

Solubility of oxygen in aqueous sodium carbonate solution at pressures up to 10 MPa

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Abstract

The solubilities of oxygen in 0.2, 0.5, 0.7 and 1.0 M Na₂CO₃ solution have been measured at 300.15 K and under pressures up to 10 MPa using a magnetically stirred autoclave and a direct sampling technique. The accuracy of apparatus was verified by duplicating the solubility of oxygen in pure water in literature. The experimental data of the solubility of oxygen in aqueous sodium carbonate solution were shown that the solubility of oxygen increases with increasing pressure and decreases with increasing salt concentration due to salting-out effect. The experimentally measured data were satisfactorily compared with the predicted values by our model based on non-primitive mean spherical approximation (MSA) and perturbation theory. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The solubility of oxygen in water and aqueous salt solution, and its variation with pressure, temperature, and salt concentration is of interest not only to the physical chemist, the biologist but also to the geochemist. The work concerned with the solubility of oxygen in water has been carried out at low temperature and atmospheric pressure. Pray et al. [1] have made investigations within the temperature interval 373–573 K and at pressures up to 20 MPa. A few solubility values at temperatures between 398 and 473 K, and pressures between 1.4 and 2.3 MPa have been reported by Anderson et al. [2]. Broden and Simonson [3] have systematically measured the solubility of oxygen in water at temperatures between 323 and 423 K and pressures from 1 to 5 MPa. The study of oxygen solubilities has now been extended to include alkaline sodium salt solutions used in technical processes. The solubilities of oxygen in sodium hydrogen carbonate and in sodium hydroxide solutions, respectively, were investigated by Broden and Simonson [3]. However, very few results relevant to the solubility of oxygen in aqueous salt solution are reported

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in the literature. No data on the solubility of oxygen in sodium carbonate solution are available in the literature. The present work is oriented toward obtaining an accurate set of measurements of the solubility of oxygen in aqueous sodium carbonate solution with different salt concentration at pressure up to 10 MPa.

Although a number of activity coefficient models such as Pitzer's equation [4] and NRTL model [5] have been developed for electrolyte solutions, the applications of these models are only limited to the case at low pressure and not suitable for salt solutions at high-pressure. Equation of state is more preferable to describe high-pressure phase equilibria for systems containing supercritical gas. In previous paper [6], we have proposed a new model for calculating high-pressure solubility of gas in aqueous electrolyte solution based on non-primitive mean spherical approximation (MSA) and perturbation theory which can predict gas solubility in aqueous salt solution only using the pure-component parameters. Although Liu et al. [7,8] also used non-primitive MSA plus SAFT for real 1:1 symmetric electrolyte solution, they did not introduce LJ dispersion term in their model, so it cannot be used to calculate solubility of gas in aqueous salt solution. In this work, the experimental data measured have successfully compared with the predicted values by new model in the range of temperature and pressure considered.

2. Experiment

2.1. Materials

The oxygen used in this experiment was obtained from Beijing Oxygen Co., Inc., its purity given as 99.99%. Distilled water of HPLC grade was used. Analyzed reagent grade Na_2CO_3 with 99.80% purity was directly used without further purification.

2.2. Apparatus and procedure

The experimental equipment was the same as that used earlier [9]. The autoclave used for solubility measurements was designed for high-pressure work, the volume being 500 ml. It was equipped with a magnetically driven stirrer for reaching rapid equilibration. The temperature of the autoclave was controlled by a regulator supported with a resistance sensor, a transmitter and a thyristor power control connected to the heating coils inside the autoclave. There were thermal insulations surrounding the autoclave. The temperature variation of system in the whole cell was within ± 0.1 K.

The salt solution with a definite concentration was prepared by weight. Then approximately 350 ml of salt solution was injected into the equilibrium cell by a high-pressure pump. The heating was started and oxygen was bubbled until no traces of nitrogen could be detected by GC-analysis. The cell was then completely sealed and heated to the temperature required. Once thermal equilibrium was achieved, the oxygen was added from oxygen cylinder, adjusting to a proper value. Subsequently, the equilibrium cell was agitated with a magnetic stirrer until equilibrium at a proper pressure was achieved. Equilibrium assumed when no cell pressure variation was observed over a 8 h period. Once equilibrium was reached, agitation was stopped and a sample of the liquid phase was withdrawn into evaporating pipe. The evaporated vapor entered gas chromatography (GC) with thermal conductivity detector and the on-line GC allowed a rapid composition analysis. At least three samples were withdrawn before the pressure was changed to a new level. The pressure variation during the sampling was within 0.01 MPa.

