salado et
27
28 al.²¹ stated that the data from Kiepe et al.¹⁰ had low credibility.

29
30
31
32
33
34
35
36
37 It is known from Takenouchi and Kennedy⁷³ and Tödheide and Franck⁷⁴ that the change of
38
39 the solubility of CO₂ with pressure at temperatures above 538 K differs sharply from that
40
41 at temperatures below 538 K. In this work, therefore, the modelling temperature is set to
42
43 lower than 538 K. Moreover, the range of salt molality of most collected data follows the
44
45 work of Maribo-Mogensen et al.⁴⁹ i.e. NaCl: 6 mol/kg water, KCl: 6 mol/kg water, CaCl₂:
46
47 3 mol/kg water, MgCl₂: 2 mol/kg water, and Na₂SO₄: 2 mol/kg water.

48
49
50
51
52
53 The solubility data of CO₂ in aqueous solutions of salts other than NaCl and CaCl₂, and the
54
55 solubility data of CH₄ in aqueous solutions of salts other than NaCl, KCl and CaCl₂ are

1
2
3
4 limited. Moreover, the overlapping space is very small, and a clear conclusion cannot be
5
6 reached regarding the reliability of these data sets. For the gas solubility in aqueous multi-
7
8 salt solutions, the experimental data are limited and scattered. Therefore, all these collected
9
10 data of aqueous multi-salt solutions are considered reliable.
11
12

13 14 **3.2 Parameter Estimation**

15
16 As presented above, e-CPA is set up for ions, i.e. the model parameters are by nature ion
17
18 specific. The pure component e-CPA parameters of an ion are: b_i , Γ_i ($= a_{0i}/Rb_i$), c_{1i} ,
19
20 $\varepsilon^{A_iB_i}$, $\beta^{A_iB_i}$, d_i and $r_{Born,i}$. The binary interaction parameters of ion and another species
21
22 are: α_{ij} , ΔU_{ij}^{ref} , $\omega_{\Delta U_{ij}}$ and $T_{\Delta U_{ij}}$. In order to minimize the number of parameters, the
23
24 following assumptions have been made⁴⁹: the CPA reduced energy parameter (Γ_i) and the
25
26 temperature dependence parameter (c_{1i} in Eq. (5)) of ions are both set to zero; the ions are
27
28 assumed to be non-associating, thus eliminating the two association parameters; the three
29
30 size parameters b_i , d_i and $r_{Born,i}$ are connected with only one adjustable parameter left⁷⁵.
31
32 the NRTL non-randomness factor and the ion-ion interaction parameters are set to zero. In
33
34 this work, ion-solvent and ion-gas interaction parameters are transformed to cation/anion-
35
36 solvent, and cation/anion-gas interaction parameters, which means that the interaction
37
38 parameter $\Delta U_{cation-solvent}$ is equal to $\Delta U_{anion-solvent}$, and $U_{cation-gas}$ is equal to Δ
39
40 $U_{anion-gas}$.
41
42
43
44
45
46
47
48
49

50 The objective function used for the regression is

$$51 \quad F = \sum \left[\frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}} \right]^2 \quad (15)$$

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]	N_p	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.

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

1
2
3
4 literature ^{7,10,62,73,81-87} and literature ⁸⁸⁻⁹⁴, respectively.
5

6 The binary systems of H₂O-NaCl, H₂O-KCl, H₂O-CaCl₂, H₂O-MgCl₂, and H₂O-Na₂SO₄
7
8 have been investigated previously. The modelling performance of e-CPA on mean ionic
9
10 activity coefficients and osmotic coefficients of these systems are shown in Figure 1, and
11
12 more details can be found in Table S3 of Supporting Information. It is readily seen that e-
13
14 CPA with the binary interaction parameters from literature⁴⁹ can correlate the mean ionic
15
16 activity coefficients and osmotic coefficients of H₂O-salt binary systems very well.
17
18
19
20
21

22 It is worth mentioning that the mean ionic activity coefficients and osmotic coefficients of
23
24 aqueous solutions of NaCl, KCl, CaCl₂, MgCl₂ and Na₂SO₄ exhibit different trends. The
25
26 activity coefficients for aqueous solutions of CaCl₂ and MgCl₂ decrease first and then
27
28 increase sharply as the salt concentration increases. These properties of the aqueous
29
30 Na₂SO₄ solutions are smaller than those of other systems.
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

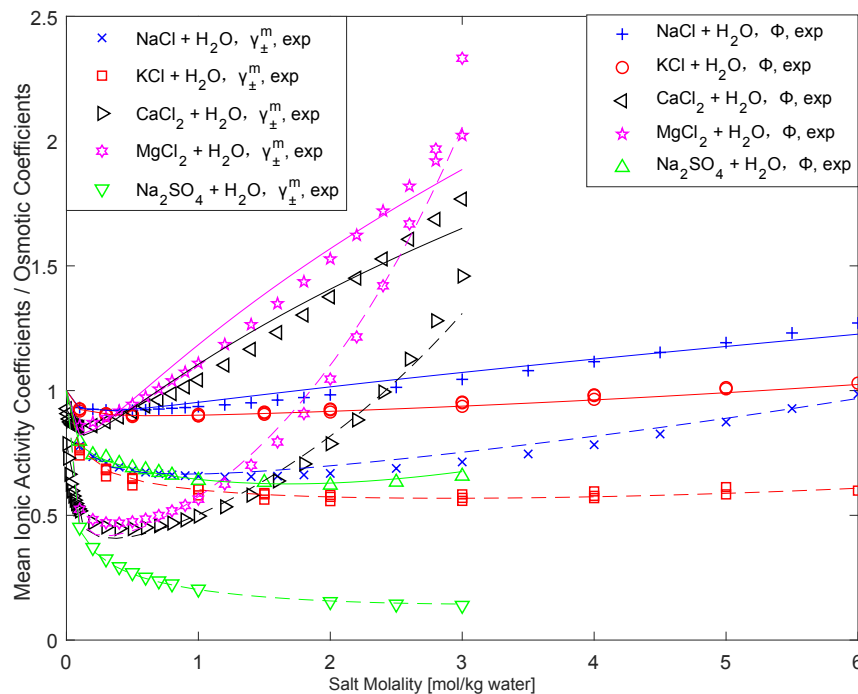


Figure 1. Experimental and calculated mean ionic activity coefficients and osmotic coefficients for binary systems at 298.15 K: $\text{H}_2\text{O}-\text{NaCl}$ ^{95,96}; $\text{H}_2\text{O}-\text{KCl}$ ⁹⁷; $\text{H}_2\text{O}-\text{CaCl}_2$ ⁹⁸; $\text{H}_2\text{O}-\text{MgCl}_2$ ⁹⁹, $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4$ ¹⁰⁰. Dash lines are for mean ionic activity coefficients and solid lines are for osmotic coefficients. γ_{\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 300K 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.

1
2
3
4 Table S4 of Supporting Information lists the details of the modelling results for all three
5
6 approaches. Approach A shows an overall better performance than Approaches B and C,
7
8 which is to be expected as there are more adjustable parameters. It needs to be pointed out
9
10 that Approach A, from a mathematical point of view, is in general more sensitive to the
11
12 data used in the parameter fitting than the two other approaches. Approach A and Approach
13
14 B can be recommended when there are enough data over a wide range of temperature
15
16 available, while Approach C is recommended if limited data are available and
17
18 extrapolations are required. With Approach C, the binary interaction parameters of Na⁺/Cl-
19
20 CO₂ and that of Na⁺/Cl-CH₄ are not the same but close to what were reported by Maribo-
21
22 Mogensen et al.⁴⁹ ($\Delta U_{ij}^{ref}/R = 816.4\text{K}$ versus 724.8 K for Na⁺/Cl-CO₂, and $\Delta U_{ij}^{ref}/R =$
23
24 1329 K versus 1128 K for Na⁺/Cl-CH₄). The small differences are due to the different
25
26 binary interaction parameters between H₂O and gas, as well as the different experimental
27
28 data. It is a good indication that Approach C is not so sensitive to the data, and with this
29
30 approach Maribo-Mogensen et al.⁴⁹ showed the predictive capability of e-CPA for the
31
32 solubility of CO₂ and CH₄ in NaCl containing systems. In the following part of this work,
33
34 Approach A is used except for the H₂O-MgCl₂-CH₄ system which is modeled with
35
36 Approach C because of the limited number of data points.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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	

