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**Solubility Modeling of Air in Aqueous Electrolyte Solutions with the e-CPA
Equation of State**

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Keywords: e-CPA; Air; Gas Solubility; Salting-out Effects

Abstract

Accurate prediction of the solubilities of air (as well as nitrogen: N_2 , oxygen: O_2 and argon) in aqueous electrolyte solutions is very important for geological studies and in the chemical industry. However, very few electrolyte equations of state have been successfully used for the calculations of these gas solubilities. This work presents a thermodynamic modeling study on the solubilities of N_2 , O_2 , argon and gas mixtures in pure water and aqueous solutions of several inorganic salts with the electrolyte Cubic Plus Association equation of state (e-CPA). The binary interaction parameters between cation/anion and gas are obtained by fitting the experimental data of gas solubilities in single-salt solutions. The results show that e-CPA can satisfactorily correlate the gas solubilities for most systems. For example, e-CPA gives deviations of 4% for the O_2 solubilities in aqueous NaCl solution. e-CPA is then applied to predict the solubilities of gas mixtures and multi-salt systems (gas mixture in pure water and gas mixture in aqueous multi-salt solutions), and satisfactory performance is achieved. For example, e-CPA gives deviations of 4% for the air solubilities in aqueous NaCl solution.

1. Introduction

Nitrogen (N_2) and oxygen (O_2) are the two most abundant gases in Earth's atmosphere, and they are also significant for the whole Earth's eco-system¹. Argon is also a main component of air. The natural fluids usually contain ions (e.g. Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} et al.)², whereas gas dissolution in the electrolyte solutions also occurs in many industrial processes³. Therefore, the investigation of air (as well as N_2 , O_2 and argon) solubilities in electrolyte solutions is a very important part for geochemistry studies⁴, chemical industry⁵ and biology studies (e.g. gas solubility in tissues and some biological systems)⁶.

Some experimental works of gas (N_2 , O_2 , argon and air) solubilities in aqueous electrolyte solutions have been reported⁷⁻⁹, but unfortunately, these experimental data are scattered and the pressure-temperature-molality (salt) ranges are limited.

Via the so-called $\varphi - \varphi$ approach, an electrolyte equation of state (e-EoS) provides a consistent thermodynamic framework to model the gas solubilities, to extrapolate the predictions beyond the range of experimental conditions, as well as to calculate other properties (e.g. density and thermal properties). Some modeling works using e-EoS have been presented for gas (e.g. carbon dioxide: CO_2 , methane: CH_4) solubility calculations¹⁰⁻²¹.

Here, we give a short review on several aspects of these e-EoS modeling works. The first aspect is related to relative static permittivity, which is a very important physical quantity for electrostatic calculations. Zuo and Guo¹², Sun and Dubessy¹⁴, Tan et al.¹⁷, and Ji et. al.¹⁵ assumed that the relative static permittivity of electrolyte solution is equal to that of the solvent. Other models^{10-11, 13, 16, 18-20} take the effect of salt presence on relative static permittivity into account. The other important aspect is the Born term. Søreide and Whitson¹³, Aasberg-Petersen et al.¹¹, Haghighi et al.¹⁶, and Sun and Dubessy^{14, 22} 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 to be important for salting-out effects and the thermodynamic modeling of other properties and behaviours.

Very few e-EoS have been presented to predict gas solubilities of N₂¹³, O₂, argon and air so far. Soreide and Whitson's model¹³ cannot predict N₂ solubilities in aqueous NaCl solution well above 300 bar, and the temperature range is narrow in their studies. To the best of our knowledge, extensive modeling works for gas mixture and multi-salt systems have not been reported with electrolyte equations of state.

The electrolyte Cubic Plus Association equation of state (e-CPA) is an extension of Cubic Plus Association equation of state (CPA), which is suitable for describing associating fluids. The e-CPA includes an ion-ion interaction term and an ion-water interaction term, and considers the effect of salt presence on relative static permittivity. e-CPA has been successfully applied in modeling the dissolution of some gases in aqueous electrolyte solutions²³. e-CPA is selected as the thermodynamic model in this work.

This work investigates a thermodynamic modeling of gas solubilities of N₂, O₂, argon and gas mixtures in pure water and aqueous electrolyte solutions. This manuscript is organized as follows: a short introduction of the thermodynamic model is first presented, followed by the parameter estimation. Then, both the correlative and predictive results are presented and discussed, followed by the conclusions. Supplementary information is available in the Supporting Information.

2. The Thermodynamic Model

2.1 The e-CPA EoS

e-CPA was developed by Maribo-Mogensen et al.²⁴, and it is an extension of CPA proposed by Kontogeorgis et al.²⁵

In terms of residual Helmholtz energy, e-CPA can be written:

$$A^{Res} = A^{SRK} + A^{Assoc} + A^{DH} + A^{Born} \quad (1)$$

Where A^{SRK} and A^{Assoc} are the two contributions from the cubic equation of state (Soave-Redlich-Kwong²⁶) and the association term, A^{DH} is from the Debye-Hückel (DH) theory²⁷ and A^{Born} is from the Born equation²⁸.