Table 1

Comparison between experimental data and values of literature [3] for the solubility of oxygen in water at 300.15 K

P (MPa)	$x_{\text{O}_2}^{\text{exp}} \times 10^5$	$x_{\text{O}_2}^{\text{lit}} \times 10^5$	A.R.D. (%)
1.00	22.36	21.08	6.07
2.00	44.11	41.38	6.61
3.00	65.80	60.69	8.42
4.00	85.23	79.01	7.87
5.00	103.61	96.33	7.56
6.00	15.88	–	–
7.00	128.63	–	–
8.00	145.62	–	–
9.00	160.11	–	–
10.00	171.01	–	–

2.3. Sample analysis

The compositions of oxygen and water were analyzed using a GC with a thermal conductivity detector and a 2 m by 5 mm diameter stainless steel packed GDX-301 for analysis of the samples. The flow rate of hydrogen carrier gas was 70 ml/min, the column temperature was 423.15 K, and the temperature of detector was 443.15 K.

2.4. Calibration of apparatus

Reproducibility and accuracy of experimental technique were verified by duplicating the data determined by Broden and Simonson [3] for the solubility of oxygen in water under various pressures. Table 1 and Fig. 1 showed a good agreement between our measurements and the literature. The absolute relative deviation (A.R.D.) between them was within 9%, which demonstrated that our apparatus could give an enough accuracy of determination.

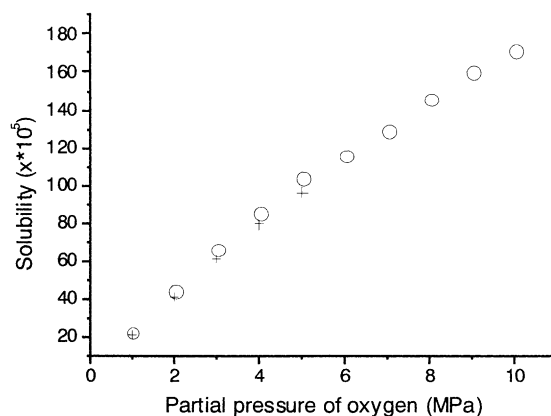


Fig. 1. The solubility of oxygen in water at 300.15 K: (O) experimental data; (+) values of literature [3].

Table 2
Experimental data of solubility of O₂ in Na₂CO₃ solution at 300.15 K

<i>P</i> (MPa)	<i>x</i> × 10 ⁵	<i>P</i> (MPa)	<i>x</i> × 10 ⁵
0.20 M			
0.76	23.00	5.82	106.31
2.07	41.66	6.98	120.25
2.84	59.27	7.75	133.40
3.99	75.88	8.93	145.84
4.83	91.54	9.98	157.60
0.50 M			
0.99	20.22	5.77	93.44
1.92	36.62	6.98	105.69
2.85	52.10	7.80	117.26
4.15	66.69	8.90	128.19
4.82	80.46	10.03	138.53
0.70 M			
1.02	18.55	6.02	85.74
2.00	33.60	6.98	96.98
2.92	47.80	7.92	107.60
3.93	61.20	8.92	117.62
5.01	73.83	9.95	127.11
1.00 M			
1.14	16.31	6.09	75.37
1.95	29.54	6.71	85.25
3.00	42.02	8.01	94.57
4.00	53.79	8.90	103.39
5.13	64.89	9.89	111.73

3. Results and correlation

The experimental data measured at 300.15 K and under pressures from 1 to 10 MPa are given in Table 2 for the oxygen solubility in sodium carbonate solution with various salt concentrations.

In Table 2, *P* is total pressure, *x* is mole fraction of dissolved oxygen, and *M* is mass mole concentration of sodium carbonate in water. The variations of solubility of oxygen with pressure and salt concentration are plotted in Fig. 2. As seen in Fig. 2, the solubility of oxygen increases with increasing pressure, whereas, the solubility of oxygen decreases with increasing salt concentration due to salting-out effect.