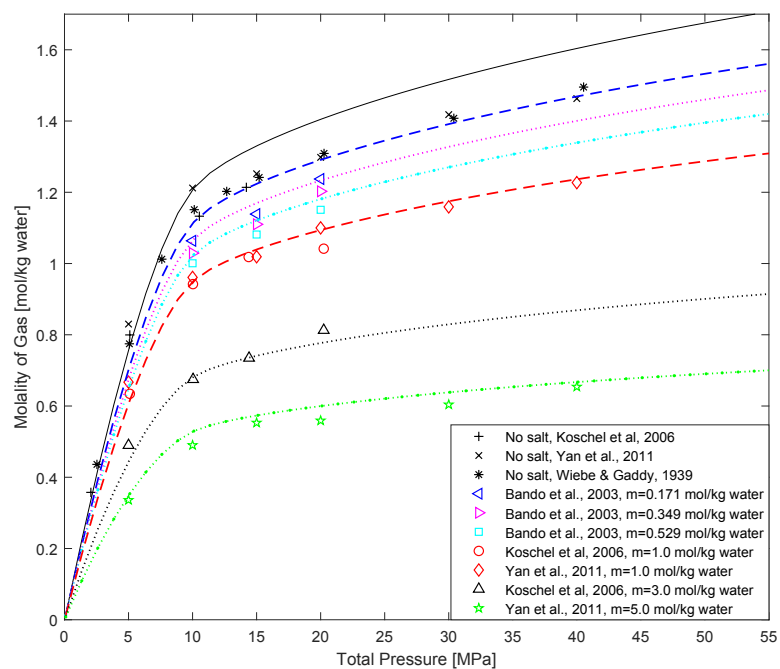
H₂O-MgCl₂-gas

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

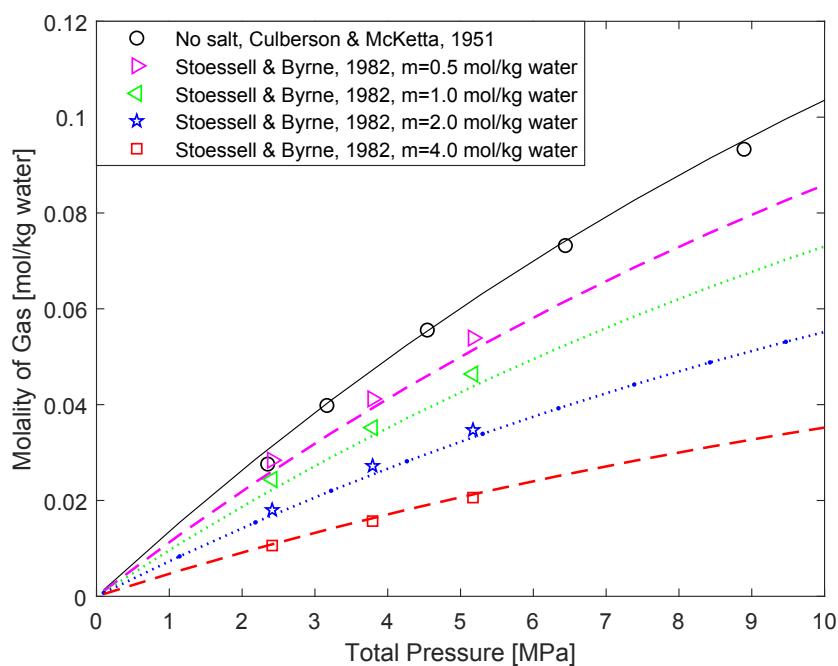
H₂O-Na₂SO₄-gas

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
-----------------	---------------	------------	------------	-----------------------	---------	-------	-------	-----

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.



(a)



(b)

Figure 2. Comparison of the model results against the experimental data of the solubility of (a) CO_2 in aqueous NaCl solution at 323.15 K^{62,65,102}; (b) CH_4 in aqueous NaCl solution at 298.15 K¹⁰⁷.

1
2
3
4 Figure 2 presents the solubilities of CO₂ and CH₄ in aqueous NaCl solution as a function
5
6 of pressure at different salinity and a constant temperature. Figure 2 (a) shows that the
7
8 solubility of CO₂ decreases as the NaCl concentration increases, which is a typical ‘salting-
9
10 out’ effect, defined as the reduction of the solubility of a gas due to the presence of ionic
11
12 species in a solvent¹¹³. Carvalho et al.¹¹⁴ and Wiebe et al.⁸² found that the increase of the
13
14 brine’s salinity led to a reduction of CO₂ dissolution, regardless of the system pressure
15
16 and temperature. They explained the reduction of the solubility of CO₂ in a brine solution
17
18 on ‘solvation’ terms: involvement of H₂O molecules in ions solvation made the dissolved
19
20 CO₂ out of the interstice of water molecules. They also pointed out that the salting-out
21
22 effect was not that pronounced at low salinities, and the pressure dependency of the
23
24 solubility reduced as the pressure increases^{82,114}.

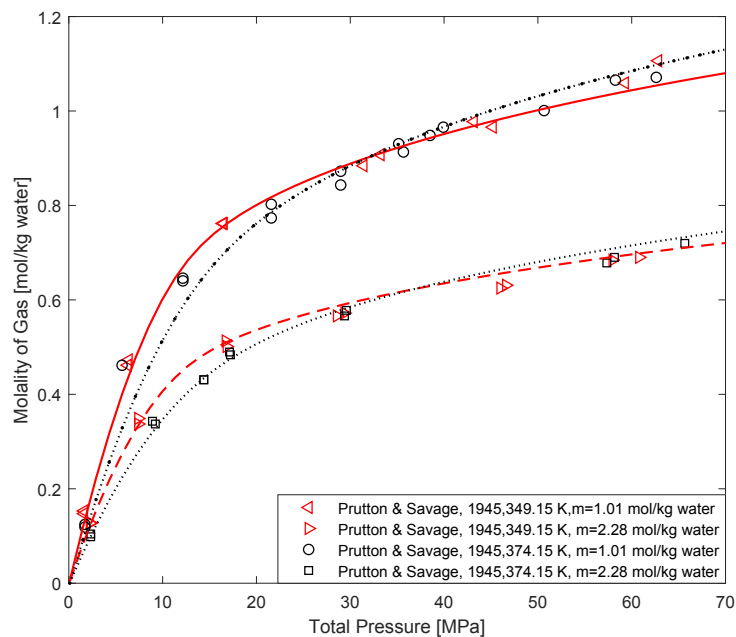
25
26
27
28
29
30
31
32 Similar with CO₂, it can be seen from Figure 2 (b) that e-CPA can correlate very well the
33
34 solubility of CH₄ in aqueous NaCl solution, and the solubility of CH₄ decreases as the NaCl
35
36 concentration increases. Combining with Figure S1, which presents the solubility of CH₄
37
38 in aqueous NaCl solution at different salinity and temperatures, it is also observed that the
39
40 solubility of CH₄ decreases as temperature increases and pressure decreases, which is
41
42 consistent with the literature^{106,107}.

43
44
45
46
47
48 Figure S2 in the Support Information show the calculated gas solubility in aqueous KCl
49
50 solution as a function of pressure at different salinity and temperatures. It can be seen,
51
52 similar to the aqueous NaCl solution, that gas solubility in aqueous KCl solution decreases
53
54 as temperature increases and as pressure decreases. As the molality of KCl increases, the
55
56
57

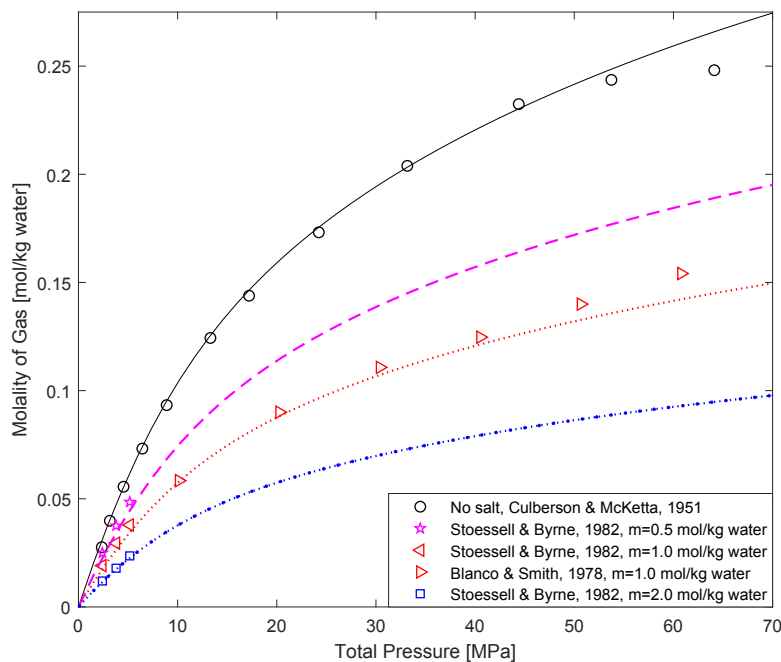
1
2
3
4 gas solubility decreases significantly, which means that KCl has a salting-out effect on the
5
6 gas solubilities of CO₂ and CH₄ in H₂O.
7

8
9 Figures 3 (a) and (b) present the modeling results of the solubilities of CO₂ and CH₄ in the
10
11 aqueous CaCl₂ solution, respectively. More modeling results of this system are presented
12
13 in the Figures S3 in the Support Information. It can be seen that CaCl₂ also has a significant
14
15 salting-out effect on the solubilities of CO₂ and CH₄ in H₂O. The solubilities of both gases
16
17 again increase as pressure increases. It is surprising that e-CPA can accurately capture the
18
19 intersection of the solubility of CO₂ in aqueous CaCl₂ solution at 349.15K and 374.15K.
20
21 This indicates that the temperature dependence of the salt-outing effect will depend on the
22
23 pressure, which can also be deduced from Figure 3 (a). The solubility of CH₄ in aqueous
24
25 CaCl₂ solution decreases as temperature increases.
26
27
28
29
30
31

32
33 Figures 4 (a) and (b) show the comparison of the modeling results and experimental data
34
35 of the solubilities of CO₂ and CH₄ in aqueous MgCl₂ solution. Figure 4 (a) clearly shows
36
37 that the solubility of CO₂ decreases as temperature increases at a constant pressure and
38
39 salinity, and the solubility of CH₄ increases as pressure increases. A significant salting-out
40
41 effect is also observed. It can be seen that e-CPA can accurately correlate the solubilities
42
43 of CO₂ and CH₄ in aqueous MgCl₂ solution. It is worth pointing out that the molality of
44
45 CaCl₂ and MgCl₂ is smaller than that of NaCl and KCl, and a more detailed comparison is
46
47
48
49
50
51 given below.
52
53
54
55
56
57
58
59
60



(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}.

