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Measurement and Modeling of CO_2 Solubility Under Offshore CCUS Conditions

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ABSTRACT

The solubility of CO_2 under ocean storage conditions affects the dissolution rate and dissolution amount of CO_2 in seawater, and then affects the final storage amount. In this study, the solubility of CO_2 in actual seawater was studied by a combination of experiments and models. Firstly, based on the literature data, the model of carbon dioxide solubility in pure water was constructed, and the *AAD* was 2.2%.Then, a solubility measurement system based on Raman spectrometer was built, and the quantitative relationship between peak intensity ratio and solubility *S*=HR/0.20225 was established by solubility method, and the solubility of CO_2 in the actual seawater in the range of 276.15-286.65 K and 2-20 MPa was further measured by using this quantitative relationship, and the measurement results showed that the sensitivity of CO_2 solubility in seawater to seawater depth was significantly reduced after the storage depth of 400m. Finally, the obtained experimental data was coupled with the model, and the *AAD* was 2.8%.

Keywords: CCUS, solubility, thermodynamic model, Raman spectroscopy

NONMENCLATURE

Abbreviations	
IR	Intensity ratio
Symbols	
f	Fugacity
φ	Fugacity coefficient
x	Mole fraction
Z	Compression factor
A^R	The residual Helmholtz energy of eCPA EoS
k_{ij}	Binary interaction coefficient
S	Solubility
S_{cal}	Calculated value of Solubility
S_{exp}	Experimental value of solubility
N	Number of data
P	Pressure
T	Temperature

1. INTRODUCTION

Carbon Capture, Utilization and Storage (CCUS) technology [1] is a promising and effective solution to the greenhouse effect, which can provide important technical support for green and low-carbon development and energy structure transformation. The solubility of CO_2 in aqueous solution is necessary to estimate the amount of CO_2 stored in seawater under marine sequestration conditions. The dissolution characteristics of CO_2 in seawater affect the CO_2 diffusion rate and CO_2 hydrate formation rate in seawater, and then affect the final storage stock, which has a crucial impact on the storage safety.

There are a number of precedents for the quantitative analysis of Raman spectroscopy for the analysis of geological fluids [2-4]. In the Raman spectroscopy of fluid composition, how to obtain the Raman quantification factor of the measurement system is a very critical issue. For the quantitative study of the solubility of gases in water, the key to obtaining the Raman quantification factor is to prepare a standard aqueous solution with a known gas concentration, and then establish a quantitative function relationship between the gas concentration and the band intensity. In this study, the solubility method was used to calibrate and determine the Raman quantification factor, that is, the Raman spectrum in equilibrium was obtained by experimental methods at specific temperatures and pressures, and the solubility was calculated by thermodynamic model. The calibration of the solubility

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method is affected by the calculation uncertainty of the thermodynamic model and the measurement system error. Systematic errors cannot be avoided, so in order to reduce them, an accurate model for calculating the solubility of CO_2 in water at low temperature and high pressure was developed to determine the quantitative relationship between CO_2 solubility and Raman peak intensity ratio. The solubility of CO_2 in seawater was measured in the range of 276.15-286.65 K and 2-20 MPa.

2. THERMODYNAMIC MODEL

2.1 Model Theory

Gas-liquid equilibrium is the theoretical basis for studying the dissolution properties of CO_2. In gas-liquid equilibrium, the fugacity of component *i* in the two phases satisfies the following relation:

$$f_i^V = f_i^L \tag{1}$$

where f_i^V and f_i^L denotes the fugacity of component *i* in the liquid phase and vapor phase, respectively. Solving solubility ultimately comes down to the determination of fugacity.

In this study, the fugacity is solved by using the equation of state, and the fugacity of component *i* in the gas-liquid phase is expressed as:

$$f_i = \varphi_i \; x_i P \tag{2}$$

where , φ_i denotes the fugacity coefficient of the gas-liquid phase, which is calculated by using the eCPA equation of state [5].