In previous paper [6], a new model based on non-primitive MSA and perturbation theory was proposed to calculate gas solubility at high-pressure in aqueous electrolyte solution. In this model, residual Helmholtz energy of system containing salt, solvent and gas is made up of the following three parts:

$$A - A^{\text{ID}} = A^{\text{HS}} + A^{\text{MSA}} + A^{\text{LJ}} \quad (1)$$

where A^{ID} is Helmholtz free energy of ideal fluid at the same volume and temperature with a real system; A^{HS} is a repulsive term for hard sphere fluid; A^{MSA} is a contribution of non-primitive MSA that arises

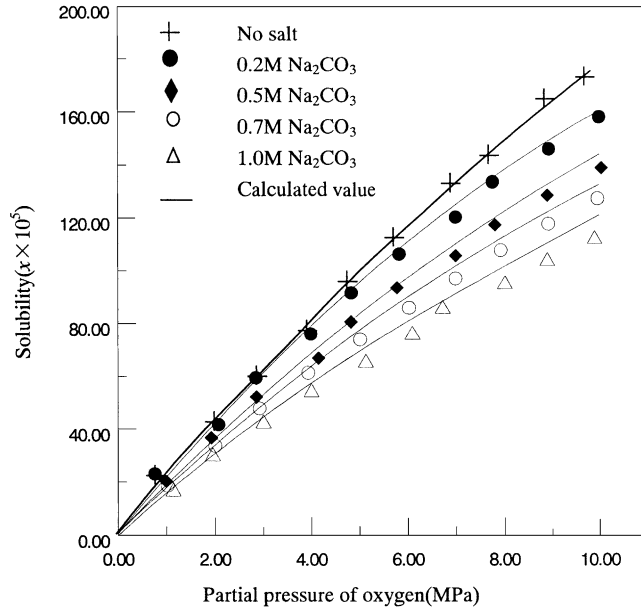


Fig. 2. The solubility of oxygen in aqueous Na₂CO₃ solution at 300.15 K.

from the interaction of ion–ion, ion–dipole and dipole–dipole; and A^{LJ} accounts for the attractive term to Lennard–Jones fluid.

A^{HS} is given by BMCSL equation [10], which is

$$A^{HS} = \frac{(3DE/F)\xi - (E^3/F^2)(E^3/F^2)}{(1 - \xi) + (1 - \xi)^2} + \left(\frac{E^3}{F^2} - 1\right) \ln(1 - \xi) \tag{2}$$

where

$$D = \sum_i x_i \sigma_i, \quad E = \sum_i x_i \sigma_i^2, \quad F = \sum_i x_i \sigma_i^3, \quad \xi = \frac{1}{6} \pi \rho F$$

where ξ is reduced density; ρ the number density and σ_i the molecular diameter.

Non-primitive MSA contribution, A^{MSA} is represented by Blum and Wei’s real non-primitive MSA model [11], which accounts for the interactions of all species (for example, salt and water) in electrolyte solution and sets the dielectric constant of water as unity. The Helmholtz free energy of the system is represented as follows:

$$-\frac{A^{MSA}}{kTV} = \frac{1}{12\pi} \left[-2\alpha_0^2 \sum_j \rho_j z_j N_j + 2\alpha_0 \alpha_2 \rho_n \beta_{10} \right] + J \tag{3}$$

where V is system volume; ρ_j the ionic number density; z_j the valence number of ion; ρ_n the number density of dipole hard sphere; $\alpha_0, \alpha_2, N_j, \beta_{10}, J$ are respectively the parameters of non-primitive MSA model.

Table 3
Molecule parameters for ions, oxygen and water

Species	σ (nm)	(ε/k) (K)	μ/D
Na ⁺	0.205	251.21	–
CO ₃ ²⁻	0.410	65.23	–
O ₂	0.3428	203.86	–
H ₂ O	0.2726 – 1.68/ <i>T</i>	79.86	2.702