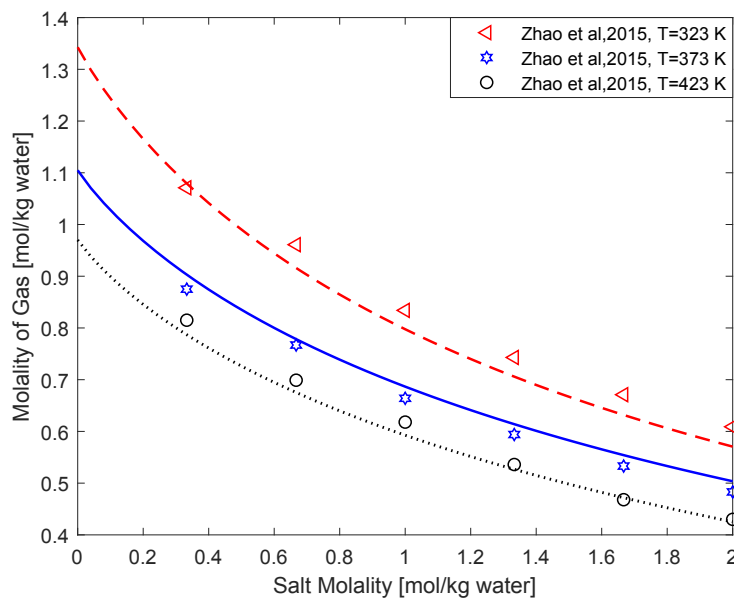
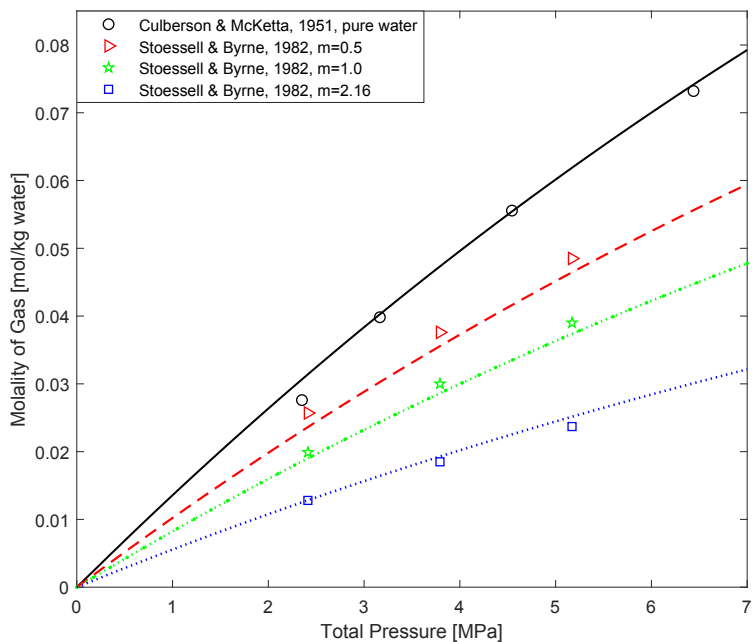
(a) Solubility of CO₂ at 15MPa(b) Solubility of CH₄ at 298.15 K

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).

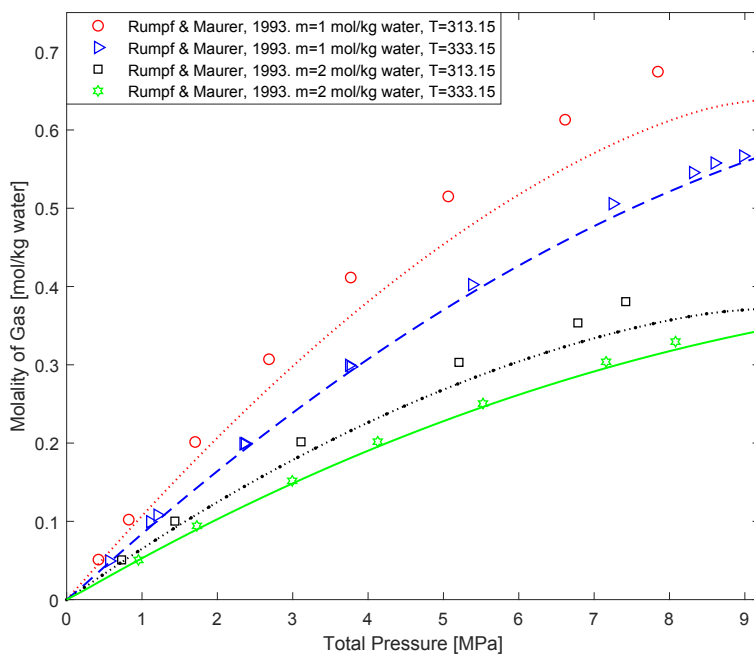


Figure 5. Comparison of the modelling results against the experimental solubility of CO₂¹⁸ in aqueous Na₂SO₄ solution.

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.

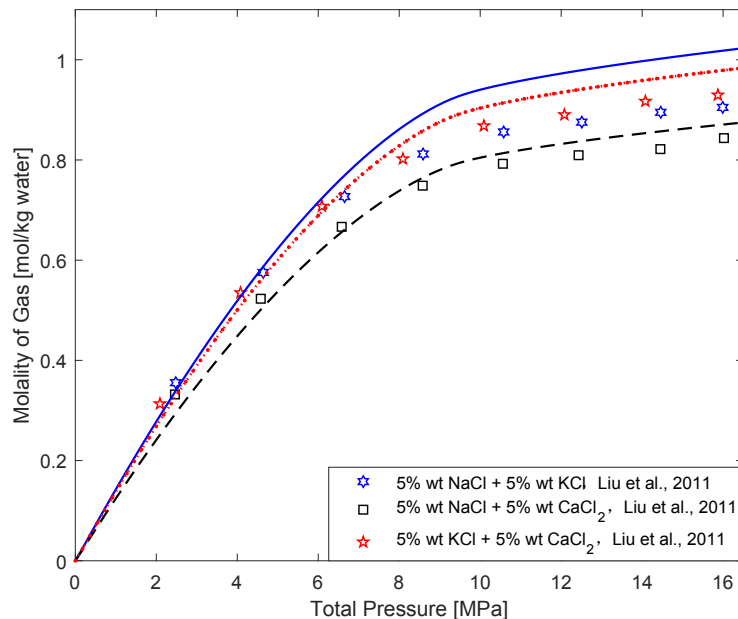


Figure 6. Comparison of the modelling results against the experimental solubility of CO₂¹⁰¹ in aqueous solutions of two salts at T= 318.15 K. The weight percentage of the two salts are given in the Figure legend.

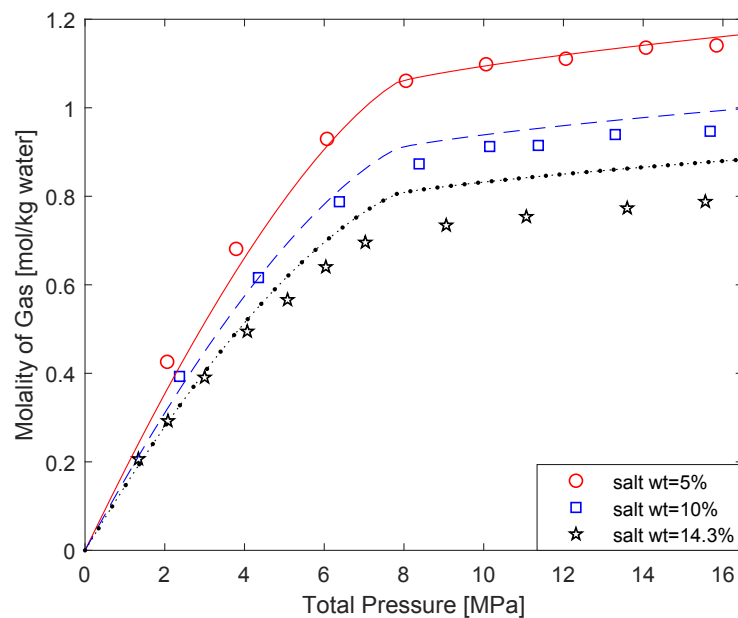


Figure 7. Comparison of the modelling results against the experimental solubility of CO₂¹⁰¹ in the aqueous solutions of three salts at T=308.15 K and different mass fraction of salts. The weight ratio of NaCl, KCl and CaCl₂ is 1:1:1.