The classical van der Waals one-fluid mixing rule is used for the energy parameter for

two non-ionic molecules, while the Huron–Vidal/NRTL mixing rule is used when an ion is involved²⁴. The HV-NRTL infinite pressure mixing rule reduces to the one-fluid mixing rule if the non-randomness parameter (α_{ji}) is set to zero and the binary interaction parameter between cation/anion and molecules (ΔU_{ij}^{ref}) is appropriately chosen, for which more details can be found in the book from Michelsen and Møllerup²⁹. More details about the e-CPA EoS can be found in Section A of Supporting Information and the original paper²⁴.

2.2 Parameter Estimation

From Section A of Supporting Information and the original e-CPA paper²⁴, it can be seen that the binary interaction parameters of ions with water or gas are: NRTL non-randomness parameter (α_{ji}), interaction parameter at the reference temperature (ΔU_{ij}^{ref}), and the two adjustable parameters of the temperature dependency ($\omega_{\Delta U_{ij}}$ and $T_{\Delta U_{ij}}$). In this work, the NRTL non-randomness factor and the ion-ion interaction parameters are set to zero. Moreover, the ion-solvent and ion-gas interaction parameters are transformed to cation/anion-solvent, and cation/anion-gas interaction parameters, which means that interaction parameters $\Delta U_{cation-solvent}$ is equal to $\Delta U_{anion-solvent}$, and $\Delta U_{cation-gas}$ is equal to $\Delta U_{anion-gas}$.

The cation/anion-solvent interaction parameters are obtained by fitting mean ionic activity coefficients and osmotic coefficients. These parameters have been presented by Maribo-Mogensen et al.²⁴ We have further validated these parameters for several H₂O+salt binary systems. The interaction parameters and the verification results can be found in Table S1 of Supporting Information.

The cation/anion-gas interaction parameters are obtained by fitting gas solubilities in aqueous single-salt solutions. In the optimizations, if the experimental data are lacking, the temperature-dependency of interaction parameters (i.e. $\omega_{\Delta U_{ij}}$ and $T_{\Delta U_{ij}}$) is not considered, i.e. only one interaction parameter (interaction parameter at the reference temperature, ΔU_{ij}^{ref}) is used.

The gas solubilities in an electrolyte solution is calculated by a two-phase PT-flash with the successive substitution method²⁹⁻³⁰. The MATLAB built-in function “fmincon” is used for the regression, for which the objective function is:

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

Where Np is the number of data points, x_i^{cal} represents the calculated values (gas solubilities), and x_i^{exp} represents the corresponding experimental values.

The results are typically presented as the relative average deviation (RAD):

$$RAD\% = \frac{1}{Np} \sum_i \left| \frac{y_i^{cal} - y_i^{exp}}{y_i^{exp}} \right| \times 100\% \quad (3)$$

Here, y_i^{cal} represents the calculated results of a given property (mean ionic activity coefficient, osmotic coefficient or gas solubility), and y_i^{exp} represents the corresponding experimental data.

In this work, the H₂O-gas interaction parameters are obtained from H₂O+single-gas systems, while the cation/anion-gas interaction parameters are obtained from the ternary H₂O+single-gas+single-salt systems. Thus, the calculations of the solubilities of single-gas in pure water and aqueous single-salt solution should be considered correlations. On the other hand, there are no additional adjustable parameters in modeling for the H₂O+gas mixture, H₂O+gas mixture+single-salt and H₂O+gas mixture+multi-salt systems, so, the calculations of these systems are predictions.

3. Gas Solubilities in Pure Water

3.1 Correlations of Solubilities of Single-Gas

Prior to modeling the gas solubilities in aqueous electrolyte solutions, the gas solubilities in pure water are considered. For such systems, e-CPA reduces to CPA due to the absence of electrolytes.

The modeling of single-gas solubilities in pure water is a correlation task. The H₂O-gas interaction parameters are obtained by fitting gas solubilities in pure water. In our previous works, the interaction parameters of H₂O-N₂³¹, H₂O-CO₂²³, and H₂O-CH₄²³

were obtained. The interaction parameters of H₂O-O₂ and H₂O-argon are obtained in this work. The H₂O-gas interaction parameters and modeling results are presented in Table 1 and Figures S1-S2 of Supporting Information. The corresponding CPA pure component parameters can be found in Table S2 of Supporting Information, in which the parameters of argon are obtained in this work by fitting the saturation pressure and liquid density. Table S3 of Supporting Information lists the H₂O-gas interaction parameters and modelling performance of gas solubilities in pure water, from which it can be seen that CPA correlates well the gas solubilities in pure water, over wide temperature and pressure ranges, especially for O₂ and argon.

