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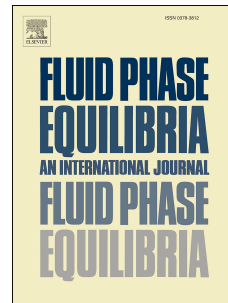
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Author contributions section

Li Sun: Conceptualization, Methodology, Software, Writing-Original Draft

Xiaodong Liang: Conceptualization, Methodology, Software, Writing-Review & Editing

Nicolas von Solms: Conceptualization, Writing-Review & Editing

Georgios M. Kontogeorgis: Conceptualization, Writing-Review & Editing, Project administration

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Thermodynamic Modeling of Gas Solubility in Aqueous Solutions of Quaternary Ammonium Salts
with the e-CPA Equation of State

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The study of gas solubility in aqueous electrolyte solutions is important, e.g. for hydrate applications, and it is also a challenging task, as metal halide salts show salting-out effects on gas in water, while some quaternary ammonium salts (QAS) show salting-in effects. This work presents a modeling study of gas solubility in aqueous solutions of several QAS (tetra-n-methyl-ammonium bromide, tetra-n-ethyl-ammonium bromide, tetra-n-propyl-ammonium bromide and tetra-n-butyl ammonium bromide) with the electrolyte Cubic-Plus-Association Equation of State (e-CPA). The ion size and ion-water interaction parameters are obtained by fitting the experimental data of mean ionic activity coefficients and osmotic coefficients of corresponding binary mixtures. The results show that e-CPA can reasonably correlate the mean ionic activity coefficients of QAS in aqueous solutions. The ion-gas interaction parameters are obtained by fitting the experimental data of gas solubility and the results show that e-CPA can correlate the gas solubilities (for nitrogen, carbon dioxide, methane and ethane) reasonably well from a quantitative point of view. For example, e-CPA gives deviations of 9.2% and 5.7% for the solubilities of carbon dioxide and methane in TBAB, respectively. The salting-in and salting-out effects and the influencing factors are also studied.

Under appropriate pressure and temperature conditions, hydrates may occur in natural gas pipelines, which can result in pipeline block and affect safe operation of pipeline. Gas hydrates also have considerable potential as storage and separation media for various gases. So, promotion and inhibition are equally important in hydrate studies. Some metal halide salts e.g. sodium chloride (NaCl) are well-known thermodynamic hydrate inhibitors, because they can make hydrates unstable by changing the phase equilibrium condition [1]. A type of quaternary ammonium salts (QAS), tetra-n-butyl ammonium bromide (TBAB) has been of great interest to gas hydrate-based investigations, as it can promote the forming of semi-clathrate hydrates [2-4].

In order to be caught in hydrate cage, the guest molecule must have a suitable size. The guest molecule needs to be larger than argon, and smaller than n-butane, Normally, these gases can be captured in hydrates clathrate: methane (CH_4), ethane (C_2H_6), propane (C_3H_8), nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S) [5]. CO_2 is the main part of flue gas, and is the main gas which causes the greenhouse effect [6], thus capture and separation of CO_2 has become an important research area to mitigate CO_2 emissions worldwide. CH_4 is another important greenhouse gas, which is the major constituent of natural gas streams and natural gas reserves in the form of hydrates in the earth [7]. As a kind of accompanied gas, N_2 is one of the major components of flue gas emitted from power plants [8]. C_2H_6 is an important part of natural gas and guest gas in natural gas hydrates [9].

The pressure, temperature, and salt concentration affect the formation conditions of hydrate systems [10], so, thermodynamic modeling of gas in aqueous electrolyte solution is an important step for hydrate-liquid-vapor modeling.

Gas solubility in aqueous electrolyte solutions can be calculated by different electrolyte Equation of State (EOS) or EOS plus activity coefficient models. Relatively few thermodynamic modeling studies of gas solubility have been proposed so far for QAS systems. Paricaud [11] used the statistical associating fluid theory for potentials of variable range for electrolyte solutions (SAFT-VRE) to describe the fluid phase. In Paricaud's modeling work, gas solubility is obtained from vapor-liquid flash calculation, and the effect of TBAB on CO_2 solubility is negligible. In Paricaud's study (and for specific conditions: at temperature=283.15 K and pressures up to 2.5 MPa) the relative average deviation (RAD) of CO_2 solubility in pure water (H_2O) is 6% (13 data points [12]), and RAD of CO_2 solubility in aqueous TBAB solution is 2% (6 data points [13]).

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Following Paricaud's work, Fukumoto et al. [14] adjusted the temperature dependency parameter in the SAFT-VRE EOS by using solid-liquid equilibrium data of salt+H₂O binary systems, and applied the approach to TBAB and other SCH systems. The authors [14] stated that the solubility of CO₂ can be predicted by neglecting the dispersion interactions between ions and CO₂ molecules. Unfortunately, no details of the model performance for the solubility calculations are provided.

Ma et al. [15] applied the modified Patel-Teja EOS (MPT) [16] to the fluid phase equilibrium of H₂O+TBAB. In MPT, chemical equilibria is considered for the CO₂+H₂O (pressures up to 1000 bar) and H₂S+H₂O systems [16], and the interaction parameter for salt-gas pairs are evaluated by fitting solubility data of gas+H₂O+salt systems under low pressures. Ma et al. [15] used a vapor-liquid flash algorithm to calculate gas solubility, while they did not provide the details of the performance of modeling the gas solubility in aqueous solutions.

Apart from the electrolyte EOS approach, Kwaterski and Herri [17] used the Soave-Redlich-Kwong EOS (SRK) plus electrolyte Non-Random Two Liquid model (e-NRTL) for aqueous TBAB solutions. They adopted Henry's constant for calculating the ideal solubility of CH₄ in the aqueous phase. Verrett et al. [18] used the Trebble-Bishnoi EOS (TB) plus e-NRTL for the aqueous TBAB solution, and in their modeling work, the gas solubility is obtained from vapor-liquid flash calculation. Verrett et al. [18] assumed that the gas solubility in the liquid phase is unaffected by the presence of TBAB, but they also pointed out that this assumption may be a source of error. Najibi et al. [19] utilized the Peng-Robinson EOS (PR) plus Mean Spherical Approximation for aqueous electrolytes including Ionic hydration and association (AMSA)-NRTL for aqueous TBAB solution. In Najibi et al.' work [19], the solubilities of CO₂ in pure H₂O and in a solution are predicted by the PR EOS and the AMSA-NRTL model respectively. Najibi et al. [19] stated that the AMSA-NRTL model accurately predicts the salting-out effect of TBAB (mass fraction of TBAB=0.09 (salt molality=0.3068 mol/kg water), temperature=283.15 K) in contact with pure H₂O. Eslamimanesh et al. [4] used the PR EOS for the vapor phase, plus NRTL for non-electrolyte compounds in the liquid phase, and they use a correlation based on the experimental data for the mean ionic activity coefficients of the electrolyte part. Eslamimanesh et al. [4] used the Krichevsky-Kasarnovsky equation [20] to calculate gas solubility in the aqueous phase. Eslamimanesh et al. [4] stated that the effect of TBAB on gas solubility are relatively small. Muromachi et al. [21] used Mao's model [22] to correlate N₂ solubility in aqueous TBAB solution, the results show that Mao's model can give good agreements with experimental data.

So far, the calculation of gas solubility in aqueous solutions of QAS has not been systematically studied for various gases, and only a few electrolyte EOS have been proposed for such studies. In this work, the electrolyte Cubic-Plus-Association (e-CPA) EOS developed by Maribo-Mogensen et al. [23] is used. The rest of the paper is organized as follows: firstly, the thermodynamic model is briefly presented, and then the modeling results are reported. Finally, the analysis and discussion of the results are presented, followed by our conclusions.