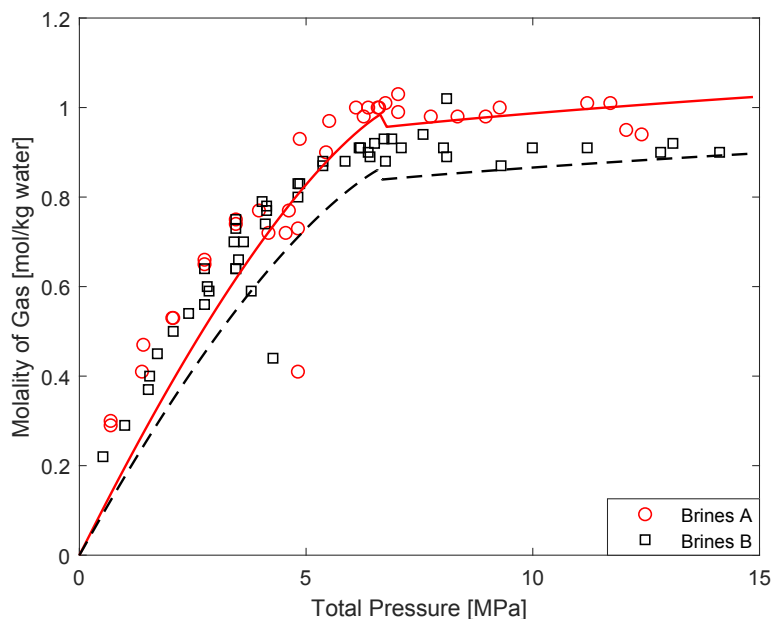


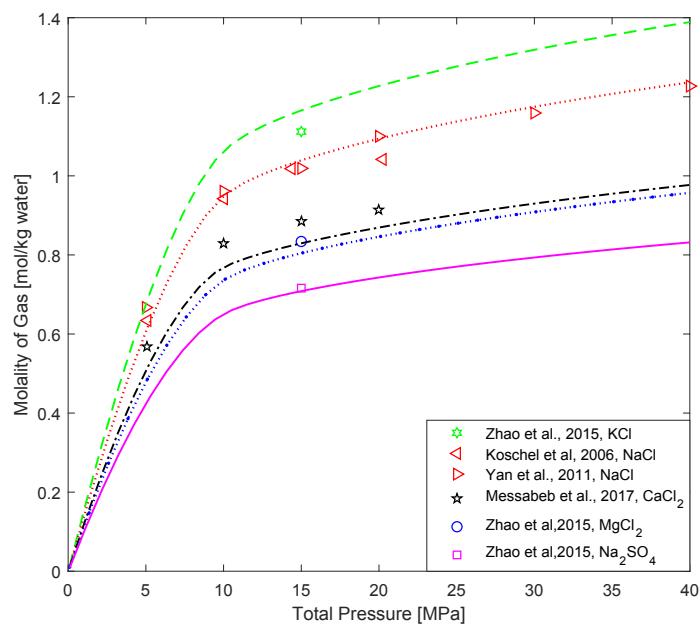
Figure 8. Comparison of the modelling results against the experimental solubility of CO_2 ¹²¹ in two aqueous salt solutions: Brines A ($m\text{NaCl}=1.001$, $m\text{KCl}=0.101$, $m\text{CaCl}_2=0.100$, $m\text{MgCl}_2=0.100$, all in mol/kg water), Brines B ($m\text{NaCl}=1.396$, $m\text{KCl}=0.047$,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

4.4 Discussion

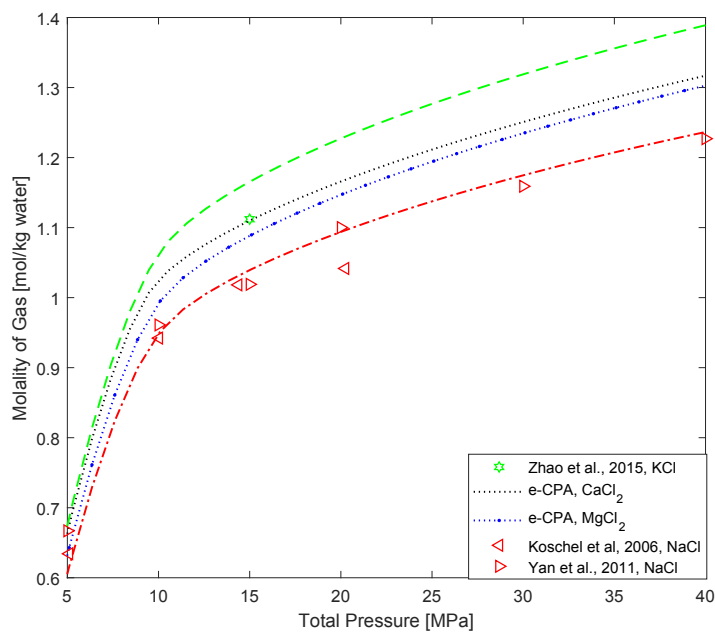
4.4.1 Salting Effects of Different Salts

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}.

1
2
3
4 It can be seen from Figure 9 (a) that different salts exhibit different salting-out effects, and
5
6 the salting-out effects on CO₂ follow a sequence of KCl<NaCl<CaCl₂ ≈ MgCl₂<Na₂SO₄
7
8 with the same molality. This is consistent with the findings from Jacob and Saylor¹²¹.
9
10 Na₂SO₄ shows the strongest salting-out effect on the solubility of CO₂ mainly because 1
11
12 mol Na₂SO₄ has 2 mol Na⁺, and this is similar to the salting-out effect on the solubility of
13
14 amino acids in water¹²⁵.
15
16

17
18 For KCl, NaCl, CaCl₂ and MgCl₂, the salting-out effect is significantly greater with
19
20 divalent cations, because the ion charge is more important than ion size in relation to the
21
22 salting-out effect in these aqueous solutions with the same salt molality.
23
24

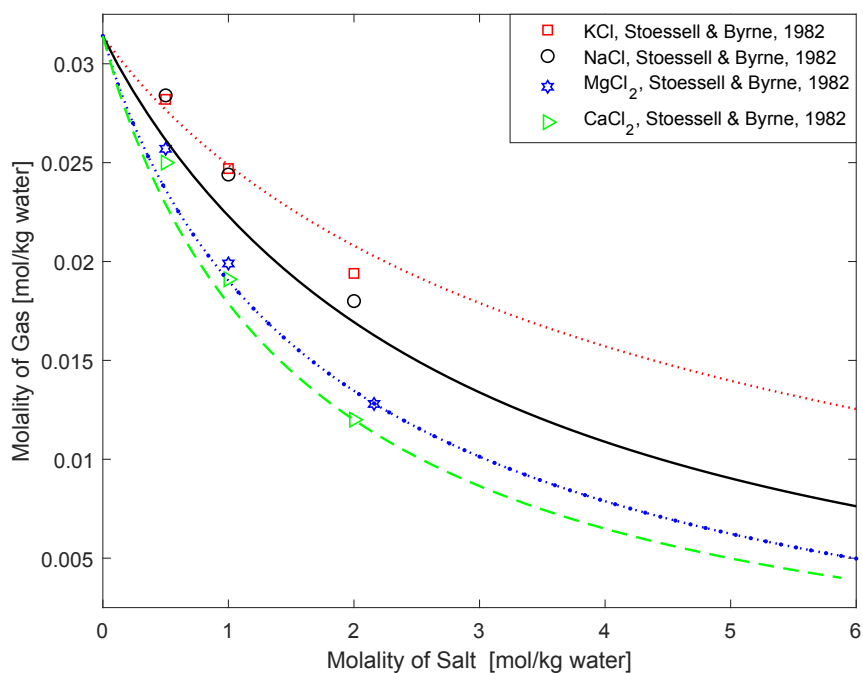
25
26 KCl shows the weakest salting-out effect, mainly because K⁺ has a low charge density and
27
28 it binds H₂O weakly, and there are more intervals to accommodate gas
29
30 molecules^{101,108,122,123}. The low charge density of K⁺ comes from that K⁺, with charge of
31
32 ‘+1’, has a relatively bigger size than Na⁺, Mg²⁺ and Ca²⁺ (Pauling Radius: K⁺-1.33 Å; Na⁺-
33
34 0.95 Å; Ca²⁺-0.99 Å; Mg²⁺-0.65 Å). Kiepe et al.¹⁰ observed that the salting-out effect of
35
36 KCl is smaller than that of NaCl on the solubility of CO₂.
37
38

39
40 Figure 9 (b) shows that the salting-out effects on CO₂ follow a sequence of
41
42 KCl<CaCl₂<MgCl₂<NaCl with the same ionic strength, and this is consistent with the work
43
44 of Zhao et al.¹⁰⁸.
45
46

47
48 It can also be observed from both Figures 9 (a) and (b) that MgCl₂ and CaCl₂ have similar
49
50 salting-out effects. Portier et al.⁸ pointed out that the salting-out effect of CaCl₂ or MgCl₂
51
52 on the solubility of CO₂ in aqueous solutions is lower than that of NaCl of equivalent ionic
53
54
55
56
57

1
2
3
4 strength, because Ca^{2+} and Mg^{2+} tended to form ion pairs easier.
5
6
7
8

9 Figure 10 shows that the salting-out effects on-the solubility of CH_4 follow a sequence of
10
11 $\text{KCl} < \text{NaCl} < \text{MgCl}_2 \approx \text{CaCl}_2$ with the same molality, and MgCl_2 and CaCl_2 have similar
12
13 salting-out effects.
14
15
16
17
18



19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40 Figure 10. Comparison of the solubility of CH_4 in different electrolyte aqueous solutions
41
42 with the same molality (1.0 mol/kg water) at 298.15 K and $P=2.41 \text{ MPa}^{107}$.
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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, Haghghi 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

1
2
3
4 a. T-dep: Temperature-dependent; b. Short-range perturbed term with Lennard-Jones
5
6 potential; c. T-ind: Temperature-independent; d. TW: This work;
7
8
9

10
11 Most of the electrolyte EOS listed in Table 6 perform satisfactorily at low salt molality.
12
13 Harvey-Prausnitz model³⁸ overestimates CO₂ solubility (AAD ≈ 10-20%) at high salt
14
15 molality. The model (ALS+DH) proposed by Aasberg-Petersen et al.³⁹ slightly
16
17 overpredicts gas solubility at high salt molality, and the deviation between calculated and
18
19 experimental values may in certain cases be 10-15%, while the deviations are somewhat
20
21 larger for the aqueous CaCl₂ solution. The MPT EOS⁴⁰ shows inaccurate results for the
22
23 CO₂ solubility in aqueous NaCl solution, and it can only be applied over narrow
24
25 temperature ranges, probably because the temperature-dependent parameters have not been
26
27 used. Although the Søreide-Whitson model³⁷ is relatively simple, it uses two different sets
28
29 of interaction parameters. Thus, it is essentially an inconsistent thermodynamic model, and
30
31 it cannot satisfactorily describe the solubility of CO₂ in aqueous solutions with high salt
32
33 molality (by more than 20% at 50 °C in NaCl solution with molality=2 mol/kg water, and
34
35 at pressures=100 bar). Tan et al.'s model⁴² (CPA+PMSA) performs poorly at high molality
36
37 and pressure. Courtial et al.⁴³ used some unreliable experimental data for modelling, and
38
39 the deviations of solubility are large. Sun and Dubessy^{44, 45} applied their model (SAFT-
40
41 LJ+MSA) to calculate the solubility of CO₂ in aqueous NaCl solution (range from 273 to
42
43 573 K, from 0 to 1000 bar, and from 0 to 6 mol/kg NaCl). The deviation for the solubility
44
45 of CO₂ with NaCl molality lower than 4 mol/kg is 3%. Schreckenberget al.⁴⁷ stated that
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 the performance of their model for calculating the solubility of CO₂ is not good at high salt
5
6 molality. It is easy to notice that the solubility of CO₂ is higher than that of CH₄ in the same
7
8 system under the same condition, which as mentioned above is probably because of the
9
10 CO₂ dissociation. The chemical equilibria have not been taken into account in this work.
11
12 For modelling the solubility of CO₂ with an electrolyte EOS considering chemical
13
14 equilibria, readers might be referred to^{126,127}. It would be interesting to make a fair and
15
16 systematic comparison for these two approaches in term of easiness of parameterization,
17
18 predictive capability and flexibility of extension to multi-salt solutions.
19
20
21
22
23
24
25
26