The residual Helmholtz energy of eCPA EoS is shown as follows:

$$A^R = A^{SRK} + A^{assoc} + A^{DH} + A^{Born} \tag{3}$$

The fugitiy coefficient is calculated as follows:

$$\ln \varphi(\vec{x}) = A^R + (Z-1) + \left(\frac{\partial A^R}{\partial x_i}\right)_{T,V} - \sum_{j=1}^{n}\left[x_j\left(\frac{\partial A^R}{\partial x_j}\right)_{T,V,i\neq j}\right] - \ln Z \tag{4}$$

2.2 Model Validation

In order to ensure the accuracy of the thermodynamic model, it is necessary to calibrate the important parameters of the model. In this study, the model was modified using the solubility data in the literature [6-9].

Fig.1. and Fig.2. shows the comparison of the experimental values in the literature between the models in the range of 273.15-298 .15 K and 0-40 MPa. Then, the effect of the model was evaluated by calculating the Average Absolute Deviation (*AAD*) [10], and the *AAD* was calculated as follows. The *AAD* of this model is 2.2%.

$$AAD = \frac{100\%}{N}\sum_i^N\left|\frac{S_{cal}-S_{exp}}{S_{exp}}\right| \tag{5}$$

where *N* represents the number of data points; S_{exp} represents the experimental value; S_{cal} represents the calculated value of the model.