2. Thermodynamic Model

Maribo-Mogensen et al. [23] extended the CPA EOS, which was proposed by Kontogeorgis et al. [24], to mixtures containing electrolytes. In e-CPA, the residual Helmholtz energy is given by:

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

In the right-hand side of Eq. (1), the first two terms are the contributions from CPA, and the remaining two contributions are from the Debye-Hückel theory [25] (for the long-range interaction of the ions) and the Born equation [26] (for ion solvation), respectively.

e-CPA is set up for ions, i.e. the model parameters are by nature ion specific, while in order to minimize the number of parameters, a series of assumptions have been made. For more details of e-CPA and how the parameters are set, the reader is referred to the Section A of Support Information, Maribo-Mogensen et al. [23] or particularly Sun et al. [27, 28]. The temperature dependency parameter ($T_{\Delta U_{ij}}$) was respectively set to 340 K and 350K for chloride salts and bromide salts in the work of Maribo-Mogensen et al.[23]. In this work, three fitting approaches have been investigated for the regression of the ion-gas binary interaction parameters, as in our previous works [27, 28]. Approaches A, B and C have respectively three, two and one adjustable parameters, and more details are given in the Table S1 of Support Information.

In this work, the following binary systems are studied: H₂O+C₂H₆, H₂O+tetra-n-methyl-ammonium bromide (TMAB), H₂O+tetra-n-ethyl-ammonium bromide (TEAB), H₂O+tetra-n-propyl-ammonium bromide (TPAB). Moreover, the following gas-containing ternary systems are studied: H₂O+NaCl+N₂, H₂O+NaCl+C₂H₆, H₂O+CaCl₂+C₂H₆, TMAB+H₂O+CH₄, H₂O+TMAB+C₂H₆, H₂O+TEAB+CH₄, H₂O+TEAB+C₂H₆, H₂O+TPAB+CH₄, H₂O+TPAB+C₂H₆, H₂O+TBAB+CO₂, H₂O+TBAB+N₂, H₂O+TBAB+CH₄, H₂O+TBAB+C₂H₆. The gas solubility in aqueous solutions is calculated by a two-phase PT-flash with the successive substitution method [29, 30], it is assumed that there is no

salt in vapor phase.

The parameter estimation procedure follows the steps: (1) validation the published interaction parameters of some binary systems; (2) H₂O-C₂H₆ binary interaction parameters are obtained by fitting C₂H₆ solubility in pure H₂O; (3) the ion size of QAS cations (TMA⁺, TEA⁺, TPA⁺) and binary interaction parameters (H₂O-TMA⁺/Br⁻, H₂O-TEA⁺/Br⁻, H₂O-TPA⁺/Br⁻) are obtained by fitting the mean ionic activity coefficients and osmotic coefficients of aqueous electrolyte solutions; (4) the binary interaction parameters between ions and gas are obtained by fitting the gas solubility in aqueous electrolyte solutions.

The physical properties and pure component e-CPA parameters are summarized in Tables S2 and S3 of Supporting Information.

3. Modeling Results and Discussion

3.1. Binary Systems

Before modelling the H₂O+salt+gas ternary systems, the performance of model for H₂O+gas, and H₂O+salt binary systems have been studied. The e-CPA reduces to CPA in the absence of electrolytes.

Table 1. Modelling performance of gas solubility in pure water.

| Gas | k_{ij}^c | This work | | |
|--|--------------------|------------|---------------|----------------|
| | | RAD [%]/Np | T-range [K] | P-range [MPa] |
| CO ₂ [31] ^a | -0.15508+0.000877T | 8.3 / 328 | 273.75-473.15 | 0.09509-82.88 |
| CH ₄ [28] ^a | 0.8243-245.33/T | 4.5 / 206 | 274.19-444.26 | 0.101325-100 |
| C ₂ H ₆ ^b | 0.6091-166.253/T | 9.5 / 308 | 274.26-444.26 | 0.101325-68.94 |
| N ₂ [32] ^a | 1.0741-368.3066/T | 5.4 / 176 | 274.1-628.0 | 0.534-101.325 |

a. Verification work: N₂+H₂O data source:[33-37], H₂O-CO₂ data source: [38-42] [13, 43-47], H₂O-CH₄ data source: [48-54]; b. Obtained in this work: C₂H₆+H₂O data source: [52, 53, 55-62]; c. k_{ij} is the binary interaction parameter.

The results for H₂O+gas systems are presented in Table 1 together with the temperature-dependent binary interaction parameters used. CO₂ is not considered as a self-associating fluid in this work. It can be seen that CPA can satisfactorily correlate the solubilities

of N₂, CH₄ and CO₂ in H₂O with the binary interaction parameters from literature, while somewhat larger deviations are found at low pressures and high temperatures. It should be pointed out that the existence of two liquid phases for H₂O+CO₂ has not been taken into account in this work. The same strategy is applied for the modelling of ternary systems below, mainly due to lack of experimental data for the two liquid phases.

The other type of binary system is H₂O+salt, the binary systems H₂O+NaCl, H₂O+CaCl₂ and H₂O+TBAB which have been studied in our previous works [23, 27].

For H₂O+salt binary systems, only Approach A is used, and the interaction parameters between ions (TMA⁺/Br⁻, TEA⁺/Br⁻, TPA⁺/Br⁻) and H₂O are obtained by fitting mean ionic activity coefficients and osmotic coefficients.

Ion radius is a very important physical parameter in electrostatic calculations. TMA⁺, TEA⁺, TPA⁺, TBA⁺ are soft and irregular organic cations, and it is not entirely clear which radii approximately reflects the physics of the electrostatic interactions. For this reason, the cation radii are chosen to be fitted together with the interaction parameters. The ion radius of TBA⁺ has been obtained in previous work [27], and other three cations' radii are obtained in this work. The fitted H₂O-ion interaction parameters and the ion radii are summarized in Table 2.

Table 2. Binary ion-H₂O interaction parameters and model performance.

| Salt | r_{cation} [Å] | $\Delta U_{ij}^{ref}/R$ [K] | $T_{\Delta U_{ij}}$ [K] | $\omega_{\Delta U_{ij}}$ [K] | T [K] | max m | RAD [%] | γ_{\pm}^m | RAD ϕ [%] |
|-----------|------------------|-----------------------------|-------------------------|------------------------------|---------------|-------|---------|------------------|----------------|
| TMAB | 1.75 | -0.70 | 61.5 | -73.1 | 298.15-308.15 | 5.5 | 3.0 | | 2.6 |
| TEAB | 2.11 | -24.42 | 622.2 | 570.9 | 298.15-308.15 | 6.0 | 4.7 | | 3.7 |
| TPAB | 2.23 | -41.77 | 950 | 331 | 298.15-308.15 | 6.0 | 4.4 | | 3.5 |
| TBAB [27] | 2.25 | -114.9 | 192.4 | 137.3 | 298.15-373.15 | 10.0 | 7.2 | | 5.9 |

In Table 2, r_{cation} is ion radius of cation, 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, m is molality [mol/kg water].

The values are obtained by fitting experimental data of mean ionic activity coefficients and osmotic

From Table 2, it can be seen that the ion radii of TMA^+ , TEA^+ , TPA^+ and TBA^+ are smaller than the published effective radii (TMA^+ : 2.51 Å, TEA^+ : 3.08 Å, TPA^+ : 3.49 Å, TBA^+ : 3.81 Å) [65], but the order of regressed radii is consistent with the values of the published effective radii. The difference between regressed values and published ones is mainly because of the structure of the cations: the hydrocarbon chains are long and soft and the positive charge comes from the centre nitrogen atom. It can be also seen from Table 2 that the absolute values of interaction parameters between H_2O and ions at reference temperature ΔU_{ij}^{ref} follow a decreasing sequence: $\text{TBAB} > \text{TPAB} > \text{TEAB} > \text{TMAB}$, which shows a strong correlation with the length of the hydrocarbon chains.