27 **5. Conclusion**

28
29
30 The solubilities of CO₂ and CH₄ in several aqueous solutions of inorganic salts have been
31
32 studied systematically with the e-CPA EOS. In this work. It can be concluded that e-CPA
33
34 gives accurate agreements with the experimental solubility data of H₂O-gas and H₂O-salt
35
36 binary systems. With temperature-dependent ion-gas interaction parameters, e-CPA gives
37
38 excellent agreement with the experimental gas solubility data over wide ranges of
39
40 temperature, pressure and salt molality. e-CPA also predicts satisfactory agreements with
41
42 the experimental gas solubility data in aqueous multi-salt solutions, without new adjustable
43
44 parameters. Moreover, e-CPA shows a good performance on the salting-out effects from
45
46 temperature and pressure as well as from ion size, charge density and salt concentration.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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.

Author Information

Corresponding author:

E-mail address: xlia@kt.dtu.dk, Tel.: 0045-4525 2877.

Reference

- (1) Fyfe, W. S.: *Fluids In The Earth's Crust: Their Significance In Metamorphic, Tectonic And Chemical Transport Process*; Elsevier, 2012; Vol. 1.
- (2) Duan, Z.; Møller, N.; Greenberg, J.; Weare, J. H. The prediction of methane solubility in natural waters to high ionic strength from 0 to 250 C and from 0 to 1600 bar. *Geochimica et Cosmochimica Acta* **1992**, *56*, 1451-1460.
- (3) Sloan Jr, E. D.; Koh, C. A.: *Clathrate hydrates of natural gases*; CRC press, 2007.
- (4) Roedder, E. The fluids in salt. *American Mineralogist* **1984**, *69*, 413-439.
- (5) Millero, F. J. Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta* **1995**, *59*, 661-677.
- (6) Li, Y. K.; Nghiem, L. X. Phase equilibria of oil, gas and water/brine mixtures from a cubic equation of state and Henry's law. *The Canadian Journal of Chemical Engineering* **1986**, *64*, 486-496.
- (7) Nighswander, J. A.; Kalogerakis, N.; Mehrotra, A. K. Solubilities of carbon dioxide in water and 1 wt.% sodium chloride solution at pressures up to 10 MPa and temperatures from 80 to 200. degree. C. *Journal of Chemical and Engineering Data* **1989**, *34*, 355-360.
- (8) Portier, S.; Rochelle, C. Modelling CO₂ solubility in pure water and NaCl-type waters from 0 to 300 C and from 1 to 300 bar: Application to the Utsira Formation at Sleipner. *Chemical Geology* **2005**, *217*, 187-199.
- (9) Li, J.; Topp hoff, M.; Fischer, K.; Gmehling, J. Prediction of gas solubilities in aqueous electrolyte systems using the predictive Soave– Redlich– Kwong model. *Industrial &*

1
2
3
4 *engineering chemistry research* **2001**, *40*, 3703-3710.

5
6
7 (10) Kiepe, J.; Horstmann, S.; Fischer, K.; Gmehling, J. Experimental determination and
8
9 prediction of gas solubility data for CO₂+ H₂O mixtures containing NaCl or KCl at
10
11 temperatures between 313 and 393 K and pressures up to 10 MPa. *Industrial &*
12
13 *Engineering Chemistry Research* **2002**, *41*, 4393-4398.

14
15
16
17 (11) García, A. V.; Thomsen, K.; Stenby, E. H. Prediction of mineral scale formation in
18
19 geothermal and oilfield operations using the Extended UNIQUAC model: Part II.
20
21 Carbonate-scaling minerals. *Geothermics* **2006**, *35*, 239-284.

22
23
24
25 (12) Sørensen, H.; Pedersen, K. S.; Christensen, P. L. Modeling of gas solubility in brine.
26
27 *Organic Geochemistry* **2002**, *33*, 635-642.

28
29
30 (13) Spycher, N.; Pruess, K.; Ennis-King, J. CO₂-H₂O mixtures in the geological
31
32 sequestration of CO₂. I. Assessment and calculation of mutual solubilities from 12 to 100
33
34 C and up to 600 bar. *Geochimica et cosmochimica acta* **2003**, *67*, 3015-3031.

35
36
37
38 (14) Spycher, N.; Pruess, K. CO₂-H₂O Mixtures in the Geological Sequestration of CO₂.
39
40 II. Partitioning in Chloride Brines at 12–100 C and up to 600 bar. *Geochimica et*
41
42 *Cosmochimica Acta* **2005**, *69*, 3309-3320.

43
44
45
46 (15) Spycher, N.; Pruess, K. A phase-partitioning model for CO₂-brine mixtures at
47
48 elevated temperatures and pressures: application to CO₂-enhanced geothermal systems.
49
50 *Transport in porous media* **2010**, *82*, 173-196.

51
52
53 (16) Rumpf, B.; Nicolaisen, H.; Öcal, C.; Maurer, G. Solubility of carbon dioxide in
54
55 aqueous solutions of sodium chloride: experimental results and correlation. *Journal of*
56
57

1
2
3
4 *solution chemistry* **1994**, 23, 431-448.

5
6
7 (17) Duan, Z.; Sun, R. An improved model calculating CO₂ solubility in pure water and
8
9 aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical geology*
10
11 **2003**, 193, 257-271.

12
13
14 (18) Rumpf, B.; Maurer, G. An experimental and theoretical investigation on the solubility
15
16 of carbon dioxide in aqueous solutions of strong electrolytes. *Berichte der*
17
18 *Bunsengesellschaft fuer physikalische chemie* **1993**, 97, 85-97.

19
20
21 (19) Zhao, H.; Fedkin, M. V.; Dilmore, R. M.; Lvov, S. N. Carbon dioxide solubility in
22
23 aqueous solutions of sodium chloride at geological conditions: Experimental results at
24
25 323.15, 373.15, and 423.15 K and 150 bar and modeling up to 573.15 K and 2000 bar.
26
27 *Geochimica et Cosmochimica Acta* **2015**, 149, 165-189.

28
29
30 (20) Masoudi, R.; Tohidi, B.; Danesh, A.; Todd, A. C. A new approach in modelling phase
31
32 equilibria and gas solubility in electrolyte solutions and its applications to gas hydrates.
33
34 *Fluid Phase Equilibria* **2004**, 215, 163-174.

35
36
37 (21) Pérez-Salado Kamps, Á.; Meyer, E.; Rumpf, B.; Maurer, G. Solubility of CO₂ in
38
39 aqueous solutions of KCl and in aqueous solutions of K₂CO₃. *Journal of Chemical &*
40
41 *Engineering Data* **2007**, 52, 817-832.

42
43
44 (22) Yan, Y.; Chen, C.-C. Thermodynamic modeling of CO₂ solubility in aqueous
45
46 solutions of NaCl and Na₂SO₄. *The Journal of Supercritical Fluids* **2010**, 55, 623-634.

47
48
49 (23) Duan, Z.; Møller, N.; Weare, J. H. An equation of state for the CH₄-CO₂-H₂O system:
50
51 II. Mixtures from 50 to 1000 C and 0 to 1000 bar. *Geochimica et Cosmochimica Acta* **1992**,

1
2
3
4 56, 2619-2631.
5

6 (24)Duan, Z.; Møller, N.; Weare, J. H. An equation of state for the CH₄-CO₂-H₂O system:
7
8 I. Pure systems from 0 to 1000 C and 0 to 8000 bar. *Geochimica et Cosmochimica Acta*
9
10
11 **1992**, 56, 2605-2617.
12

13
14 (25)Peng, D.-Y.; Robinson, D. B. A new two-constant equation of state. *Industrial &*
15
16
17 *Engineering Chemistry Fundamentals* **1976**, 15, 59-64.
18

19 (26)Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state.
20
21
22 *Chemical engineering science* **1972**, 27, 1197-1203.
23

24 (27)Redlich, O.; Kwong, J. N. On the thermodynamics of solutions. V. An equation of
25
26
27 state. Fugacities of gaseous solutions. *Chemical reviews* **1949**, 44, 233-244.
28

29 (28)Avlonitis, D.; Danesh, A.; Todd, A. Prediction of VL and VLL equilibria of mixtures
30
31
32 containing petroleum reservoir fluids and methanol with a cubic EoS. *Fluid Phase*
33
34
35 *Equilibria* **1994**, 94, 181-216.
36

37 (29)Gross, J.; Sadowski, G. Perturbed-chain SAFT: An equation of state based on a
38
39
40 perturbation theory for chain molecules. *Industrial & engineering chemistry research* **2001**,
41
42
43 *40*, 1244-1260.
44

45 (30)Gross, J.; Sadowski, G. Application of the perturbed-chain SAFT equation of state to
46
47
48 associating systems. *Industrial & engineering chemistry research* **2002**, 41, 5510-5515.
49

50 (31)Li, J.; Polka, H.-M.; Gmehling, J. A gE model for single and mixed solvent electrolyte
51
52
53 systems: 1. Model and results for strong electrolytes. *Fluid Phase Equilibria* **1994**, 94, 89-
54
55
56 114.
57

1
2
3
4 (32)Thomsen, K.; Rasmussen, P. Modeling of vapor–liquid–solid equilibrium in gas–
5 aqueous electrolyte systems. *Chemical Engineering Science* **1999**, *54*, 1787-1802.