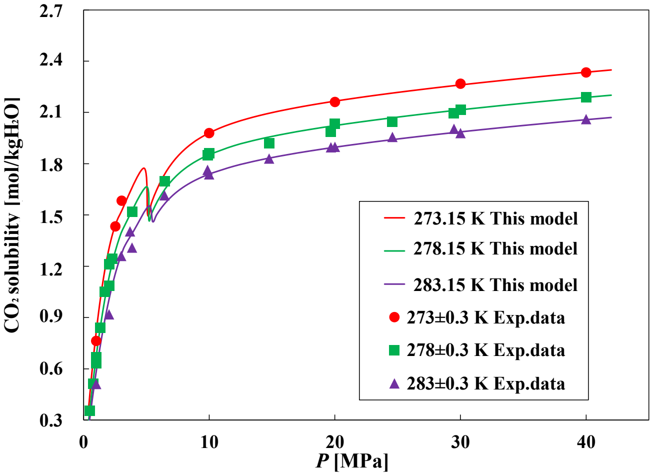


Fig. 1. Comparison of data at 273.15-283.15K

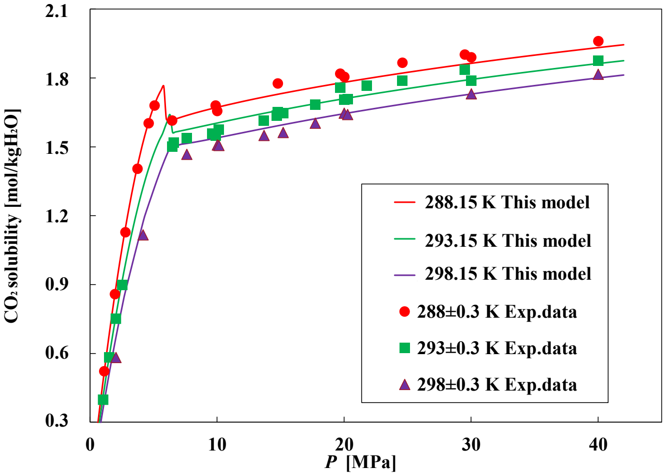


Fig. 2. Comparison of data at 288.15-298.15K

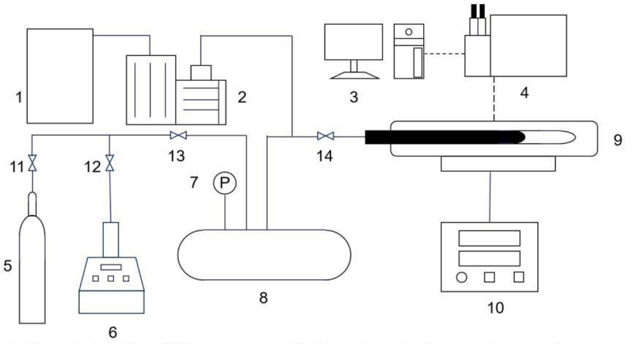
3. EXPERIMENTAL PART

3.1 Experimental principle

Raman spectroscopy is a widely used non-destructive measurement technique that can be used to characterize the composition of substances in liquid, gas, and solid phases at different temperatures and pressures. In this study, CO_2 dissolution experiments were carried out in a tubular transparent high-pressure chamber constructed of quartz capillaries, and the experimental system is shown in Fig.3.

3.2 Experimental procedure

Before the solubility measurement experiment, the quantitative relationship between the CO_2 concentration in the aqueous phase and the ratio of Raman peak height was first calibrated. After the calibration is completed, dissolution experiments in seawater are performed and the peak-to-height ratio is obtained, and the CO_2 solubility can be calculated from the quantitative relationship obtained. The specific steps include: (1) Prepare a quartz capillary sample tube filled with pure water; (2) Fix the quartz capillary sample tube on the hot and cold stage and connect the CO_2 pipeline; (3) Vacuum extraction of all pipelines to eliminate the influence of air on the experiment; (4) When the pipeline is in a vacuum state, open the valve to enter CO_2; (5) Adjust the temperature and pressure to the target working conditions; (6) After standing for 1 hour; (7) The observation point was selected within 100 microns from the aqueous side of the gas-liquid interface, and the Raman spectrum was measured and obtained; (8) Raman spectra were analyzed to obtain IR; (9) The thermodynamic model is used to calculate the solubility value of the corresponding working conditions; (10) Fitting the quantitative relationship between solubility and peak height ratio; (11) Refer to steps 1-8 to obtain the IR in seawater; (12) The solubility of CO_2 in seawater is obtained by using quantitative relationship.



1. Discarded bottles; 2. Vacuum pump; 3. Computers; 4. Raman micro-spectroscope; 5. CO_2 cylinder; 6. Pressure pump; 7. Pressure sensor; 8. Intermediate containers; 9. Cooling and heating station; 10. Temperature controller; 11~14. Valve.

Fig. 3. Experimental system

4. RESULTS AND DISCUSSION

4.1 Raman quantitative relationship

Raman quantitative experiments were divided into two groups according to the pressure, 5 MPa and 15 MPa, and the Raman spectra of the solution near the gas-liquid interface were collected in the temperature range of 276.15-290.15 K, and the relationship between CO_2 solubility and Raman peak intensity ratio (IR) was established. In the process of determining the Raman quantitative relationship, CO_2 solubility is expressed by the number of moles of CO_2 dissolved per kilogram of water *S*, and the resulting IR/*S* values are shown in Tab. 1.

Fig.4. illustrates the relationship between IR value and solubility *S*. As can be seen from Fig.4., there is a linear relationship between HR and S, and the obtained IR/S values are all around 0.2, and the average IR/S value is taken as the quantitative relationship in this study: IR/*S*=0.20225→*S*=IR/0.20225.

Tab 1. Raman quantitative experimental data

T [K]	*P* [MPa]	IR	S[mol/kgH_2O]	IR/S
290.15	5	0.26838	1.33627	0.20084
288.15	5	0.28788	1.40042	0.20556
286.15	5	0.30187	1.46179	0.20650
284.15	5	0.31422	1.52622	0.20588
282.15	5	0.32113	1.59021	0.20194
280.15	5	0.33362	1.65434	0.20166
278.15	5	0.34235	1.71685	0.19941
276.15	5	0.36010	1.78186	0.20209
290.15	15	0.33582	1.66299	0.20194
288.15	15	0.34677	1.69550	0.20452
286.15	15	0.34855	1.71947	0.20270
284.15	15	0.34974	1.74735	0.20015
282.15	15	0.35664	1.77810	0.20057
280.15	15	0.36084	1.82148	0.19810
278.15	15	0.38140	1.88063	0.20280
276.15	15	0.38700	1.92364	0.20118