Figure S1 of Supporting Information presents modelling results of gas solubilities for the three main components (N₂, O₂ and argon) of air in pure water, and it shows that CPA represents well the experimental data of gas solubilities. The experimental data and the model show that N₂ has the lowest solubility values, while argon shows the largest solubility ability in pure water, with the O₂ solubility being somewhat smaller compared to argon.

There are two mechanisms of the gas dissolution. These are (1) the vacancy mechanism³² (also called as insertion mechanism³³ or hydrophobic mechanism³⁴), i.e. the filling of interstices (vacancies)^{32, 35} and (2) the solvation mechanism³² (also called as insertion-substitution mechanism³³ or hydrophilic mechanism³⁴), which is the substitution of water molecules in the structural framework of water^{32, 65}.

From Figures S1 and S2 of Supporting Information, it can be seen that, at different temperatures and pressures, the solubilities of O₂ are about twice as high compared to N₂, and in fact, this phenomenon is not unique to water³⁶. One explanation is the “distorting effects on hydrogen-bonding network of the surrounding water”³⁶⁻³⁹. The McGowan volume of N₂ (22.22 cm³/mol) is 21% greater than that of O₂ (18.30 cm³/mol)³⁷, so small hydrophobic solutes can enter the bulk water system without severely distorting the hydrogen-bonding network of the surrounding water molecules³⁸⁻³⁹. The N₂-H₂O interaction is approximately twice as high as the O₂-H₂O interaction³⁸⁻³⁹. In other words, more energy is required in order to form a cavity for N₂

than for O₂ in the aqueous solvent³⁷. N₂ causes a greater distortion of this hydrogen-bonding network than O₂, leading to lower solubilities of N₂³⁶. This explanation is based on the hydrophobic mechanism³⁴.

Battino and Seybold³⁶ suggest that molecular simulations could be applied to investigate this phenomenon.

From Figures S3-S5 of Supporting Information, it can be clearly seen that, with increasing temperature, the solubilities of N₂, O₂ and argon reach a minimum and then increase.

Kuenen⁴⁰ pointed out that, the existence of a minimum is a common phenomenon and is not associated with the specific properties of the solvent and the dissolved gas. Moreover, the gas solubility minima are encountered also in non-aqueous solvents⁴¹⁻⁴². It has been reported⁴³ that the minima in the solubilities of the majority of gases in water occur in the range 323-343K. Most studies have been done for O₂. The minimum solubility of O₂ in pure water is reported at 373 K⁴⁴ (Pressure=0.1 MPa), 348 K⁴⁴ (Pressure=10 MPa), 385 K⁴⁵ (Pressure ≈ 0.7-3.5 MPa and 7-14 MPa), approximately 373 K⁴⁴ (Pressure ≈ 2-6 MPa), and approximately 373 K⁴⁶⁻⁴⁷ (Pressure=1-5 MPa). In these studies, it has also been found out that an increase in pressure from 0.7 to 5 MPa hardly affects the minimum temperature point⁴⁵⁻⁴⁶, but a further increase in pressure from 7 to 10 MPa leads to a decrease of the minimum temperature point⁴⁸.

Groisman and Khomutov⁴⁴ reviewed the explanations of this phenomenon. According to the works of Winkler⁴⁹, the changes in the internal friction (viscosity) and density of the liquid as a function of temperature affect the solubilities of the gas in opposite ways. This leads to a minimum in the temperature variation of the solubilities of the gas in the liquid. Tammann⁴³ presented another theoretical study, which is on the basis of the hydration theory (hydrophilic mechanism): temperature increase causes the reduction of the vacancy contribution, and also an increase of the solvation contribution. These two opposing contributions are responsible for the presence of a minimum in the curves of the temperature variation of the solubilities of O₂ (as well as of other non-polar gases in water)³².

3.2 Predictions of Solubilities of Gas Mixtures

Actually, both in nature and in the chemical industry, the existence of gas mixtures is more common than the existence of single gases. Air is the most common gas mixture in nature, and air can be simplified to contain three gases, N₂ (78.084% by volume), O₂ (20.9476% by volume), and argon⁵⁰. Gas mixtures like CH₄+CO₂ and N₂+CO₂ are common in petroleum and geological fluids⁵¹⁻⁵³.

Table 1 presents the predictions of the solubilities of gas mixtures in pure water we have obtained with CPA using no interaction parameters between the gases.

Table 1. Predictive performance of CPA for the solubilities of gas mixtures in pure water.

Gas mixture	T [K]	P [MPa]	Np	RAD (xGas, %)
Air (N ₂ +O ₂ +Ar)	273.15-343.15	0.101-25.000	121 ⁵⁴⁻⁵⁶	4.9 (Air)
	273.72-308.32	0.101	14 ⁵⁷⁻⁵⁸	1.5 ^a (O ₂)
CO ₂ +N ₂	308.15-318.15	8.000-16.000	42 ⁵²	2.0 (CO ₂)/8.1 (N ₂)
CH ₄ +CO ₂	344.15	10.000-100.000	9 ⁵¹	3.3 (CH ₄)/6.1 (CO ₂)
	324.00-376.20	10.500-50.600	21 ³	5.2 (CH ₄)/4.1 (CO ₂)

a. the experimental studied are reported for H₂O+Air, but only experimental solubilities of O₂ are given.

