Measurement and prediction model of carbon dioxide solubility in aqueous solutions containing bicarbonate anion

Yong Tang [a,*], Xiaoqiang Bian [a], Zhimin Du [a], Changquan Wang [b]

[a] The State Key Laboratory of Oil & Gas Reservoir Geology and Exploitation Engineering, Southwest Petroleum University, Chengdu 610500, PR China
[b] Petroleum Engineer College, Yangtze University, Jingzhou 434023, PR China

ABSTRACT

The solubility of CO_2 in aqueous solutions containing bicarbonate anion was determined at 308.15, 328.15, 368.15, and 408.15 K up to 40 MPa. In comparison with Cl^-, HCO_3^- has a larger size and higher molecular weight, which leads to the opposite salting-out effect. HCO_3^- can suppress CO_2 dissolution because of equilibrium reaction between CO_2 and H_2O to form HCO_3^-. Cooperation of the three effects leads to slightly variable solubility of CO_2 in the solution containing HCO_3^-. It is found that the Duan model can more accurately predict the CO_2 solubility at low salt concentration, while the PR–HV model shows smaller error at high salt concentration. Moreover, the solubility of CO_2 in natural ground water was measured at different temperatures and pressures, and the results verified the presented mathematical model.

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1. Introduction

The concentration of carbon dioxide (CO_2) in the atmosphere has increased considerably because of fossil fuel combustion, leading to a significant climate change. Serious efforts are likely to be made during the coming decades to reduce CO_2. A particular technology for achieving these reductions in the relatively near future is carbon capture and sequestration (CCS) [1]. Geological storage, which injects CO_2 into deep saline aquifers, depleted hydrocarbon reservoirs, or deep coalbeds, is currently attracting much attention because of the large capacity [2].

Effective estimation of the total amount of the stored CO_2 requires the solubility of CO_2 in aqueous solutions. Generally, CO_2 dissolution into the aqueous phase is limited by its solubility, which in turn depends upon the water temperature, pressure, and salt concentration and composition. These parameters can change significantly from one location to another. Salt composition and concentration in deep formation waters may thus vary substantially among different formations depending on their depth, thermal conditions, geomorphology, and reservoir minerals.

Currently, many systems, such as CO_2–H_2O [3–9], CO_2–H_2O–NaCl [10–12], CO_2–H_2O–KCl [11,13], CO_2–H_2O–Na_2SO_4 [14], CO_2–seawater [15] and CO_2–brine [6], have been studied at different ranges of pressure and temperature. Many models including the Duan model [16,17] and the Peng [18] equation of state combined with Huron–Vidal [19] mixing rules (PR–HV model) for predicting CO_2 aqueous solubility have been developed in studies over recent decades using a combination of phase-equilibrium and empirical relationships [16,17,20–26]. Despite these contributions, the limitation of the current work is the relative rarity of investigations on the effect of anion of salts. In addition to halogen ion (Cl^-, Br^-, I^-) and SO_4^{2-}, three noteworthy anionic examples are nitrate (NO_3^-), acetate (CH_3COO^-), and phosphate, which exhibit different effects on CO_2 solubility [27,28]. To the best of our knowledge, no measurement and prediction model of CO_2 solubility for salt solutions containing bicarbonate anion (HCO_3^-) are reported in the current literatures, although prediction of CH_4 and N_2 solubility for salt solutions containing bicarbonate anion was successfully achieved [29]. Indeed, HCO_3^- is commonly present in natural ground waters although NaCl is often the major component, and HCO_3^- can also be formed because of reaction between CO_2 and water. Therefore, it can be anticipated that HCO_3^- should show important effects on CO_2 solubility.

In this paper, the solubility of CO_2 was determined in an aqueous solution containing HCO_3^- in the range of 308.15–408.15 °C and 8–40 MPa. Moreover, available experimental data from various conditions were used to compare the performance of several models in predicting CO_2 solubility. The Duan and PR–HV models can provide accurate prediction for CO_2 solubility in aqueous solutions containing HCO_3^-. It is interesting to note that the Duan model is shown to fit better at low salt concentration, while the PR–HV model is more suitable for high salt concentration.

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2. Experimental

2.1. Materials

CO_2 (purity 99.99%) was supplied by Chengdu Dongfang Electric Gas Co., Ltd. The salts of NaCl, KCl, $NaHCO_3$, $KHCO_3$ and $CaCl_2$ supplied by Sinopharm Chemical Reagent Co., Ltd. were of analytical grade with a purity of >99% (see Table 1). This purity is acceptable, with the uncertainty taken to be approximately 0.5% for the NaCl and KCl and 2% for the $CaCl_2$ and $MgCl_2$. The reagents were used without further purification. The water used to prepare solutions was twice-distilled water (conductivity <5 mS/cm). The solvent mixture was prepared gravimetrically.

2.2. Preparation of aqueous solutions

Aqueous solution samples with different concentrations were prepared by mixing the desired amount of NaCl, $MgCl_2$, $CaCl_2$, and $NaHCO_3$. They were weighted on an analytic balance with sensitivity ±0.1 mg and then dissolved in distilled water.

The ground water samples collected from the Jilin Oilfield Group formation, China, was measured by ICP-AES and the titrimetric method to determine the components. ICP-AES measurement for determining metal ionic was performed on an IRIS Advantage (HR) spectrometer. The compositions and concentration of aqueous solutions are listed in Table 2.