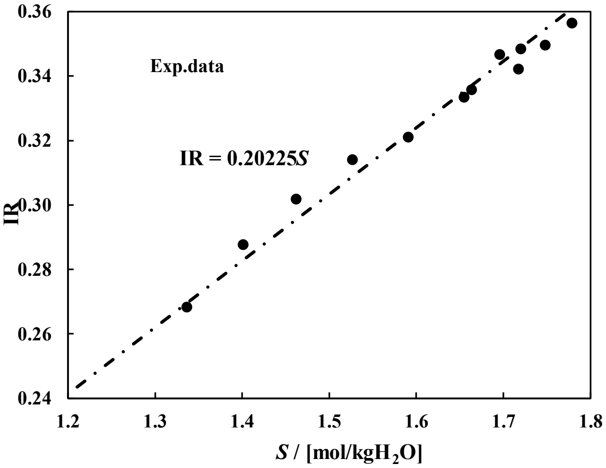


Fig. 4. Relationship between IR and *S*

4.2 Solubility measurement results

After determining the quantitative relationship, a total of 15 groups of CO_2 solubility measurements in seawater with a pressure range of 2-20 MPa and a temperature range of 276.15-286.65 K were completed through the experimental steps proposed in the experimental part, and the measurement conditions were selected according to the actual working conditions of seawater. When using the thermodynamic model, all the salts in the seawater are converted into NaCl , then the calculated value Scal with *AAD* is 2.8%. The specific experimental data and the predicted results of the model and their deviations are shown in Tab.2.

Tab. 2. Experimental data of solubility measurement

T [K]	*P* [MPa]	IR	Solubility		AD
			S_{exp}	S_{cal}	
286.65	2	0.15800	0.78126	0.76535	2.0%
283.83	3	0.18949	0.93694	0.90734	3.2%
281.81	4	0.27331	1.35138	1.30043	3.8%
281.03	4.5	0.28195	1.39413	1.30462	6.4%
280.33	5	0.28995	1.43367	1.33929	6.6%
279.25	6	0.29245	1.44604	1.39278	3.7%
277.86	8	0.29901	1.47847	1.49546	1.1%
277.42	9	0.30216	1.49406	1.54558	3.4%
277.23	9.5	0.30500	1.50811	1.56637	3.9%
277.06	10	0.30775	1.52168	1.58495	4.2%
276.54	12	0.32784	1.62102	1.64352	1.4%
276.15	14	0.33872	1.67483	1.68745	0.8%
276.15	16	0.34312	1.69659	1.71626	1.2%
276.15	18	0.35246	1.74276	1.74114	0.1%
276.15	20	0.35949	1.77856	1.76352	0.8%

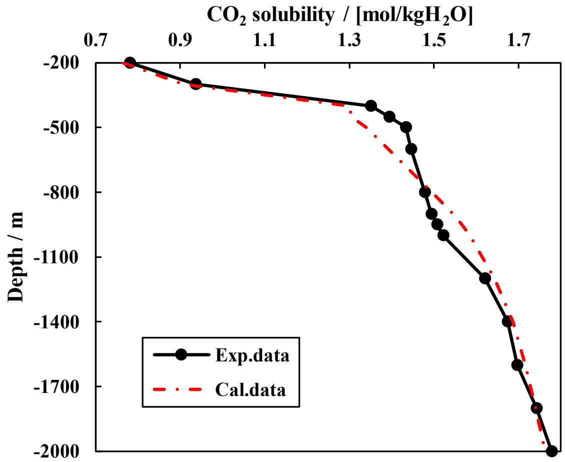


Fig. 5. Solubility varies with depth

Fig.5 shows the variation of solubility with sea depth, and it can be seen that the solubility increases with the increase of sea depth. At depths of less than 400 m, solubility changes rapidly with depth, but after reaching depths of 400 m, solubility changes slowly with depth. Through thermodynamic analysis, it can be seen that when CO_2 is in the gaseous state, the fugitiveness is more sensitive to pressure changes than in the liquid state. Therefore, when the depth is increased to 400 m, the CO_2 changes from gaseous to liquid state, resulting in a decrease in the sensitivity of solubility to depth changes.