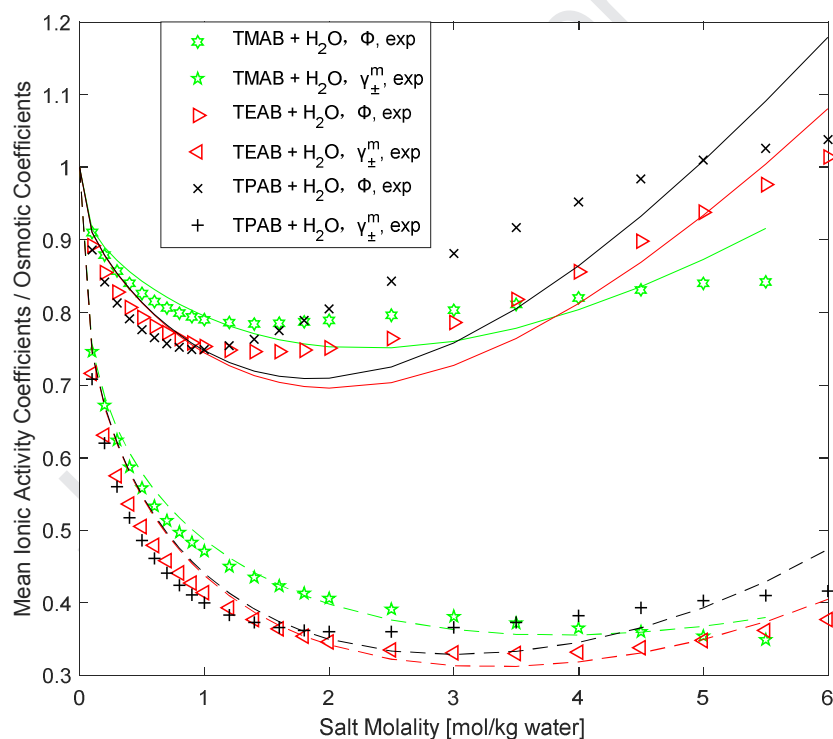


Figure 1. Experimental and predicted mean ionic activity coefficients and osmotic coefficients for binary systems at 298.15 K: $\text{H}_2\text{O} + \text{TMAB}$ [63]; $\text{H}_2\text{O} + \text{TEAB}$ [63]; $\text{H}_2\text{O} + \text{TPAB}$ [63].

Figure 1 shows the model performance of mean ionic activity coefficients and osmotic coefficients for the aqueous solutions of TPAB, TEAB and TMAB. It can be seen that e-CPA can reasonably correlate the mean ionic activity coefficients from a quantitative point of view. For the osmotic coefficients of $\text{TEAB} + \text{H}_2\text{O}$ and $\text{TPAB} + \text{H}_2\text{O}$ systems, the deviations between calculated and

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experimental values are relatively large at moderate salt concentrations (molality > 2.0 mol/kg water), with the deviations following a decreasing sequence: TPAB > TEAB > TMAB, which links to the length of hydrocarbon chains of cations, and the deviations may be attributed to the hydrophobic effects caused from hydrocarbon chains [27]. The interaction parameters between ions and H₂O provided in Table 2 are used for modelling ternary systems, and the hydrocarbon chain is believed playing an important role in the phase behaviour of aqueous QAS solutions.

3.2. Ternary Systems

In the Section D of Support Information, the solubility data of N₂ and CO₂ in aqueous TBAB solution have been analyzed: We have compared the CO₂ solubility data from Muromachi et al. [66] and data from Lin et al. [3] at 298.15 K. The deviations between the two data sets are small, so, the two data sets of CO₂ solubility are both included in this work. But for the N₂ solubility data, the experimental uncertainties of Muromachi et al. [21] data are too large (uncertainty of gas mole fraction in liquid is 0.00012, while the mole fraction of N₂ in pure water is 0.0003 at 292.15 K and 3.0 MPa [21]) and they are not considered here.

For the gas solubility of other gases in aqueous solutions of QAS, the experimental data are limited, and the overlap regions of the different data sets are rather narrow, thus comparisons and detailed analysis are difficult. So, all these data are used in the present work.

For the systems for which the experimental data are over a wide temperature range, all the three aforementioned approaches are investigated. For the systems for which the experimental data are within a narrow temperature range, or only few data are available, the one adjustable interaction parameter approach (Approach C) is investigated.

3.2.1. Dissolution of Gas

Table 3 summarizes the ion-gas interaction parameters and the performance of e-CPA for the correlation of gas solubility. Table S4 of Supporting Information lists the details of the modelling results for each data source with all the three approaches. It can be seen that overall e-CPA performs well for most systems, and over a wide range of temperature. It can be seen from Table S4 that, for most QAS systems, the e-CPA on one hand performs similarly with temperature-dependent parameters or temperature-independent parameters. This means that Approach C can be used for practical applications for safer extrapolation. On the other hand,

Approach A performs better than other approaches when the system covers a wide range of temperature. Therefore, in the following parts, interaction parameters and results with Approach A are discussed for the systems which have data over a wide range of temperature.

Table 3. Ion-gas interaction parameters and performance of e-CPA for gas solubility correlation.

| Gas | T [K] | P [MPa] | m [kg/mol water] | Np^a | $\Delta U_{ij}^{ref}/R$ [K] | $T_{\Delta U_{ij}}$ [K] | $\omega_{\Delta U_{ij}}$ [K] | RAD [%] |
|---|---------------|--------------|------------------|--------------------|--------------------------------|----------------------------|---------------------------------|---------|
| H ₂ O+NaCl+gas | | | | | | | | |
| N ₂ | 303.15-398.15 | 1.241-61.605 | 1.0-5.47 | 62 [35, 36, 67] | 1206.18 | 303.41 | 5233.21 | 5.9 |
| C ₂ H ₆ | 273.15-348.15 | 0.101-1.601 | 0.25-5.4 | 208 [59, 68-70] | 1252.69 | 648.08 | 3573.26 | 9.7 |
| H ₂ O+CaCl ₂ +gas | | | | | | | | |
| C ₂ H ₆ | 273.15 | 0.101-1.60 | 0.5-1.5 | 22 [68] | 866.71 | 204.31 | 933.22 | 4.1 |
| H ₂ O+TMAB+gas | | | | | | | | |
| CH ₄ | 278.15-308.15 | 0.101 | 0.176-0.302 | 7 [71] | 662.90 | - | - | 0.2 |
| C ₂ H ₆ | 278.15-308.15 | 0.101 | 0.165-0.325 | 6 [71] | 904.73 | - | - | 1.1 |
| H ₂ O+TEAB+gas | | | | | | | | |
| CH ₄ | 278.15-393.15 | 0.101-60.795 | 0.093-1.0 | 39 [71, 72] | 802.16 | 596.06 | -604.27 | 1.9 |
| C ₂ H ₆ | 278.15-308.15 | 0.101 | 0.098-0.436 | 8 [71] | 778.39 | - | - | 2.3 |
| H ₂ O+TPAB+gas | | | | | | | | |
| CH ₄ | 278.15-308.15 | 0.101 | 0.097-0.706 | 21 [71] | 773.23 | 202.01 | 678.61 | 2.1 |
| C ₂ H ₆ | 278.15-308.15 | 0.101 | 0.102-0.805 | 17 [71] | 788.24 | 325.61 | 194.26 | 2.3 |
| H ₂ O+TBAB+gas | | | | | | | | |
| CO ₂ | 286.15-303.1 | 0.2-4.0 | 0.342-2.074 | 145[3, 66] | 519.72 | 896.62 | 374.48 | 9.2 |
| CH ₄ | 278.15-308.15 | 0.101 | 0.096-4.01 | 43 [71, 73] | 628.42 | 679.29 | 3559.04 | 5.7 |
| N ₂ | 283.15-298.15 | 0.101 | 0-1.0 | 24 [74] | 643.47 | 499.38 | 2770.81 | 1.4 |
| C ₂ H ₆ | 278.15-308.15 | 0.101 | 0.099-0.304 | 8 [71] | 544.19 | - | - | 1.9 |

a. Np is the number of data points.