From Table 1, it can be seen that CPA can overall predict well the solubilities of gas mixtures in pure water. Investigation of the model performance of a specific gas solubilities (e.g. the O₂ solubilities for H₂O+air system) is more helpful for validating the predictive ability of model. Unfortunately, there are few experimental data points for specific gas solubilities in gas mixture systems (most experimental data points present the total solubilities⁵⁴⁻⁵⁶, and only few data points give solubilities of the specific gases⁵⁷⁻⁵⁸). For further studies of air solubilities, more experimental data of specific gas are suggested.

Figures 1 and S6 of Supporting Information show the solubilities of air in pure water. From these two figures, it can be seen that CPA can predict well the gas solubilities of air.

Figure 1. Solubilities of air and O_2 (in air) in pure water at atmospheric pressure⁵⁶⁻⁵⁷.

Figure 1 shows gas solubilities of air and O_2 (in air) in pure water at atmospheric pressure. The solubilities of air (N_2+O_2 +argon) are almost three times of those of O_2 , which is consistent with Figure S1 of Supporting Information. For the H_2O +air system, the volume fraction ($N_2:O_2 \approx 78.1:20.9$) and solubility abilities of pure-gas ($N_2:O_2 \approx 1:2$) result in the mole fraction of specific gas (in air) in pure water ($N_2:O_2 \approx 2:1$).

Figure S6 of Supporting Information shows the air solubilities in pure water at different temperatures and pressures. The difference in air solubilities between different temperatures becomes larger with increasing pressure, and this trend seems smaller at high temperature.

From the above results, it can be seen that CPA can predict satisfactorily the solubilities

of gas mixtures without interaction parameters between the gases.

4. Gas Dissolution in Aqueous Electrolyte Solutions

When electrolyte solutions are considered, the electrostatic terms (DH and Born) are used as well as the HV-NRTL infinite pressure mixing rule and therefore the electrolyte CPA (e-CPA) EoS is applied.

4.1 Correlations of Solubilities of Single-Gas in Aqueous Single-Salt Solutions

Modeling of solubilities of single-gas in aqueous single-salt solutions is a correlation task, in which the cation/anion-gas interaction parameters are obtained by fitting the experimental data of gas solubility.

In our previous works, the solubilities of CH₄ and CO₂ in aqueous electrolyte solutions are studied, as well as the solubilities of N₂ in an aqueous NaCl solution. In this section, solubility studies of N₂, O₂, and argon in aqueous electrolyte solutions are presented. It should be pointed out that, in some experimental works, the unit of salt concentration is molarity (mol/L solution), but in our calculations, we convert molarity to molality (mol/kg water) before modeling (by using experimental correlations of the liquid density⁵⁹).

Although NaCl, KCl and CaCl₂ are common electrolytes in the chemical industry and geological fluids, investigation of other electrolytes is helpful to systematically study the gas solubilities in aqueous electrolyte solutions and thus such systems are useful for evaluating the capabilities of the model. In this work, we have considered many systems where experimental data have been found in the literature.

Table 2 presents the cation/anion-N₂ interaction parameters and the modeling performance of e-CPA for N₂ solubilities in aqueous electrolyte solutions.

Table 2. Cation/anion-N₂ interaction parameters and performance of e-CPA for the

correlation of N₂ solubilities.

Salt	T [K]	P [MPa]	m ^b	N _p	$\Delta U_{ij}^{ref}/R$ [K]	$T_{\Delta U_{ij}}$ [K]	$\omega_{\Delta U_{ij}}$ [K]	RAD [%]
KCl	273.15-513.15	9.810	0.0-2.1	24 ⁶⁰	2017.9	200.7	505.4	8.1
CaCl ₂	303.15	1.240-7.600	0.5-4.0	18 ⁷	476.8	201.6	624.1	9.7
BaCl ₂	278.15-298.15	0.101 ^a	0.0-0.8	35 ⁶¹	1578.4	218.7	9980.8	2.5
Na ₂ SO ₄	298.15-303.15	0.101-6.980	0.0-2.2	21 ^{7, 62}	2053.5	200.5	-6210.8	6.1
MgSO ₄	303.15	1.520-6.980	1.3-2.6	9 ⁷	1313.1 ^c	-	-	11.8

a. partial pressure of N₂; b. molality of salt [mol/kg water]; c. temperature-independent cation/anion-gas interaction parameter due to lack of plentiful experimental data.

The uncertainty of the adjustable parameters is 0.05.

Figure 2. Solubilities of N₂ in aqueous KCl solution at 9.81 MPa⁶⁰.