5. CONCLUSIONS

In this study, a thermodynamic model was constructed to calculate the solubility of carbon dioxide in water based on the eCPA equation of state. Based on the available experimental data, the accuracy of the improved model was 2.2% for the experimental data in the literature. A solubility measurement system based on Raman spectrometer was built to measure the solubility of CO_2 in the actual seawater in the range of 276.15-286.65 K and 2-20 MPa, which supplemented the CO_2 solubility data under marine storage conditions. The measured solubility showed that after the sequestration depth of 400 m, the sensitivity of CO_2 solubility in seawater to seawater depth was significantly reduced. Finally, the solubility of CO_2 in seawater was predicted by using this model, and the *AAD* was 2.8% compared with the experimental data in this paper.

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DECLARATION OF INTEREST STATEMENT

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. All authors read and approved the final manuscript.

REFERENCE

[1] Zhao J., Zheng J., Ren L., et al. A review on geological storage of marine carbon dioxide: Challenges and prospects. Marine and petroleum geology 2024;163: 106757.

[2] Geng L., Qu K., Lu W., et al. In situ Raman spectroscopic study of the pressure effect on the concentration of CO_2 in water at hydrate-liquid water equilibrium up to 900 bar. Fluid Phase Equilibria 2017;438: 37-43.

[3] Sa J., Kwak G., Lee B. R., et al. Phase equilibria and characterization of CO_2 and SF_6 binary hydrates for CO_2 sequestration. Energy 2017;126: 306-311.

[4] Guo H., Chen Y., Hu Q., et al. Quantitative Raman spectroscopic investigation of geo-fluids high-pressure phase equilibria: Part I. Accurate calibration and determination of CO_2 solubility in water from 273.15 to 573.15 K and from 10 to 120 MPa. Fluid Phase Equilibria 2014;382: 70-79.

[5] Maribo-Mogensen B., Thomsen K., Kontogeorgis G. M. An electrolyte CPA equation of state for mixed solvent electrolytes. Aiche journal 2015;61(9): 2933-2950.

[6] Servio P., Englezos P. Effect of temperature and pressure on the solubility of carbon dioxide in water in the presence of gas hydrate. Fluid phase equilibria 2001;190(1): 127-134.

[7] Stewart P. B., Munjal P. J. Solubility of carbon dioxide in pure water, synthetic sea water, and synthetic sea water concentrates at -5 to 25℃ and 10 to 45 atm. pressure. Journal of chemical and engineering 1970;15: 67-71.

[8] Li Z., Guo X. Q., Tian H. Calculation for solubility of methane and carbon dioxide in water in presence of hydrate. Huagong Xuebao 2010;61: 1341-1348.

[9] Guo H., Chen Y., Hu Q., et al. Quantitative Raman spectroscopic investigation of geo-fluids high-pressure phase equilibria: Part I. Accurate calibration and determination of CO2 solubility in water from 273.15 to 573.15 K and from 10 to 120 MPa. Fluid Phase Equilibria 2014;382: 70-79.

[10] Clarke M. A., Chen Z., Ahmadi M. A comparison of the CPA equation of state and the Trebble-Bishnoi equation of state for use in correlating methane hydrate formation conditions in the presence of aqueous amino acids. Fluid Phase Equilibria 2023;573: 113878.

[11] Sun L., Kontogeorgis G. M., von Solms N., et al. Modeling of Gas Solubility Using the Electrolyte Cubic Plus Association Equation of State. Industrial & engineering chemistry research 2019;58(37): 17555-17567.

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