6
7
8
9 (33)Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions
10 for liquid mixtures. *AIChE Journal* **1968**, *14*, 135-144.

11
12
13
14 (34)Pitzer, K. The Nature of the Chemical Bond and the Structure of Molecules and
15 Crystals: An Introduction to Modern Structural Chemistry. *Journal of the American*
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

(35)Chen, C. C.; Britt, H. I.; Boston, J.; Evans, L. Local composition model for excess
Gibbs energy of electrolyte systems. Part I: Single solvent, single completely dissociated
electrolyte systems. *AIChE Journal* **1982**, *28*, 588-596.

(36)Song, Y.; Chen, C.-C. Symmetric electrolyte nonrandom two-liquid activity
coefficient model. *Industrial & Engineering Chemistry Research* **2009**, *48*, 7788-7797.

(37)Søreide, I.; Whitson, C. H. Peng-Robinson predictions for hydrocarbons, CO₂, N₂,
and H₂ S with pure water and NaCl brine. *Fluid Phase Equilibria* **1992**, *77*, 217-240.

(38)Harvey, A. H.; Prausnitz, J. M. Thermodynamics of high-pressure aqueous systems
containing gases and salts. *AIChE Journal* **1989**, *35*, 635-644.

(39)Aasberg-Petersen, K.; Stenby, E.; Fredenslund, A. Prediction of high-pressure gas
solubilities in aqueous mixtures of electrolytes. *Industrial & engineering chemistry*
research **1991**, *30*, 2180-2185.

(40)Zuo, Y.-X.; Guo, T.-M. Extension of the Patel—Teja equation of state to the prediction
of the solubility of natural gas in formation water. *Chemical Engineering Science* **1991**,

1
2
3
4 46, 3251-3258.
5

6 (41) Haghghi, H.; Chapoy, A.; Tohidi, B. Methane and water phase equilibria in the
7 presence of single and mixed electrolyte solutions using the cubic-plus-association
8 equation of state. *Oil & Gas Science and Technology-Revue de l'IFP* **2009**, *64*, 141-154.
9
10

11 (42) Tan, S. P.; Yao, Y.; Piri, M. Modeling the solubility of SO₂+ CO₂ mixtures in brine
12 at elevated pressures and temperatures. *Industrial & Engineering Chemistry Research* **2013**,
13
14
15
16
17
18
19
20
21
22 52, 10864-10872.

23 (43) Courtial, X.; Ferrando, N.; De Hemptinne, J.-C.; Mougín, P. Electrolyte CPA equation
24 of state for very high temperature and pressure reservoir and basin applications.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Geochimica et Cosmochimica Acta **2014**, *142*, 1-14.

(44) Sun, R.; Dubessy, J. Prediction of vapor–liquid equilibrium and PVT_x properties of
geological fluid system with SAFT-LJ EOS including multi-polar contribution. Part I:
Application to H₂O–CO₂ system. *Geochimica et Cosmochimica Acta* **2010**, *74*, 1982-1998.

(45) Sun, R.; Dubessy, J. Prediction of vapor–liquid equilibrium and PVT_x properties of
geological fluid system with SAFT-LJ EOS including multi-polar contribution. Part II:
Application to H₂O–NaCl and CO₂–H₂O–NaCl System. *Geochimica et Cosmochimica
Acta* **2012**, *88*, 130-145.

(46) Rozmus, J.; de Hemptinne, J.-C.; Galindo, A.; Dufal, S.; Mougín, P. Modeling of
strong electrolytes with ePPC-SAFT up to high temperatures. *Industrial & Engineering
Chemistry Research* **2013**, *52*, 9979-9994.

(47) Schreckenber, J. M.; Dufal, S.; Haslam, A. J.; Adjiman, C. S.; Jackson, G.; Galindo,

1
2
3
4 A. Modelling of the thermodynamic and solvation properties of electrolyte solutions with
5
6 the statistical associating fluid theory for potentials of variable range. *Molecular Physics*
7
8 **2014**, *112*, 2339-2364.

9
10
11 (48) Ji, X.; Tan, S. P.; Adidharma, H.; Radosz, M. SAFT1-RPM approximation extended
12
13 to phase equilibria and densities of CO₂-H₂O and CO₂-H₂O-NaCl systems. *Industrial*
14
15 *& engineering chemistry research* **2005**, *44*, 8419-8427.

16
17
18 (49) Maribo-Mogensen, B.; Thomsen, K.; Kontogeorgis, G. M. An electrolyte CPA
19
20 equation of state for mixed solvent electrolytes. *AIChE Journal* **2015**, *61*, 2933-2950.

21
22 (50) Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An equation of
23
24 state for associating fluids. *Industrial & engineering chemistry research* **1996**, *35*, 4310-
25
26 4318.

27
28 (51) Debye, P.; Huckel, E. *Phys. Z.*, *24*, 185 (1923); P. Debye. *Phys. Z* **1924**, *25*, 93.

29
30 (52) Born, M. Volumen und hydrationswärme der ionen. *Zeitschrift für Physik A Hadrons*
31
32 *and Nuclei* **1920**, *1*, 45-48.

33
34 (53) Breil, M. P.; Kontogeorgis, G. M.; Behrens, P. K.; Michelsen, M. L. Modeling of the
35
36 thermodynamics of the acetic acid- water mixture using the cubic-plus-association
37
38 equation of state. *Industrial & Engineering Chemistry Research* **2011**, *50*, 5795-5805.

39
40 (54) Michelsen, M. L.; Mollerup, J. Thermodynamics models; fundamentals and
41
42 computational aspects. **1996**.

43
44 (55) Wertheim, M. Fluids with highly directional attractive forces. I. Statistical
45
46 thermodynamics. *Journal of statistical physics* **1984**, *35*, 19-34.

1
2
3
4 (56)Wertheim, M. Fluids with highly directional attractive forces. II. Thermodynamic
5
6 perturbation theory and integral equations. *Journal of statistical physics* **1984**, *35*, 35-47.

7
8
9 (57)Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New reference equation of
10
11 state for associating liquids. *Industrial & Engineering Chemistry Research* **1990**, *29*, 1709-
12
13 1721.

14
15
16 (58)Michelsen, M. L.; Hendriks, E. M. Physical properties from association models. *Fluid*
17
18 *phase equilibria* **2001**, *180*, 165-174.

19
20
21 (59)Myers, J. A.; Sandler, S. I.; Wood, R. H. An equation of state for electrolyte solutions
22
23 covering wide ranges of temperature, pressure, and composition. *Industrial & engineering*
24
25 *chemistry research* **2002**, *41*, 3282-3297.

26
27
28 (60)Ben-Naim, A. Thermodynamics of aqueous solutions of noble gases. I. *The Journal of*
29
30 *Physical Chemistry* **1965**, *69*, 3240-3245.

31
32
33 (61)Maribo-Mogensen, B.; Kontogeorgis, G. M.; Thomsen, K. Modeling of dielectric
34
35 properties of aqueous salt solutions with an equation of state. *The Journal of Physical*
36
37 *Chemistry B* **2013**, *117*, 10523-10533.

38
39
40 (62)Yan, W.; Huang, S.; Stenby, E. H. Measurement and modeling of CO₂ solubility in
41
42 NaCl brine and CO₂-saturated NaCl brine density. *International Journal of Greenhouse*
43
44 *Gas Control* **2011**, *5*, 1460-1477.

45
46
47 (63)Drummond, S. Boiling and Mixing of Hydrothermal Fluids: Chemical Effects on
48
49 Mineral Precipitation. **1982**.

50
51
52 (64)Takenouchi, S.; Kennedy, G. C. The solubility of carbon dioxide in NaCl solutions at
53
54
55

- 1
2
3
4 high temperatures and pressures. *American journal of science* **1965**, 263, 445-454.
5
6
7 (65)Koschel, D.; Coxam, J.-Y.; Rodier, L.; Majer, V. Enthalpy and solubility data of CO₂
8
9 in water and NaCl (aq) at conditions of interest for geological sequestration. *Fluid phase*
10
11 *equilibria* **2006**, 247, 107-120.
12
13
14 (66)Blanco C, L. H.; Smith, N. O. The high pressure solubility of methane in aqueous
15
16 calcium chloride and aqueous tetraethylammonium bromide. Partial molar properties of
17
18 dissolved methane and nitrogen in relation to water structure. *The Journal of Physical*
19
20 *Chemistry* **1978**, 82, 186-191.
21
22
23 (67)Blount, C. W.; Price, L. C.; Wenger, L. M.; Tarullo, M. Methane solubility in aqueous
24
25 NaCl solutions at elevated temperatures and pressures. *Proc. 4th US* **1979**, 1225-1262.
26
27
28 (68)Price, L.; Blount, C.; Gowan, D.; Wenger, L.; Bebout, D.; Bachman, A. *Methane*
29
30 *solubility in brines with application to the geopressured resource*1981.
31
32
33 (69)Duffy, J. R.; Smith, N. O.; Nagy, B. Solubility of natural gases in aqueous salt
34
35 solutions—I: Liquidus surfaces in the system CH₄-H₂O-NaCl₂-CaCl₂ at room
36
37 temperatures and at pressures below 1000 psia. *Geochimica et Cosmochimica Acta* **1961**,
38
39 24, 23-31.
40
41
42 (70)Michels, A.; Gerver, J.; Bijl, A. The influence of pressure on the solubility of gases.
43
44 *Physica* **1936**, 3, 797-808.
45
46
47 (71)Barta, L.; Bradley, D. J. Extension of the specific interaction model to include gas
48
49 solubilities in high temperature brines. *Geochimica et cosmochimica Acta* **1985**, 49, 195-
50
51 203.
52
53
54
55
56
57
58
59
60

1
2
3
4 (72)Duan, Z.; Mao, S. A thermodynamic model for calculating methane solubility, density
5
6 and gas phase composition of methane-bearing aqueous fluids from 273 to 523 K and from
7
8 1 to 2000 bar. *Geochimica et Cosmochimica Acta* **2006**, *70*, 3369-3386.