Figure 2 shows the N₂ solubilities in aqueous KCl solution at 9.81 MPa. The presence of KCl decreases the N₂ solubilities in water, in other words, KCl shows significant salting-out effects on N₂ in water, and the salting-out effects increase with increasing salt molality. It can also be seen from Figure 2 that the phenomenon of a minimum

solubility is also observed in electrolyte systems.

It is of interest to compare the salting-out effects on N_2 between different salts. Figure 3 shows the solubilities of N_2 in different electrolyte solutions.

Figure 3. Solubilities of N_2 in different aqueous solutions at different pressures at 303.15 K and 2.50 MPa⁷.

As can be seen from Figure 3, different salts have different salting-out effects, and the difference comes from the different ion hydration abilities. An ion with higher charge density (i.e. higher charge and smaller ion size) has higher ion hydration abilities. The ion hydration can reduce the number of the water molecular cavities (which can catch gas molecules), leading to lower gas solubilities. Figure 3 shows that the salting-out effects of different salts follow a sequence of $NaCl < CaCl_2 < MgSO_4 \approx KCl < Na_2SO_4$ with the same molality. In our previous work, the salting-out effects on CO_2 follow a sequence of $KCl < NaCl < CaCl_2 < Na_2SO_4$ with the same molality. An unexpected thing (due to ion hydration abilities) is that, KCl does not show the weakest salting-out effects. The reasons for this may be due to the interaction between N_2 and KCl, or the

experimental data being in narrow pressure range cannot reflect the extensive salting-out effects. For a more accurate explanation, experimental data over wider temperature ranges are needed.

Table 3 presents the cation/anion-O₂ interaction parameters and modeling performance for O₂ solubilities. The experimental data are available over wide salt molality ranges, but in narrow temperature ranges and only available at atmospheric pressure. For most systems, e-CPA yields good agreement with experimental data, while the deviations for KCl and CaCl₂ systems are a little bit larger. Figures 4-8 show graphically the results for some systems.

Table 3. Cation/anion-O₂ interaction parameters and performance of e-CPA for the correlation of O₂ solubilities.

Salt	T [K]	P ^a [MPa]	m ^b	N _p	$\Delta U_{ij}^{ref}/R$ [K]	$T_{\Delta U_{ij}}$ [K]	$\omega_{\Delta U_{ij}}$ [K]	RAD [%]
NaCl	273.15-310.15	0.101	0.0-5.6	66 ^{9, 63-69}	1401.1	399.9	-4761.1	3.8
KCl	273.15-310.15	0.101	0.0-4.7	53 ^{9, 66-68, 70}	1256.3	288.9	9989.7	7.9
CaCl ₂	298.15-310.15	0.101	0.0-5.2	34 ^{9, 68, 70}	823.5	151.9	2111.1	7.4
MgCl ₂	273.15-310.15	0.101	0.0-4.3	37 ^{9, 67-68, 70}	629.5	291.5	9998.1	4.8
LiCl	273.15-293.15	0.101	0.0-2.3	8 ⁶⁷	918.9 ^c	-	-	4.3
Na ₂ SO ₄	288.15-310.15	0.101	0.0-1.9	41 ^{9, 62, 68}	2117.1	548.9	-9984.9	2.5
K ₂ SO ₄	288.15-310.15	0.101	0.2-0.6	19 ^{9, 68-69}	2165.5	334.5	-138.4	2.2
MgSO ₄	288.15-310.15	0.101	0.0-2.7	59 ^{9, 68, 70}	1792.5	530.1	-4504.3	3.8
NaNO ₃	298.15	0.101	0.0-6.2	9 ⁷⁰	1400.0 ^c	-	-	1.6
Ca(NO ₃) ₂	298.15	0.101	0.0-2.7	8 ⁷⁰	987.6 ^c	-	-	2.2
NaOH	288.15-308.15	0.101	0.0-6.6	38 ⁶⁹⁻⁷⁰	1486.0	487.4	-4994.9	3.1
KOH	288.15-298.15	0.101	0.6-1.2	8 ⁶⁹	1264.4 ^c			0.8

a. partial pressure of O₂; b. molality of salt [mol/kg water]; c. temperature-independent cation/anion-gas interaction parameter due to lack of plentiful experimental data.

The uncertainty of the adjustable parameters is 0.05.

Figure 4. Solubilities of O₂ in aqueous NaCl solutions at atmospheric pressure^{65, 67-69}.

Figure 5. Solubilities of O₂ in aqueous KCl solutions at atmospheric pressure^{9, 67-68, 70}.

Figures 4 and 5 show the modeling results of O₂ solubilities in aqueous solutions of NaCl and KCl. The O₂ solubilities decrease with increasing temperature (in the

experimental temperature ranges), and NaCl and KCl both show significant salting-out effects on O₂ in water.

Figure 6. Solubilities of O₂ in aqueous solutions of CaCl₂ and MgCl₂ at atmospheric pressure and different temperatures^{9, 68, 70}.