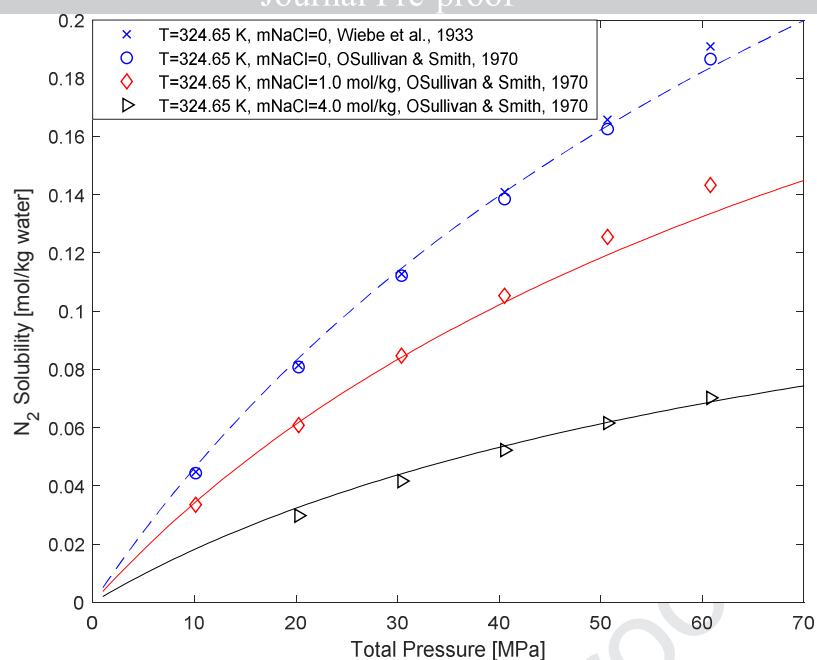


Figure 2. Comparison of the model calculations against the experimental solubility of N_2 in pure H_2O [36, 75] and aqueous $NaCl$ solution [36].

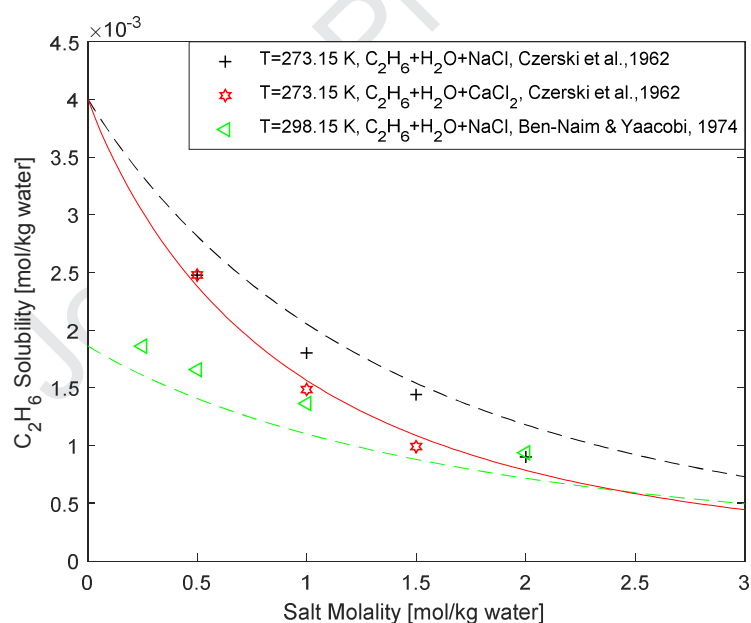
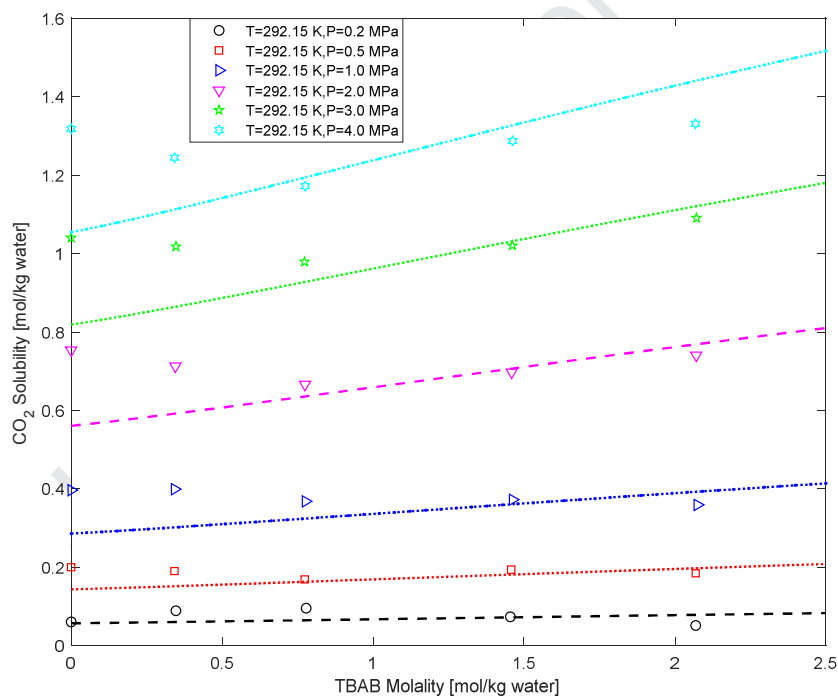


Figure 3. Comparison of the model calculations against the experimental C_2H_6 solubility in aqueous solutions of $NaCl$ [68, 76] and $CaCl_2$ [68].

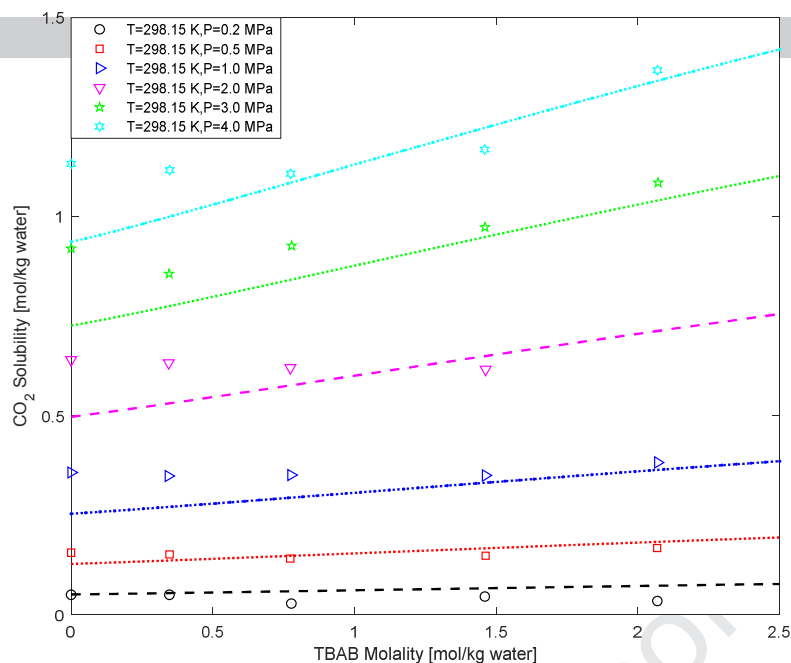
Figures 2-8 show the modeling results for metal halide salts and QAS systems. It can be seen from figures 2 and 3 that e-CPA can accurately correlate the solubilities of N_2 and C_2H_6 in aqueous $NaCl$ solution and that of C_2H_6 in aqueous $CaCl_2$ solution. Figure 2 shows that with increasing $NaCl$ molality, the solubility of N_2 decreases significantly. It can be concluded that $NaCl$ has a significant

'salting-out' effect on the solubility of N_2 in H_2O , and the salting-out effect becomes more significant at high pressure. Figure 3 shows that the solubility of C_2H_6 decreases as the $NaCl$ and $CaCl_2$ concentration increases, which reveal that they both show apparent 'salting-out' effect on the solubility of C_2H_6 in H_2O .

CO_2 is the most studied gas in gas solubility studies in aqueous TBAB solutions. On one hand, some researchers consider that the presence of TBAB does not affect the gas solubility of CO_2 in H_2O , Kamata et al. [77] reported that the CO_2 solubility in a solution (mass fraction of salt=0.1, salt molality=0.3447 mol/kg water) were almost equal to that in pure H_2O at atmospheric pressure. On the other hand, some researchers [3, 66] found that the presence of TBAB does affect the solubility of CO_2 in H_2O . Figure 4 illustrates the performance for modelling the solubility of CO_2 in aqueous TBAB solution.