The Helmholtz free energy of LJ fluid, A^{LJ} is presented in terms of the equation proposed by Cotterman et al. [12], that is

$$\frac{A^{\text{LJ}}}{NkT} = \frac{A_1^{\text{LJ}}}{T_R} + \frac{A_2^{\text{LJ}}}{T_R^2} \quad (4)$$

where

$$\begin{aligned} \frac{A_1^{\text{LJ}}}{RT} &= \rho_R(-8.5959 - 4.5424\rho_R - 2.2168\rho_R^2 + 10.285\rho_R^3), \\ \frac{A_2^{\text{LJ}}}{RT} &= \rho_R(-1.9075 + 9.9724\rho_R - 22.216\rho_R^2 + 15.904\rho_R^3), \\ \rho_R &= \frac{\eta}{\tau} \quad \tau = \frac{\pi\sqrt{2}}{6}, \quad \eta = \frac{\pi\rho\sigma^3}{6}, \quad T_R = \frac{kT}{\varepsilon} \end{aligned} \quad (4)$$

where σ is diameter of particle; ε the energy parameter of LJ fluid.

In order to calculate gas solubility in aqueous electrolyte solution at high-pressure using the molecular thermodynamic model described above, the molecule parameters of particles (ions, gas and water) have to be first evaluated. The molecule parameters of water are given in Table 3 by fitting the experimental saturated vapor pressure data of water from 298.15 to 573.15 K. The expression of mean ionic activity coefficient could be obtained from Eq. (1) according to thermodynamic relation between residual chemical potential and residual Helmholtz energy. For ions, diameter σ and Lennard–Jones energy parameter ε/k are also shown in Table 3 by fitting the experimental mean ionic activity coefficients of Na₂CO₃ salt solution taken from the compilation of Robinson and Stokes [13]. The molecule parameters of oxygen are also represented in Table 3 by using the experimental data of high-pressure solubility of oxygen in water, which are from the values determined in this work at 300.15 K and within the range of 10 MPa.

To calculate gas–liquid equilibria, we require for each component that its fugacity is the same in every phase, that is

$$f_i^{\text{L}}(T, x, \rho^{\text{L}}) = f_i^{\text{V}}(T, y, \rho^{\text{V}}) \quad (5)$$

$$x_i P \hat{\phi}_i^{\text{L}} = y_i P \hat{\phi}_i^{\text{V}} \quad (6)$$

The fugacity coefficient can be determined from the residual chemical potential μ_i^{r} by the relation

$$\ln \hat{\phi}_i = \frac{\mu_i^{\text{r}}}{RT} - \ln Z \quad (7)$$

In Eq. (7), $Z = (P/\rho KT) = \rho[(\partial(A/RT)/\partial\rho)]_{T,n}$ is the compressibility factor. The residual chemical potential μ_i^r is derived from the relation

$$\mu_i^r = \left[\frac{\partial(A - A^{\text{ID}})}{\partial n_i} \right]_{T,V,n_j=i} \quad (8)$$

The concrete expressions of μ^r and Z could be referred to the appendix of literature [6].

Fig. 2 shows the predicted result on high-pressure gas solubility for oxygen in aqueous sodium carbonate solution with various concentrations. The figure indicates that the agreement between predicted results and experimental data is good even if at very high-pressure by using our model based on non-primitive MSA and perturbation theory. The model proposed by us is reliable for predicting high-pressure solubility of gas in aqueous salt system only using the molecule parameters of pure component.

4. Conclusion

In the present paper, an apparatus for measuring gas solubility at high-pressure has been developed to provide accurate and reproducible gas solubility measurement. The solubilities of oxygen in pure water and aqueous sodium carbonate solution with various concentration of salt have been determined experimentally at 300.15 K and pressures up to 10 MPa. The measured data could be satisfactorily compared with the predicted values by our model based on non-primitive MSA and perturbation theory.

List of symbols

A	Helmholtz free energy
k	Boltzmann's constant $\approx 1.381 \times 10^{-23}$ (J/K)
L	liquid phase
n	mole number
P	pressure (Pa)
T	absolute temperature (K)
V	vapor phase
x	mole fraction in liquid phase
y	mole fraction in vapor phase
Z	compressibility factor

Greek letters

ε	Lennard–Jones energy parameter
$\hat{\phi}$	partial fugacity coefficient
μ	dipole moment (Debye)
μ_i	chemical potential
ρ	number density (m^{-3})
σ	diameter of particle (m)

Superscript

HS	hard sphere
LJ	Lennard–Jones

MSA mean spherical approximation

r residual

Subscripts

i, j component indices

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