Figure 7. Solubilities of O₂ in aqueous solutions of chloride salts at 298.15 K and atmospheric pressure^{67, 69-70}.

Figure 8. Solubilities of O_2 in aqueous solutions of different salts at 310.2 K and atmospheric pressure^{9, 68}.

Figures 6-8 show the modeling results for O_2 solubilities in different aqueous electrolyte solutions. Similar to other gas systems, different salts show different salting-out effects on O_2 in water. Figure 6 shows the modeling results of $CaCl_2$ and $MgCl_2$ systems, where these two salts have similar salting-out effects on O_2 in water. The Pauling Radius of Ca^{2+} is 0.99 Å, while the Pauling Radius of Mg^{2+} is 0.65 Å. This implies that Mg^{2+} has stronger ion hydration effects than that of Ca^{2+} , but $CaCl_2$ and $MgCl_2$ both have two Cl^- , so, the contributions from anion also need to be considered. The combined effects of cation and anion resulted in $CaCl_2$ and $MgCl_2$ have similar salting-out effects.

From Figure 7, it can be seen that the salting-out effects on O_2 in water at 298.15 K follow a sequence of $KCl < NaCl < CaCl_2 \approx MgCl_2$ with the same molality. This order is the same as our previous study for CO_2 ²³.

In Figure 8, the salts with two cations (K_2SO_4 and Na_2SO_4) have stronger salting-out effects than the corresponding monovalent salts (KCl and $NaCl$), because cations contribute more than anions to ion hydration. It can also be observed that $MgSO_4$ has

stronger salting-out effects than MgCl_2 ; this phenomenon may be explained by an additional equilibrium of dissolution of SO_4^{2-} and the difference of the ion-association between MgCl_2 and MgSO_4 .

Table 4 presents cation/anion-argon interaction parameters and modeling performance for argon solubilities. As in the case with O_2 , the experimental data cover wide salt molality ranges, but only narrow temperature and pressure ranges. The e-CPA modeling results are in good agreement with experimental data for these systems. Figures 9-13 show graphically the results for some systems.

Table 4. Cation/anion-argon interaction parameters and performance of e-CPA for the correlation of argon solubilities.

Salt	T [K]	P [MPa]	m^b	N_p	$\Delta U_{ij}^{ref}/R$ [K]	$T_{\Delta U_{ij}}$ [K]	$\omega_{\Delta U_{ij}}$ [K]	RAD [%]
NaCl	273.15-313.15	0.101 ^a	0.0-6.0	52 ^{8, 67, 71-73}	1227.5	539.5	4998.5	4.3
KCl	278.15-303.15	0.101 ^a	0.0-4.6	18 ^{8, 71, 73}	1339.8	325.3	155.6	4.1
CaCl_2	298.15	0.101 ^a	0.0-5.4	3 ⁷¹	281.2 ^c	-	-	2.1
MgCl_2	298.15	0.101 ^a	0.0-5.0	3 ⁷¹	-72.3 ^c	-	-	2.1
LiCl	278.15-313.15	0.101 ^a	0.0-6.8	52 ^{8, 71-73}	574.0	329.6	4942.2	4.1
RbCl	283.15-313.15	0.101	0.0-2.4	23 ⁷²	1294.6	342.2	-100.7	3.3
NaBr	303.15	0.101	0.0-2.0	4 ⁸	1296.7 ^c	-	-	2.3
KBr	278.15-313.15	0.101	0.0-2.1	34 ⁷²⁻⁷³	1279.2	266.6	-3498.0	2.6
CsBr	283.15-313.15	0.101	0.0-2.4	24 ⁷²	1235.0	260.0	-110.7	3.6
SrCl_2	298.15	0.101 ^a	0.0-3.6	3 ⁷¹	671.6 ^c	-	-	4.4
BaCl_2	298.15	0.101 ^a	0.0-1.7	3 ⁷¹	1335.5 ^c	-	-	4.7
NaI	278.15-313.15	0.101	0.0-3.9	48 ^{8, 72-73}	1179.8	268.3	-2.7	5.9
KI	278.15-313.15	0.101	0.0-4.0	45 ⁷²⁻⁷³	1399.0	250.4	-17.4	6.0
KOH	288.15-298.15	0.101 ^a	0.6-1.2	8 ⁶⁹	1659.4 ^c	-	-	2.0

a. partial pressure of argon; b. molality of salt [mol/kg water]; c. temperature-

independent cation/anion-gas interaction parameter due to lack of plentiful experimental data.

The uncertainty of the adjustable parameters is 0.05.

Figure 9. Solubilities of argon in aqueous NaCl solutions at atmospheric pressure^{67, 72}.

Figure 10. Solubilities of argon in aqueous LiCl solutions at atmospheric pressure⁷².

Figure 11. Solubilities of argon in aqueous KBr solutions at atmospheric pressure⁷².