9
10
11 (73)Takenouchi, S.; Kennedy, G. C. The binary system H₂O-CO₂ at high temperatures
12
13 and pressures. *American Journal of Science* **1964**, *262*, 1055-1074.

14
15
16 (74)Tödheide, K.; Franck, E. Das Zweiphasengebiet und die kritische Kurve im System
17
18 Kohlendioxid–Wasser bis zu Drucken von 3500 bar. *Zeitschrift für Physikalische Chemie*
19
20 **1963**, *37*, 387-401.

21
22
23 (75)Sun, L.; Liang, X.; Von Solms, N.; Kontogeorgis, G. M. Modeling Tetra-n-butyl
24
25 ammonium halides aqueous solutions with the electrolyte cubic plus association equation
26
27 of state. *Fluid Phase Equilibria* **2019**, *486*, 37-47.

28
29
30 (76)Liang, X. Numerical aspects of phase equilibrium calculations with the cubic and
31
32 association models. *Industrial & Engineering Chemistry Research* **2018**, *57*, 14273-14285.

33
34
35 (77)Silberberg, M. S.: *Principles of general chemistry*; McGraw-Hill Higher Education
36
37 New York, 2007.

38
39
40 (78)Reid, R. C.; Prausnitz, J. M.; Poling, B. E. The properties of gases and liquids. **1987**.

41
42
43 (79)Yan, W.; Kontogeorgis, G. M.; Stenby, E. H. Application of the CPA equation of state
44
45 to reservoir fluids in presence of water and polar chemicals. *Fluid Phase Equilibria* **2009**,
46
47 *276*, 75-85.

48
49
50 (80)Tsvintzelis, I.; Kontogeorgis, G. M.; Michelsen, M. L.; Stenby, E. H. Modeling phase
51
52 equilibria for acid gas mixtures using the CPA equation of state. Part II: Binary mixtures
53
54
55
56
57

1
2
3
4 with CO₂. *Fluid Phase Equilibria* **2011**, *306*, 38-56.

5
6 (81) King, M.; Mubarak, A.; Kim, J.; Bott, T. The mutual solubilities of water with
7
8
9
10
11
12
13 supercritical and liquid carbon dioxides. *The Journal of Supercritical Fluids* **1992**, *5*, 296-
302.

14 (82) Wiebe, R.; Gaddy, V. The solubility in water of carbon dioxide at 50, 75 and 100, at
15
16
17
18
19
20
21 pressures to 700 atmospheres. *Journal of the American Chemical Society* **1939**, *61*, 315-
318.

22 (83) Valtz, A.; Chapoy, A.; Coquelet, C.; Paricaud, P.; Richon, D. Vapour-liquid equilibria
23
24
25
26
27
28
29 in the carbon dioxide-water system, measurement and modelling from 278.2 to 318.2 K.
Fluid phase equilibria **2004**, *226*, 333-344.

30 (84) Bamberger, A.; Sieder, G.; Maurer, G. High-pressure (vapor+ liquid) equilibrium in
31
32
33
34
35
36
37 binary mixtures of (carbon dioxide+ water or acetic acid) at temperatures from 313 to 353
K. *The Journal of Supercritical Fluids* **2000**, *17*, 97-110.

38 (85) Wiebe, R.; Gaddy, V. The solubility of carbon dioxide in water at various temperatures
39
40
41
42
43
44
45 from 12 to 40 and at pressures to 500 atmospheres. Critical phenomena. *Journal of the*
American Chemical Society **1940**, *62*, 815-817.

46 (86) Müller, G.; Bender, E.; Maurer, G. Das Dampf-Flüssigkeitsgleichgewicht des ternären
47
48
49
50
51
52
53
54
55 Systems Ammoniak-Kohlendioxid-Wasser bei hohen Wassergehalten im Bereich
zwischen 373 und 473 Kelvin. *Berichte der Bunsengesellschaft für physikalische Chemie*
1988, *92*, 148-160.

56 (87) Lin, W.; Delahaye, A.; Fournaison, L. Phase equilibrium and dissociation enthalpy for
57
58
59
60

1
2
3
4 semi-clathrate hydrate of CO₂+ TBAB. *Fluid Phase Equilibria* **2008**, 264, 220-227.

5
6 (88)Lekvam, K.; Bishnoi, P. R. Dissolution of methane in water at low temperatures and
7
8 intermediate pressures. *Fluid Phase Equilibria* **1997**, 131, 297-309.

9
10 (89)Culberson, O.; McKetta Jr, J. Phase equilibria in hydrocarbon-water systems III-the
11
12 solubility of methane in water at pressures to 10,000 psia. *Journal of Petroleum Technology*
13
14
15
16
17 **1951**, 3, 223-226.

18
19 (90)Dodson, C.; Standing, M. In *Tilte*1944; American Petroleum Institute.

20
21 (91)Claussen, W.; Polglase, M. Solubilities and structures in aqueous aliphatic
22
23 hydrocarbon solutions. *Journal of the American Chemical Society* **1952**, 74, 4817-4819.

24
25 (92)Culberson, O.; Horn, A. B.; McKetta Jr, J. Phase equilibria in hydrocarbon-water
26
27 systems. *Journal of Petroleum Technology* **1950**, 2, 1-6.

28
29 (93)Morrison, T.; Billett, F. 730. The salting-out of non-electrolytes. Part II. The effect of
30
31 variation in non-electrolyte. *Journal of the Chemical Society (Resumed)* **1952**, 3819-3822.

32
33 (94)Yang, S.; Cho, S.; Lee, H.; Lee, C. Measurement and prediction of phase equilibria for
34
35 water+ methane in hydrate forming conditions. *Fluid Phase Equilibria* **2001**, 185, 53-63.

36
37 (95)Lindenbaum, S.; Boyd, G. Osmotic and activity coefficients for the symmetrical
38
39 tetraalkyl ammonium halides in aqueous solution at 25. *The Journal of Physical Chemistry*
40
41
42
43
44
45
46
47
48 **1964**, 68, 911-917.

49
50 (96)Robinson, R. A.; Stokes, R. H. Tables of osmotic and activity coefficients of
51
52 electrolytes in aqueous solution at 25 C. *Transactions of the Faraday Society* **1949**, 45,
53
54
55
56
57 612-624.

(97) Pabalan, R. T.; Pitzer, K. S. Apparent molar heat capacity and other thermodynamic properties of aqueous potassium chloride solutions to high temperatures and pressures.

Journal of Chemical and Engineering Data **1988**, *33*, 354-362.

(98) Rard, J. A.; Habenschuss, A.; Spedding, F. H. A review of the osmotic coefficients of aqueous calcium chloride at 25. degree. C. *Journal of Chemical and Engineering Data*

1977, *22*, 180-186.

(99) Rard, J. A.; Miller, D. G. Isopiestic determination of the osmotic and activity coefficients of aqueous magnesium chloride solutions at 25. degree. C. *Journal of*

Chemical and Engineering Data **1981**, *26*, 38-43.

(100) El Guendouzi, M.; Marouani, M. Water activities and osmotic and activity coefficients of aqueous solutions of nitrates at 25 C by the hygrometric method. *Journal of*

solution chemistry **2003**, *32*, 535-546.

(101) Liu, Y.; Hou, M.; Yang, G.; Han, B. Solubility of CO₂ in aqueous solutions of NaCl, KCl, CaCl₂ and their mixed salts at different temperatures and pressures. *The*

Journal of supercritical fluids **2011**, *56*, 125-129.

(102) Bando, S.; Takemura, F.; Nishio, M.; Hihara, E.; Akai, M. Solubility of CO₂ in aqueous solutions of NaCl at (30 to 60) C and (10 to 20) MPa. *Journal of Chemical &*

Engineering Data **2003**, *48*, 576-579.

(103) Markham, A. E.; Kobe, K. A. The solubility of carbon dioxide and nitrous oxide in aqueous salt solutions. *Journal of the American Chemical Society* **1941**, *63*, 449-454.

(104) Messabeb, H.; Contamine, F. o.; Cézac, P.; Serin, J. P.; Gaucher, E. C.

1
2
3
4 Experimental Measurement of CO₂ Solubility in Aqueous NaCl Solution at Temperature
5
6 from 323.15 to 423.15 K and Pressure of up to 20 MPa. *Journal of Chemical & Engineering*
7
8 *Data* **2016**, *61*, 3573-3584.

9
10
11 (105) Guo, H.; Huang, Y.; Chen, Y.; Zhou, Q. Quantitative Raman Spectroscopic
12
13 Measurements of CO₂ Solubility in NaCl Solution from (273.15 to 473.15) K at p=(10.0,
14
15 20.0, 30.0, and 40.0) MPa. *Journal of Chemical & Engineering Data* **2015**, *61*, 466-474.

16
17
18 (106) O'Sullivan, T. D.; Smith, N. O. Solubility and partial molar volume of nitrogen
19
20 and methane in water and in aqueous sodium chloride from 50 to 125. deg. and 100 to 600
21
22 atm. *The Journal of Physical Chemistry* **1970**, *74*, 1460-1466.