2.3. Apparatus and procedures

The experiments were performed with apparatus based on the static approach. Details of the experimental arrangement were given before [30]. A schematic of the experimental set-up for CO_2 solubility measurement is shown in Fig. 1. The apparatus was composed mainly of a CO_2 gas cylinder, a RUSKA pump (a computer-controlled metering syringe pump), a JEFRI equilibrium view cell with a sapphire window, a thermostatic air bath, a sampling bomb, a pressure transducer, gas meters and an electronic balance. The temperature of the thermostatic air bath was controlled by a temperature controller.

In a typical experiment, the equilibrium cell and lines are evacuated using a vacuum pump prior to introducing the aqueous solution and CO_2 gas. The desired amount of salt solution was introduced into the view cell, the view cell was placed in the air bath, whose temperature was controlled to the desired temperature with an immersed thermocouple by an electric furnace, then CO_2 was charged into the system by using the pressure amplifier and the cell pressure was controlled to reach the desired pressure. The aqueous phase in the view cell was stirred by the magnetic stirrer. The stirring of the aqueous phase ensured a homogeneous temperature inside the view cell. The temperature was held constant to within ±0.1 K by a thermocouple and the pressure was monitored by a transducer with a precision of 0.01 MPa. The system was considered to have reached equilibrium if the pressure

Table 2
Molar concentration of ions in aqueous solutions at temperature T = 298 K and pressure P = 0.101 MPa.[a]

Samples	Ionic	c (mol/Kg)
No. 1[b]	Na^+	0.0595 ± 0.0002
	Ca^{2+}	0.0899 ± 0.0005
	Mg^{2+}	0.1040 ± 0.0003
	Cl^-	0.3913 ± 0.0006
	HCO_3^-	0.0595 ± 0.0002
	Total[c]	0.7041 ± 0.0004
No. 2[b]	Na^+	0.1190 ± 0.0004
	Ca^{2+}	0.1798 ± 0.0006
	Mg^{2+}	0.2079 ± 0.0002
	Cl^-	0.7825 ± 0.0003
	HCO_3^-	0.1190 ± 0.0005
	Total[c]	1.4083 ± 0.0004
Groundwater	K^+	0.0153 ± 0.0005
	Na^+	0.1261 ± 0.0006
	Ca^{2+}	0.0087 ± 0.0003
	Mg^{2+}	0.0012 ± 0.0005
	Fe^{2+}	0.0005 ± 0.0002
	Cl^-	0.0917 ± 0.0004
	SO_4^{2-}	0.0051 ± 0.0004
	HCO_3^-	0.0098 ± 0.0003
	Total[c]	0.2586 ± 0.0004

[a] Standard uncertainties u are $u(T)$ = 0.1 K, $u(P)$ = 0.01 MPa.
[b] No.1 and No.2 aqueous solution samples were obtained by mixing the desired amount of NaCl, $MgCl_2$, $CaCl_2$, and $NaHCO_3$ in distilled water.
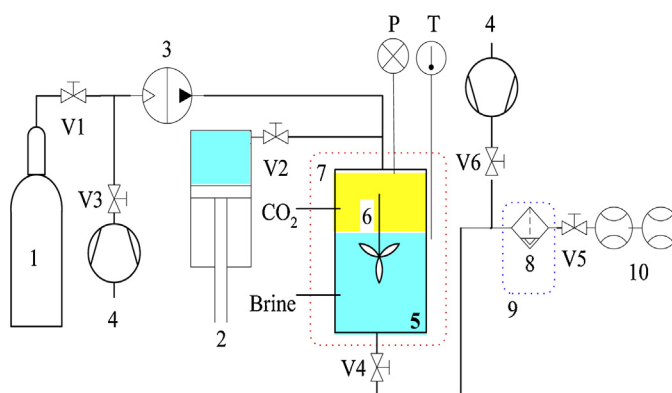[c] Molar concentration of the total ions in aqueous solutions.

Fig. 1. Schematic diagram of the experimental apparatus.

of the system had been unchanged for 3 h. Then the pressure of the system was recorded. The valve of the sampling cylinder was opened slowly to collect a sample in a sampling cylinder. At the same time, the volume of the view cell was adjusted to keep the pressure unchanged during the sampling process. The sampling valve was closed after a large enough liquid sample had been

Table 1
Source and purity of the reagents used.

Compounds	CAS number	Source	Molar mass (g/mol)	Purity (mass fraction)	Analysis method
CO_2	124-38-9	Chengdu Dongfang Electric Gas Co., Ltd.	44.01	0.9999	GC[a]
NaCl	7647-14-5	Sinopharm Chemical Reagent Co., Ltd.	58.5	0.995	None
KCl	7447-40-7	Sinopharm Chemical Reagent Co., Ltd.	74.551	0.995	None
$NaHCO_3$	144-55-8	Sinopharm Chemical Reagent Co., Ltd.	84.01	0.999	None
$KHCO_3$	298-14-6	Sinopharm Chemical Reagent Co., Ltd.	100.12	0.99	None
$CaCl_2$	10043-52-4	Sinopharm Chemical Reagent Co., Ltd.	110.98	0.99	None

[a] Gas–liquid chromatography.