Figures 9-11 show the modeling results of argon solubilities in aqueous solutions of NaCl, LiCl and KBr respectively. It can be seen that e-CPA can correlate well the argon solubilities in these systems. These salts show significant salting-out effects on argon in water.

Figure 12. Solubilities of argon in aqueous solutions of chloride salts at 283.15 K and

atmospheric pressure⁷².

Figure 12 shows the modeling results of argon solubilities in aqueous solutions of three chloride salts. The Pauling radii of Rb^+ , Na^+ and Li^+ are 1.48 Å, 0.95 Å and 0.6 Å respectively. According to the ion hydration ability, the salting-out effects on argon should follow a sequence of $\text{RbCl} < \text{NaCl} < \text{LiCl}$ with the same molality. But the experimental data show that the salting-out effects on argon follow the sequence of $\text{LiCl} < \text{RbCl} < \text{NaCl}$ with the same molality, that is to say LiCl does not show strongest salting-out effects as expected. A possible explanation is that the mean ionic activity coefficients of LiCl show a special phenomenon⁷⁴ i.e. at moderate-high salt molality ranges, the mean ionic activity coefficients of LiCl do not increase as the salt molality increasing, as those of other salts do. This phenomenon may be caused by ion-association. Ion-association reduces the number of free ions, and this may cause unexpected salting-out effects.

Figure 13. Solubilities of argon in aqueous solutions of bromine salts and iodine salts at 283.15 K and atmospheric pressure⁷²⁻⁷³.

Figure 13 shows the modeling results of argon solubilities in aqueous solutions of bromine and iodine salts. These salts also show significant salting-out effects on argon

in water. The salting-out effects of KBr are more pronounced than those of CsBr, because the Pauling radius of K^+ (1.33 Å) is smaller than that of Cs^+ (1.69 Å), which means that KBr has stronger ion hydration abilities than CsBr. As expected, NaI (with Pauling radius=0.95 Å for Na^+) has higher salting-out effects than KI (with Pauling radius=1.33 Å for K^+), but this cannot be seen from the experimental data. The few experimental data points available show that NaI and KI have very similar salting-out effects on argon in water.

4.2 Predictions of Solubilities of Air in Aqueous Solutions of Single-Salt

In this sub-section, we present the prediction of solubilities of Air in aqueous single-salt solutions for the systems for which experimental data are available. No further adjustable parameters are introduced between gases, i.e. these results are pure predictions.

Table 5 shows the temperature-pressure-molality ranges of experimental data, as well as the deviations. The results from Table 5 show that e-CPA can predict in good agreement with the experimental data the air solubilities in aqueous single-salt solutions. Most experimental works are presented at atmosphere pressure, and most experimental works only give the liquid mole fraction of O_2 .

Table 5. Predictive performance of e-CPA for air solubilities in aqueous single-salt solutions.

Salt	T [K]	P [MPa]	m^a	N_p	RAD [%]
NaCl	273.19-318.54	0.101	0.0-6.0	182 ^{57-58, 75-76}	6.1 ^b
	298.15-338.15	6.900-24.300	0.0-6.0	88 ⁵⁵	4.3
KCl	278.15-318.15	0.101	0.0-5.1	59 ⁷⁵⁻⁷⁷	5.1 ^b
CaCl ₂	298.15	0.101	0.0-3.0	14 ⁷⁵⁻⁷⁶	5.7 ^b
Na ₂ SO ₄	278.3-318.3	0.101	0.0-2.6	92 ^{57-58, 76, 78}	3.9 ^b
MgSO ₄	278.08-318.24	0.101	0.0-2.9	75 ⁵⁷⁻⁵⁸	3.7 ^b

a. molality of salt [mol/kg water]; b. the experimental works are made for Air+H₂O, but

only solubilities of O_2 is given.

There are no cation/anion-argon interaction parameters for Na_2SO_4 and $MgSO_4$, and the volume fraction of argon is very small in air. Therefore, we simplify air to N_2 (79% by volume)+ O_2 (21% by volume) in the calculations of these salts⁷⁹, that is, the $H_2O+air+Na_2SO_4$ and $H_2O+air+MgSO_4$ systems are simplified to $H_2O+N_2+O_2+Na_2SO_4$ and $H_2O+N_2+O_2+MgSO_4$.

Figures 14-15 and S8 of Supporting Information show graphically the modeling results for some systems. Figure 14 shows the air solubilities in aqueous $NaCl$ solution at 338.15 K. The gas solubility difference between different pressures decrease with increasing salt molality.

Figure 14. Solubilities of air in aqueous $NaCl$ solutions⁵⁵ at 338.15K.

Figure S8 of Supporting Information shows the air (as well as N_2 and O_2) solubilities in the aqueous $NaCl$ solution. From the modeling results, it can be seen that N_2 contributes about 2/3 to the air solubilities, and O_2 contributes about 1/3 to the air solubilities.