(a) $T=292.15\text{ K}$



(b) T=298.15 K

Figure 4. Comparison of the model calculations against the experimental CO₂ solubility in aqueous TBAB solution [66].

It can be seen from Figure 4 that e-CPA can overall correlate well the solubility of CO₂ in aqueous TBAB solution. Moreover, as it is noticed that the deviations are large for the solubility at low salt molality, the e-CPA results therefore further compared with other experimental data (Figure S3 of Support Information). With all these results, it may be suspected that the data of Muromachi et al. [66] at low molality may have relatively large experimental uncertainties. For CO₂ dissolution in aqueous TBAB solutions, the salt effects of TBAB on CO₂ in H₂O are complex. Lin et al. [3] stated that salting-in effect obviously exists at 298.15 K with a mass fraction of TBAB=0.4 (salt molality=2.068 mol/kg water), and salting-out effect exists at 290.15 K with mass fraction of TBAB=0.2 (salt molality=0.7755 mol/kg water), and the CO₂ solubility in aqueous TBAB solution at 290.15 K with mass fraction of TBAB=0.4 (salt molality=2.068 mol/kg water) is quite close to that in pure H₂O. Lin et al. [3] also observed that temperature increase facilitated the salting-in in mass fraction of TBAB=0.4 (salt molality=2.068 mol/kg water), and salting-in effects exist at high temperature and high TBAB concentration for H₂O+TBAB+CO₂ system. From the experimental investigations, there is no explicit salting-in or salting-out effect region for TBAB on CO₂ (RAD=9.2 %).

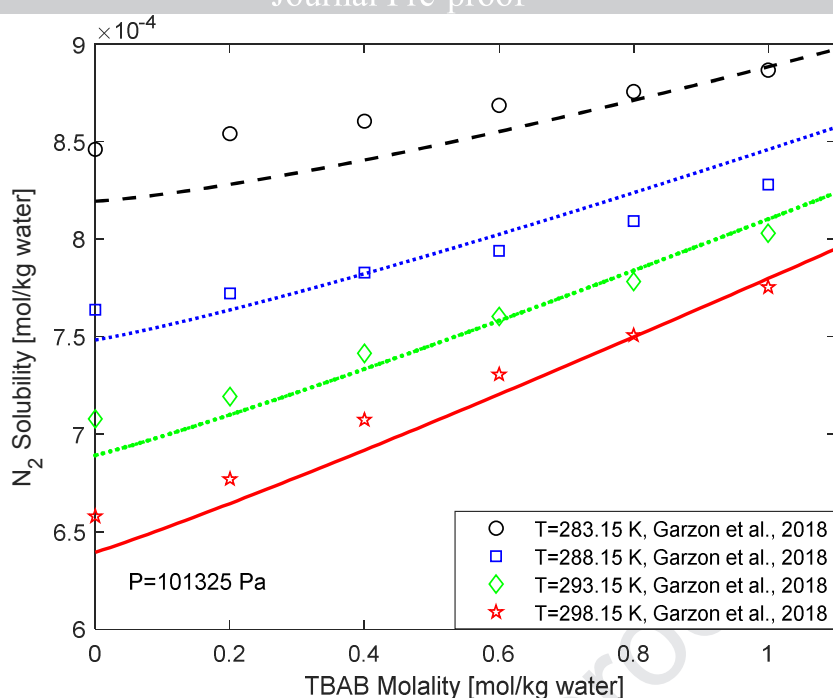


Figure 5. Comparison of the model calculations against the experimental N₂ solubility in aqueous TBAB solution [74].

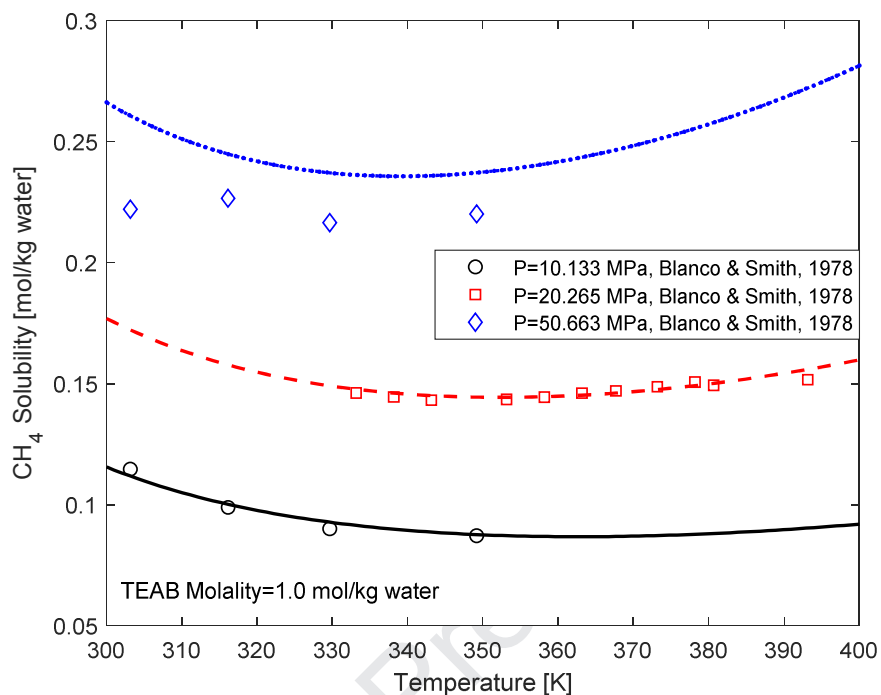
Figure 5 shows the model performance of N₂ solubility in aqueous TBAB solution. It can be seen that e-CPA can correlate well the high-temperature data, but the deviations are a bit larger at low temperature and low molality. The solubility of N₂ decreases with increasing temperature and increases with increasing TBAB concentration. TBAB shows salting-in effects on the solubility of N₂ in H₂O, and the salting-in effects are stronger at higher temperatures.

Garzon et al. [74] found that the solubility of N₂ increases as the TBAB concentration increases at a certain pressure-temperature-molality range (in a concentration interval ranging from 0.2 to 1.0 mol/kg and temperatures between 283.15 K and 298.15 K, at 101.325 kPa partial gas pressure). Garzon et al. [74] stated that the salting-in effects are not caused by micelle formation.

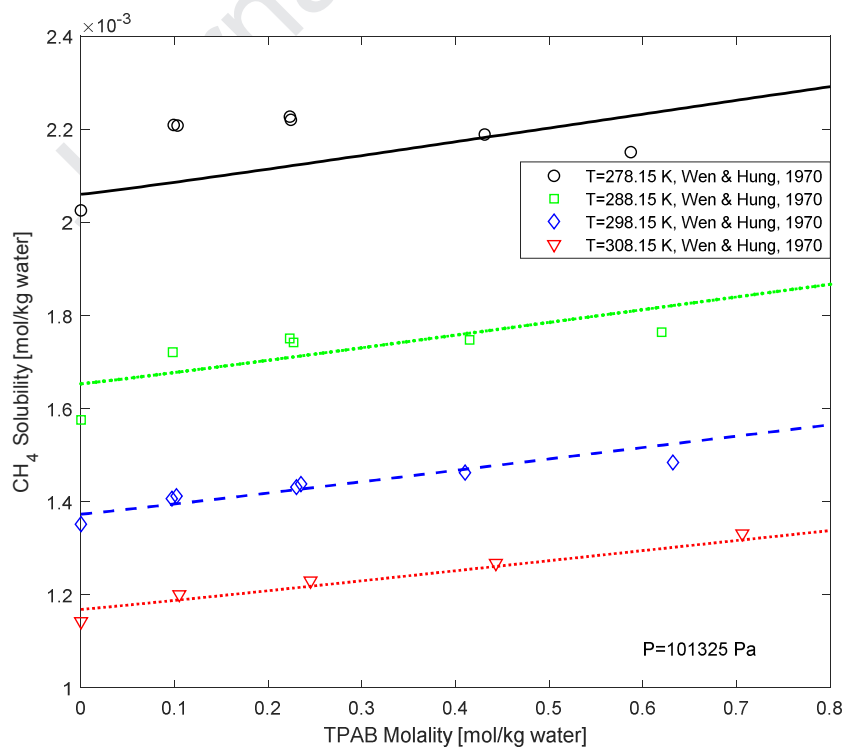
The solubility of N₂ in pure H₂O is about 1/100 of that of CO₂, so more accurate data are needed for the measurement of the solubility of N₂. Due to the low solubility of N₂, and high uncertainty of the measurements, it is hard to obtain very clear salt-effects regions [74].