23
24
25 (107) Stoessell, R. K.; Byrne, P. A. Salting-out of methane in single-salt solutions at 25
26
27 C and below 800 psia. *Geochimica et Cosmochimica Acta* **1982**, *46*, 1327-1332.

28
29
30 (108) Zhao, H.; Dilmore, R. M.; Lvov, S. N. Experimental studies and modeling of CO₂
31
32 solubility in high temperature aqueous CaCl₂, MgCl₂, Na₂SO₄, and KCl solutions. *AIChE*
33
34 *Journal* **2015**, *61*, 2286-2297.

35
36
37 (109) Kiepe, J.; Horstmann, S.; Fischer, K.; Gmehling, J. Experimental determination
38
39 and prediction of gas solubility data for methane+ water solutions containing different
40
41 monovalent electrolytes. *Industrial & engineering chemistry research* **2003**, *42*, 5392-5398.

42
43
44 (110) Tong, D.; Trusler, J. M.; Vega-Maza, D. Solubility of CO₂ in aqueous solutions
45
46 of CaCl₂ or MgCl₂ and in a synthetic formation brine at temperatures up to 423 K and
47
48 pressures up to 40 MPa. *Journal of Chemical & Engineering Data* **2013**, *58*, 2116-2124.

49
50
51 (111) Messabeb, H.; Contamine, F. o.; Cézac, P.; Serin, J. P.; Pouget, C. m.; Gaucher,

- 1
2
3
4 E. C. Experimental Measurement of CO₂ Solubility in Aqueous CaCl₂ Solution at
5
6 Temperature from 323.15 to 423.15 K and Pressure up to 20 MPa Using the
7
8 Conductometric Titration. *Journal of Chemical & Engineering Data* **2017**, *62*, 4228-4234.
- 9
10
11 (112) Prutton, C.; Savage, R. The solubility of carbon dioxide in calcium chloride-water
12
13 solutions at 75, 100, 120 and high pressures¹. *Journal of the American Chemical Society*
14
15 **1945**, *67*, 1550-1554.
- 16
17
18 (113) Hyde, A. M.; Zultanski, S. L.; Waldman, J. H.; Zhong, Y.-L.; Shevlin, M.; Peng,
19
20 F. General principles and strategies for salting-out informed by the Hofmeister series.
21
22 *Organic Process Research & Development* **2017**, *21*, 1355-1370.
- 23
24
25 (114) Carvalho, P. J.; Pereira, L. M.; Gonçalves, N. P.; Queimada, A. J.; Coutinho, J. A.
26
27 Carbon dioxide solubility in aqueous solutions of NaCl: Measurements and modeling with
28
29 electrolyte equations of state. *Fluid Phase Equilibria* **2015**, *388*, 100-106.
- 30
31
32 (115) Dinane, A.; El Guendouzi, M.; Mounir, A. Hygrometric determination of water
33
34 activities, osmotic and activity coefficients of (NaCl+ KCl)(aq) at T= 298.15 K. *The*
35
36 *Journal of Chemical Thermodynamics* **2002**, *34*, 423-441.
- 37
38
39 (116) Saad, D.; Padova, J.; Marcus, Y. Thermodynamics of mixed electrolyte solutions.
40
41 VI. An isopiestic study of a pseudo-ternary system: NaCl– KCl– MgCl₂– H₂O at 25° C.
42
43 *Journal of Solution Chemistry* **1975**, *4*, 983-993.
- 44
45
46 (117) Wood, J. R. Thermodynamics of brine-salt equilibria—I. The systems NaCl-KCl-
47
48 MgCl₂-CaCl₂-H₂O and NaCl-MgSO₄-H₂O at 25 C. *Geochimica et Cosmochimica Acta*
49
50
51
52
53
54
55
56 **1975**, *39*, 1147-1163.

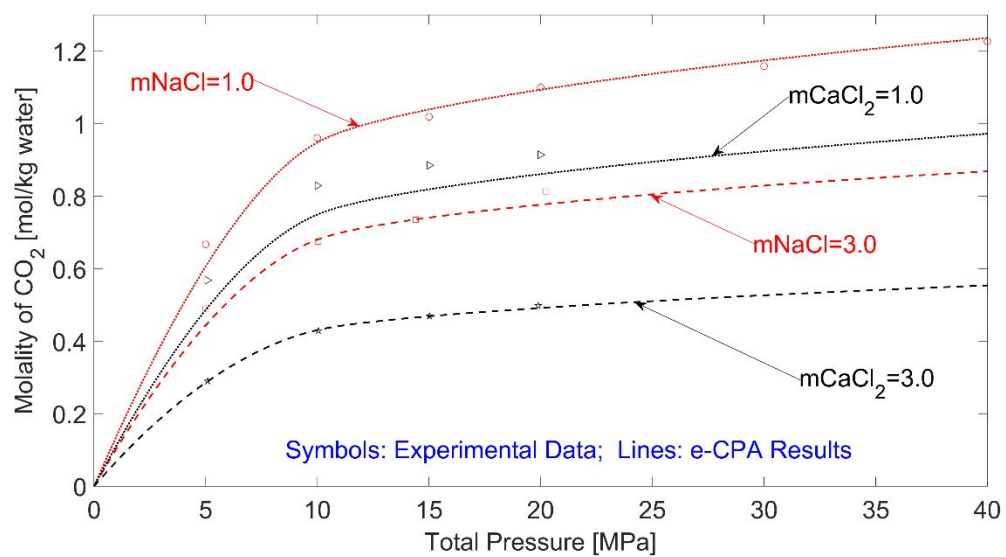
- 1
2
3
4 (118) Robinson, R.; Covington, A. The thermodynamics of the ternary system: Water-
5 potassium chloride-calcium chloride at 25 C. *J. Res. Natl. Bur. Stand. A* **1968**, *72*, 239.
6
7
8
9 (119) Christov, C. Isopiestic determination of the osmotic coefficients of an aqueous
10 MgCl₂+ CaCl₂ mixed solution at (25 and 50)° C. Chemical equilibrium model of solution
11 behavior and solubility in the MgCl₂+ H₂O and MgCl₂+ CaCl₂+ H₂O systems to high
12 concentration at (25 and 50)° C. *Journal of Chemical & Engineering Data* **2008**, *54*, 627-
13 635.
14
15
16
17
18
19
20
21
22 (120) Byrne, P. A.; Stoessel, R. K. Methane solubilities in multisalt solutions.
23
24 *Geochimica et Cosmochimica Acta* **1982**, *46*, 2395-2397.
25
26
27 (121) Jacob, R.; Saylor, B. Z. CO₂ solubility in multi-component brines containing
28 NaCl, KCl, CaCl₂ and MgCl₂ at 297 K and 1–14 MPa. *Chemical Geology* **2016**, *424*, 86-
29 95.
30
31
32
33
34
35 (122) Samoilov, O. Y. A new approach to the study of hydration of ions in aqueous
36 solutions. *Discussions of the Faraday Society* **1957**, *24*, 141-146.
37
38
39
40 (123) Collins, K. D. Charge density-dependent strength of hydration and biological
41 structure. *Biophysical journal* **1997**, *72*, 65-76.
42
43
44
45 (124) Görgényi, M.; Dewulf, J.; Van Langenhove, H.; Héberger, K. Aqueous salting-
46 out effect of inorganic cations and anions on non-electrolytes. *Chemosphere* **2006**, *65*, 802-
47 810.
48
49
50
51
52
53 (125) Held, C.; Reschke, T.; Muller, R.; Kunz, W.; Sadowski, G. Measuring and
54 modeling aqueous electrolyte/amino-acid solutions with ePC-SAFT. *The Journal of*
55
56
57

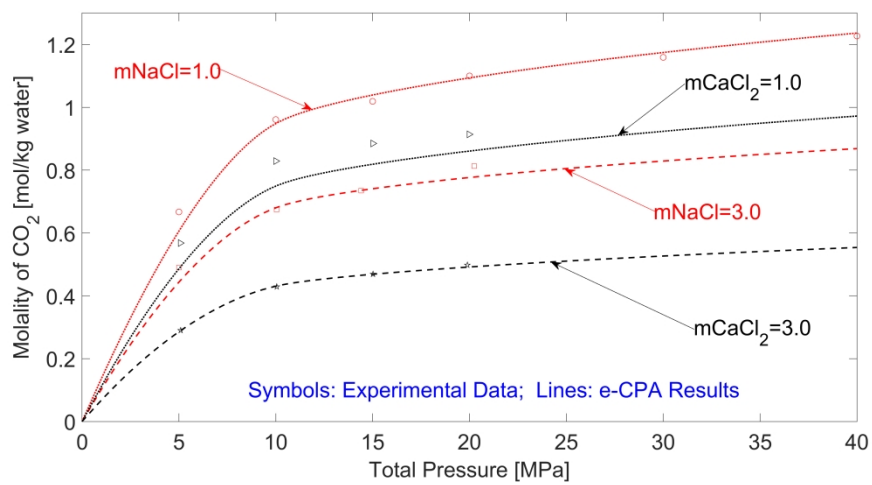
1
2
3
4 *Chemical Thermodynamics* **2014**, 68, 1-12.

5
6 (126) Uyan, M.; Sieder, G.; Ingram, T.; Held, C. Predicting CO₂ solubility in aqueous
7 N-methyldiethanolamine solutions with ePC-SAFT. *Fluid Phase Equilibria* **2015**, 393, 91-
8
9
10
11
12 100.

13
14 (127) Wangler, A.; Sieder, G.; Ingram, T.; Heilig, M.; Held, C. Prediction of CO₂ and
15
16
17 H₂S solubility and enthalpy of absorption in reacting N-methyldiethanolamine /water
18
19
20 systems with ePC-SAFT. *Fluid Phase Equilibria* **2017**, 461, 15-27.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Table of Contents Only





362x183mm (300 x 300 DPI)