Figure 15. Solubilities of O_2 (in air) in aqueous solutions of different salts at 298.15 K and atmospheric pressure.

Figure 15 shows the air solubilities in different aqueous electrolyte solutions at 298.15 K and atmospheric pressure. It can be seen from Figure 15 that the salting-out effects on air in water at 298.15 K follow the sequence of $KCl < NaCl < CaCl_2 < MgSO_4 < Na_2SO_4$ with the same molality. This order corresponds to the ion hydration abilities, and it is the same as the salting-out effects on N_2 (Figure 3), if KCl is ignored.

4.3 Predictions of Solubilities of Gas Mixtures in Aqueous Multi-Salt Solutions

Earth and industrial fluids always contain more than one salt, so extension of thermodynamic models to multi-salt systems is important. In this work, there are no interaction parameter between different salts (ions) considered, i.e. no new adjustable parameters are introduced. That means the modeling results of multi-salt systems are straight predictions.

Prior to modeling the gas solubilities in aqueous multi-salt solutions, the model is validated for aqueous multi-salt solutions. Table 6 shows the modelling performance

for osmotic coefficients and gas solubilities of aqueous multi-salt solutions. Figure 16 shows graphically the air solubilities in multi-salt systems.

Table 6. Predictive performance of e-CPA for osmotic coefficients Φ (at 298.15 K) and O₂ (in air) solubilities in aqueous multi-salt solutions at 298.15 K.

Salts	Φ			O ₂ solubilities					
	I ^a	N _p	RAD [%]	I ^c	T [K]	P [MPa]	Gas mixture	N _p	RAD [%]
Na ₂ SO ₄ +MgSO ₄ ^b	0.8-12.0	49 ⁸⁰	7.9	0.0-10.5	298.15	0.101	Air (N ₂ +O ₂)	8 ⁵⁸	3.8 ^d
NaCl+Na ₂ SO ₄ ^b	0.5-10.8	157 ⁸⁰	2.1	0.0-6.0	298.15	0.101	Air (N ₂ +O ₂)	10 ⁵⁸	6.9 ^c
NaCl+KCl+CaCl ₂	14.0	2 ⁵²	2.7	1.0	308.15	8.000	N ₂ +CO ₂	7 ⁵²	5.1 ^e /6.4 ^f

a. ionic strength [mol/kg water]; b. In the experimental data of Na₂SO₄+MgSO₄ and NaCl+Na₂SO₄ systems, the molality of each salt is very similar with each other. In the calculations for these systems, we assume that each salt has the same molality; c. salt molality: Na₂SO₄+MgSO₄ (Na₂SO₄: 0-1.5, MgSO₄: 0-1.5), NaCl+Na₂SO₄ (NaCl: 0-1.49, Na₂SO₄: 0-1.49), NaCl+KCl+CaCl₂ (NaCl: 0.30, KCl: 0.24, CaCl₂: 0.16); d. the experimental studies are made for H₂O+Air, but only solubilities of O₂ is given; e. solubilities of N₂; f. solubilities of CO₂.

It should be noted that, there are no cation/anion-argon interaction parameters for Na₂SO₄ as discussed above, so it is assumed that there is no argon in the H₂O+air+Na₂SO₄+MgSO₄ and H₂O+air+NaCl+Na₂SO₄ systems. From the results in Table 6 and Figure 16, it can be seen that e-CPA has a good performance for the solubilities of gas mixtures in aqueous multi-salt solutions.

Figure 16. Solubilities of O₂ (in air) in aqueous multi-salt solutions at 298.15 K and atmospheric pressure.

5. Conclusions

The solubilities of N₂, O₂ and argon in pure water and several aqueous electrolyte solutions have been systematically studied in this work with the e-CPA EoS. O₂ and argon have similar solubilities in pure water, and the solubilities of O₂ are about twice those of N₂. The existence of a minimum is a common phenomenon for gas dissolution in pure water and aqueous electrolyte solutions. Different salts show different salting-out effects on gases in water, partly because of different ion hydration abilities. The existence of ion-association may cause unexpected salting-out effects. From the modeling results, it can be concluded that e-CPA provides good agreement with the experimental solubility data. The modeling studies include also gas mixtures and multi-salt systems. In these cases and without additional adjustable parameters, e-CPA can also accurately predict the gas solubilities for these complex systems (gas mixtures and multi-salt solutions). Moreover, e-CPA shows a good performance on the salting-out effects.

It can be overall concluded that e-CPA is an accurate and easy-to-use model, which can be adapted for new systems. For further studies, more experimental data over wider temperature-pressure-molality ranges would be useful.

Supporting Information

Supporting Information consists of three parts: The e-CPA EoS (Section A); Verification work for H₂O+salt systems (Section B); CPA parameters of water and gases (Section C); Modeling results of gas solubility (Section D). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Caption:
Dissolution of Air in Aqueous Electrolyte Solutions

Graphic**Dissolution of Air in Aqueous Electrolyte Solutions**