Muromachi et al. [21] also stated that their measurements were not accurate enough to evaluate the temperature dependency in pure H₂O. Despite the low accuracy of their measurements, Muromachi et al. [21] still proposed the salting effects based on their experimental data: The aqueous TBAB solutions with mass fractions of 0.10 and 0.20 (salt molality=0.3447 and 0.7755

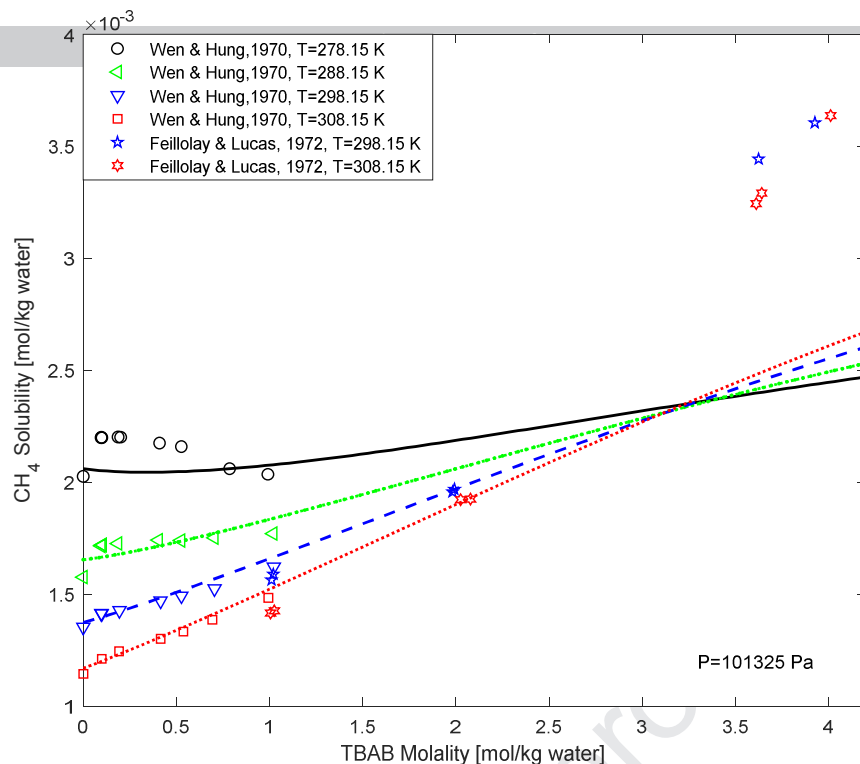
mol/kg water) presents similar solubility of N_2 as that in pure H_2O , and with mass fraction of 0.32 and 0.40 (salt molality=1.4598 and 2.068 mol/kg water), TBAB has slight salting-in effects on the solubility of N_2 in H_2O .



(a) CH_4 in aqueous solution of TEAB



(b) CH_4 in aqueous solution of TPAB



(c) CH₄ in aqueous solution of TBAB

Figure 6. Comparison of the model calculations against the experimental CH₄ solubility in aqueous solutions of (a) TEAB [72], (b) TPAB [71] and (c) TBAB [71, 73].

Figure 6 shows the model performance for the solubility of CH₄ in aqueous solutions of TEAB, TPAB and TBAB. Overall, e-CPA gives good agreement for the solubility of CH₄. It can be seen from Figure 6 (a) that TEAB shows slight salting-in effects on the solubility of CH₄ in H₂O at high temperatures, and slight salting-out effects at low temperatures. Figure 6 (b) presents that TPAB shows salting-in effects on the solubility of CH₄ in H₂O at high temperatures, and a transition that from salting-in (lower molality) to salting-out (higher molality) at low temperatures. Similar with TPAB, it can be seen from Figure 6 (c) that TBAB shows slight salting-out effects at low temperatures, and apparent salting-in effects at high temperatures.

From the experimental data of the solubility of CH₄ in aqueous TBAB solution, the data of Wen and Hung [71] show that the presence of TBAB increases the solubility of CH₄ at 288.15 K, 298.15 K, and 308.15 K. In the particular case at 278.15 K, the solubility increases slightly as the salt molality increases from 0 to 0.2 mol/kg water but then decreases with the further increase of the concentration (with salt molality increases from 0.2 to 1.0 mol/kg water). The data from Wen and Hung [71] and Feillolay and Lucas [73] have been used in the regression. TBAB shows larger

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salting-in effects at high salt molality than low molality. The e-CPA equation of state cannot represent well the salting-in effects at high salt molality.

There are only few scatter data of the solubility of C_2H_6 in aqueous QAS solutions, except for aqueous TPAB solutions, for which the model performance is shown in Figure 7. It can be seen that e-CPA can correlate well the solubility of C_2H_6 in aqueous TPAB solution. TPAB shows slight salting-in effects on the solubility of C_2H_6 in H_2O , and the effects become stronger at high temperatures.

Different salts present different salt effects on gas solubility and Figure 8 illustrates visually the different effects. The presence of NaCl can decrease gas solubility in H_2O , while the salt effects of QAS on gas are complex functions of temperature, pressure, and salt concentration, and there are no clear salting-in effect and salting-out effect regions. A general trend is that salting-in effects will appear at high temperature, pressure and QAS concentration.

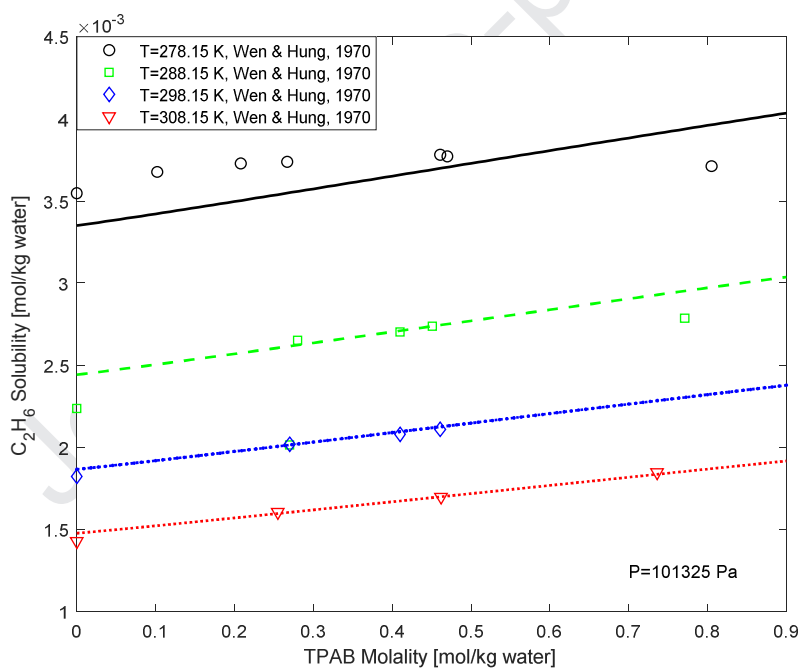
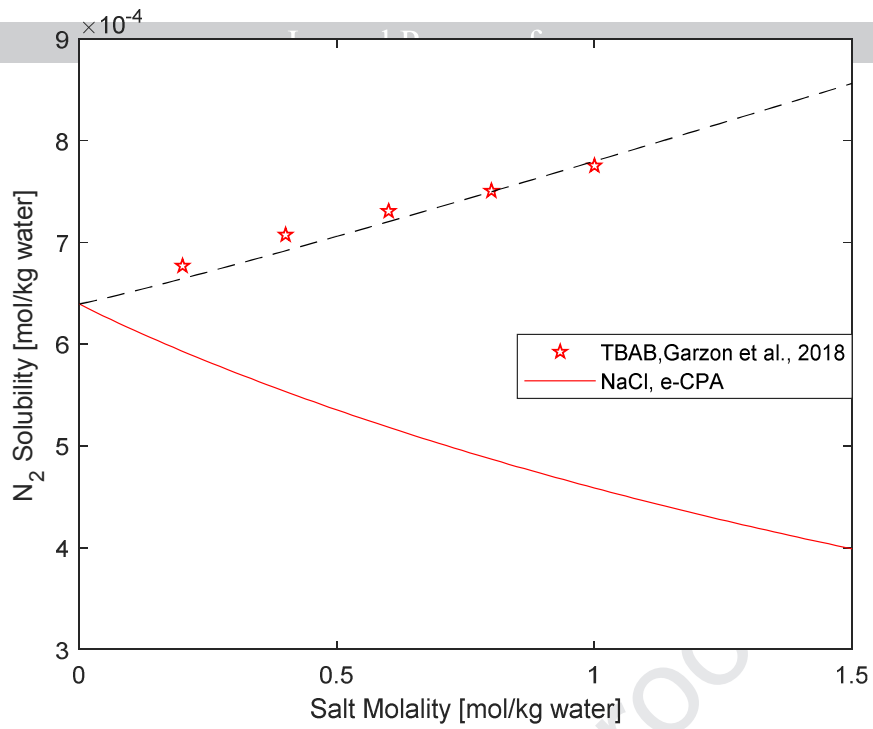
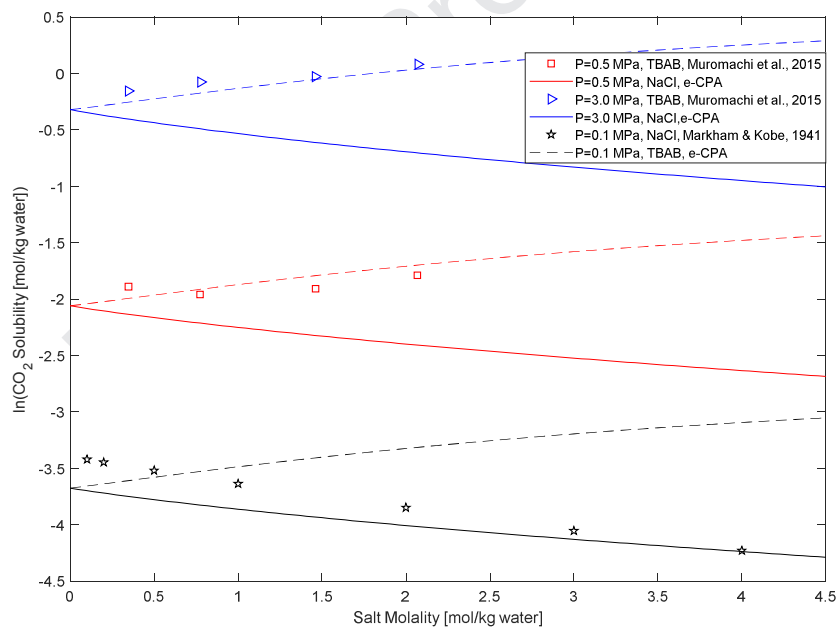


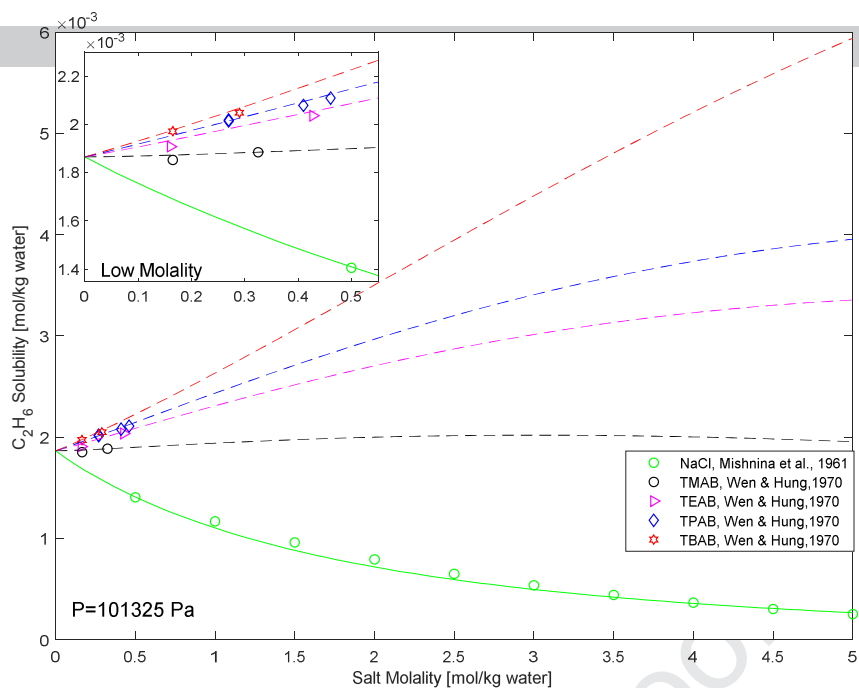
Figure 7. Comparison of the model calculations against the experimental C_2H_6 solubility in aqueous TPAB solution [71].



(a) N_2 solubility in aqueous solutions of NaCl [74] and TBAB [74] at $P=101325$ Pa and $T=298.15$ K



(b) CO_2 solubility in aqueous solutions of NaCl [78] and TBAB [66] at 298.15 K



(c) C_2H_6 solubility in aqueous solutions of NaCl [79] and QAS [71]

Figure 8. Comparison of the model calculations against the experimental gas solubility in aqueous solutions of NaCl and QAS.

3.3. Discussion

3.3.1. Salt Effects

To better understanding the mechanism of gas dissolution, it is useful to review theories presented in literature. The definition of gas solubility is the maximum quantity of gas that can dissolve in a certain quantity of solvent or quantity of solution at a specified temperature or pressure (in the case of gaseous solutes) [80]. Salting-in and salting-out are defined as the increment and reduction of the solubility of a gas due to the presence of ionic species in a solvent [81].

H_2O is a poor solvent for non-polar solutes [82]. CO_2 , N_2 , CH_4 and C_2H_6 are not very soluble in H_2O . The salting-out effects of some salts (such as NaCl) on gas is mainly from the ions solvation, which reduces the interstice of H_2O molecules, and the dissolved gas molecules will escape to vapor phase [83]. However, some salt ions, such as quaternary ammonium cations (R_4N^+), may cause the salting-in effects on gas molecules under certain conditions [82, 84].

The presence of QAS has complex effects on gas dissolution in H_2O and some researchers have proposed explanations for these effects [3, 71, 82]. Similar with ion hydration of normal ions, Wen and Hung [71] proposed 'cage effect' theory (R_4N^+ hiding in the H_2O molecular cage) to explain the

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salting-out effects of R_4N^+ on gas. They stated that this cage is not for the small solutes but for hiding the hydrocarbon chain of R_4N^+ ions.

Based on Monte Carlo simulations, Hribar et al. [82] found that the TMA^+ structure allows deep penetration by a first shell of H_2O , and this first H_2O shell sets up a second H_2O shell, these two shells shaped to act as a receptacle which can bind the nonpolar solute. Hribar et al. [82] stated that this is the main reason for salting-in effects of TMA^+ .

For the dissolution of CO_2 in aqueous TBAB solutions, Lin et al [3] concluded that there is a competition between two opposite trends with temperature and TBAB concentration change. TBAB reorganizes the H_2O molecule to accommodate more CO_2 molecules or enhances the H_2O structure (cage effect) thereby repelling CO_2 . Lin et al. [3] stated that the 'reorganizing effect' seemed to be important at a higher temperature (at 298.15 K), while the 'cage effect' of H_2O becomes important at lower temperatures (at 290.15 K). Moreover, lower TBAB concentration (mass fraction of TBAB=0.2 (salt molality= 0.7755 mol/kg water)) showed lower reorganizing ability and thereby resulting in salting-out for CO_2 at 290.15 K and 293.15 K. At a certain temperature and TBAB concentration, these two competing factors might have similar contributions, which cancel out the salinity effect on the solubility of CO_2 , as exemplified for the mass fraction of TBAB=0.40 (salt molality=2.068 mol/kg water) at $T=293.1$ K, and the mass fraction of TBAB=0.20 (salt molality=0.7755 mol/kg water) and $T=303.1$ K. For the solubility of CH_4 , Lin et al. [3] applied the 'cage effect' [71] to explain the salting-out effect of TBAB, which was observed at 278.1 K and mass fraction of TBAB=0.11 to 0.20 (salt molality=0.3834 to 0.7755 mol/kg water).

Lin et al. [3] did not provide a clear explanation of 'disorganization of H_2O molecule'. Here, this 'disorganization effect' is treated similar with the theory of Hribar et al. [82], and it is called 'disorganization effect' in the following discussion.

In this work, the influencing factors on gas solubility in aqueous QAS solution are summarized in four main aspects, and the details are listed in Table 4.

Table 4. A summary of salt effects of QAS on gas in H₂O.

| No | Effects | Ions | Theory | Influencing Factors |
|----|-------------|--------|-------------------------------|--|
| 1 | Salting-out | Anion | Ion hydration | Weakens with increasing temperature; Enhances with increasing salt molality |
| 2 | Salting-out | Cation | 'cage effect' [71] | Weakens with increasing temperature; Enhances with increasing salt molality (from 0.1 to 1.0 mol/kg water) |
| 3 | Salting-in | Cation | 'disorganization effect' [82] | Enhances with increasing temperature and salt molality |
| 4 | Salting-in | Cation | 'hydrophobic bond' [85][86] | Only for hydrocarbons; Enhances with increasing temperature |

The dissolution of gas in aqueous QAS solutions is complex and it depends on temperature, pressure, salt concentration, organic cation and gas molecule. It is believed that the hydrophobic effect also plays an important role in gas dissolution.

As for the effects on hydrate formation, gas solubility is just one factor. Su et al. [87] and Gupta et al. [88] observed that TBAB is a hydrate promoter, but TPAB, TEAB and TMAB are hydrate inhibitors. Nguyen and Nguyen [89] explained that the hydrophobic part of QAS (organic cation) acts as a hydrate promoter, while the hydrophilic part (anion) acts as a hydrate inhibitor. It creates two competitive effects on gas hydrate formation, the effects of salt depend on which effect is dominant in the working condition. Obviously, TBAB has a longer hydrocarbon chain and therefore it is more hydrophobic in comparison with TPAB, TEAB, and TMAB (the molecular structures can be seen in Section E of Support Information).

3.3.2. Model Suitability

There are actually only two electrolyte EOS in literature which have been applied for modelling the gas solubility in aqueous QAS solutions: SAFT-VRE [11] and MPT [15], and only MPT [15] considers the salt effects of QAS on gas. Unfortunately, Ma et al. [15] did not give details for the solubility calculations. Though some activity coefficient models can perform well for gas solubility calculations in aqueous solutions of QAS, the reported ranges of temperature and molality are

e-CPA takes into account ion hydration, and introduces a new model for the static permittivity calculation, which eliminates the kinetic depolarization effect. The cations of QAS are soft and have long alkyl chains. In order to obtain more physical cation radii, in this presented e-CPA approach, the cation radii of QAS are first fitted to the experimental data of mean ionic activity coefficients and osmotic coefficients.

e-CPA shows some limitations. For instance, it cannot reflect the complex salt effects of QAS on the solubility of gas in H_2O . A potential solution could be taking the hydrophobic effects into account in the model.

4. Conclusions

This work presents a theoretical study on the thermodynamic modeling for aqueous solutions of quaternary ammonium salts (QAS) by using the e-CPA EOS, which includes the Debye–Hückel and Born terms for electrostatic contributions. The representation of gas solubility in aqueous QAS solutions is challenging, as the cations of QAS have large alkyl chains, thus exhibiting hydrophobic-like character. Another reason is that the salt effects of QAS on the solubility of gas are complex and these effects come from different competing factors which depend on temperature and salt concentration. The cation size of QAS and the temperature-dependent ion-solvent interaction parameters are estimated from mean ionic activity coefficients and osmotic coefficients. e-CPA provides good agreement with the experimental data of H_2O +QAS binary systems. The temperature-dependent ion-gas interaction parameters are estimated from gas solubility in aqueous solutions and e-CPA yields successful correlation results.

Adding dissociation equilibrium to the model is a potential solution for organic salt solutions where ion-pairs and hydrophobic effects exist. In order to provide a detailed analysis for salt effects of QAS on gas, more accurate experimental data are also needed.

Acknowledgments

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List of symbols/abbreviations

| | |
|-------------------------------|--|
| AMSA | Mean Spherical Approximation for Aqueous Electrolytes includes Ionic Hydration and Association |
| CPA | Cubic-Plus-Association |
| CH ₄ | methane |
| C ₂ H ₆ | ethane |
| C ₃ H ₈ | propane |
| CO ₂ | carbon dioxide |
| CaCl ₂ | calcium chloride |
| e-CPA | electrolyte Cubic-Plus-Association |
| e-NRTL | electrolyte Non-Random Two Liquid model |
| EOS | Equation of State |
| H ₂ S | hydrogen sulfide |
| H ₂ O | water |
| MPT | Modified Patel-Teja |
| m | molality [mol/kg water] |
| NRTL | Non-Random Two Liquid model |
| N ₂ | nitrogen |
| NaCl | sodium chloride |
| N _p | number of data points |
| PR | Peng–Robinson |
| RK | Redlich-Kwong |
| RAD | relative average deviation; $\text{RAD} = \frac{1}{N_p} \sum_i^{N_p} \left \frac{y_i^{\text{cal}} - y_i^{\text{exp}}}{y_i^{\text{exp}}} \right \times 100\%$ |
| SCH | Semi-Clathrate Hydrate |
| SAFT-VRE | Statistical Associating Fluid Theory with Variable Range for Electrolytes |
| SRK | Soave–Redlich–Kwong |
| TB | Trebble–Bishnoi |
| TBA ⁺ | Tetra-n-butyl Ammonium Cation |
| TBP ⁺ | Tetra-n-butyl Phosphonium Cation |
| TMA ⁺ | Tetra-n-methyl Ammonium Cation |
| TEA ⁺ | Tetra-n-ethyl Ammonium Cation |

| | |
|-------------------------------|---|
| TPA ⁺ | Tetra-n-propyl Ammonium Cation |
| TBAX | Tetra-n-butyl Ammonium Halides |
| TBAB | Tetra-n-butyl Ammonium Bromide |
| TBAC | Tetra-n-butyl Ammonium Chloride |
| TBAF | Tetra-n-butyl Ammonium Fluoride |
| TBPB | Tetra-n-butyl Phosphonium Bromide |
| TMAB | Tetra-n-methyl Ammonium bromide |
| TEAB | Tetra-n-ethyl Ammonium bromide |
| TPAB | Tetra-n-propyl Ammonium bromide |
| R ₄ N ⁺ | quaternary ammonium cations |
| QAS | quaternary ammonium salts |
| A^r | residual Helmholtz energy |
| A^{SRK} | residual Helmholtz energy contribution for the cubic Soave–Redlich–Kwong EOS [J/mol] |
| A^{ASSOC} | residual Helmholtz energy contribution for association [J/mol] |
| A^{DH} | residual Helmholtz energy contribution from the Debye–Hückel theory [J/mol] |
| A^{Born} | residual Helmholtz energy contribution Born hydration model [J/mol] |
| k_{ij} | binary interaction parameter between solvents |
| P | pressure |
| r_i | radius of the ion i [Å] |
| T | temperature [K] |
| $T_{\Delta U_{ij}}$ | an adjustable parameter of the temperature dependency [K] |
| γ_{\pm}^m | mean ionic activity coefficient |
| ΔU_{ij}^{ref} | binary interaction parameter between ion and water at the reference temperature [J/mol] |
| Φ | osmotic coefficient |
| $\omega_{\Delta U_{ij}}$ | linear dependency in interaction energy calculation [K] |

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: