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Viscosity of Aqueous NaCl Solutions with Dissolved CO_2 at (30 to 60) °C and (10 to 20) MPa

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The viscosity of aqueous NaCl solutions with dissolved CO_2 was measured at conditions representing an underground aquifer at a depth of (1000 to 2000) m for the geological storage of CO_2 (i.e., (30 to 60) °C and (10 to 20) MPa at a mass fraction of NaCl between 0 and 0.03 by using a sedimenting solid particle type viscometer with an estimated uncertainty of ±2%). On the basis of this experimental data, an empirical equation for predicting this viscosity as a function of the temperature and mole fraction of CO_2 for these conditions was derived.

Introduction

The geological storage of CO_2 has been investigated as an option for reducing the concentration of CO_2 in the atmosphere.[1] The storage of CO_2 in deep saline aquifers is technically feasible, as demonstrated at the Sleipner gas field in the Norwegian North Sea. Since 1996, 1 million metric tons of CO_2 have been injected annually into saltwater-saturated sands at depths below 800 m[1]. In Japan, the Research Institute of Innovative Technology for the Earth (RITE) and the Engineering Advancement Association of Japan (ENAA) will begin geological sequestration field experiments in 2003 in which CO_2 will be injected into an aquifer.[2] When a large amount of CO_2 is injected into an aquifer, a prediction of the dynamic action of CO_2 in an aquifer is necessary. However, clarifying the diffusion action of the injected CO_2 first requires quantitative data pertaining to the dissolution and diffusion action of CO_2. The viscosity of aqueous NaCl solutions containing CO_2 has been measured[3,4] at pressure and temperature conditions of the deep ocean, but the viscosity of such solutions saturated with CO_2 at underground conditions has not.

In this study, such data was obtained by measuring the viscosity of aqueous NaCl solutions (NaCl mass fraction between 0 and 0.03) saturated with CO_2 at pressure and temperature conditions of an underground aquifer, namely, (30 to 60) °C and (10 to 20) MPa. Because a falling capillary tube viscometer that uses mercury cannot remain in contact with an electrolyte solution for the long time required to produce solutions saturated with CO_2, we used a sedimenting solid particle-type viscometer. On the basis of the results, a prediction equation for the viscosity as a function of temperature and CO_2 mole fraction was derived.

Materials and Methods

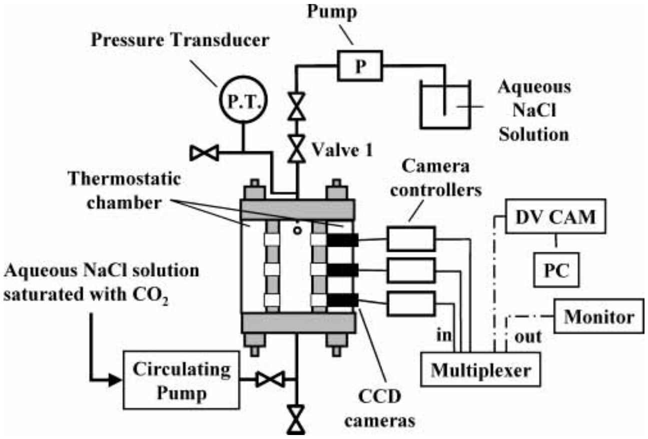

Figure 1. Schematic of the apparatus for determining the viscosity of aqueous NaCl solutions saturated with CO_2.

Figure 1 shows a schematic of the experimental apparatus used to measure the viscosity of the saturated solution. A detailed description of the apparatus and experimental procedure to produce homogeneous aqueous NaCl solutions containing CO_2 is described elsewhere.[5] The apparatus to measure viscosity consisted of a high-pressure vessel with a thermostatic chamber, a pressure transducer for the range of (0 to 25) MPa (TEAC, TP-AP 20 MPa) with an accuracy of ±0.2MPa, an amplifier (TEAC, SA-59), a temperature bath, a pump for pressurizing water (GL Science, PU610−0X), a pump for pressurizing CO_2 (Nippon Seimitsu Kagaku, NP−S-701), a CO_2 gas cylinder, a circulating pump (AKICO Co.), a CCD color video camera (SONY, DXC-LS1), four input duplex color multiplexer cameras (SONY, YS-DX504), a monitor (SONY, KV-21SF1), and a DVCAM compact half-rack digital VTR (SONY, DSR-45). The test section's temperature was measured with platinum resistance thermometers (SHIMADEN, RD-11S) within an accuracy of ±0.2 °C. The mass of CO_2 and water was measured by using a gravimetric balance (Sartorius, LP1200S).

The high-pressure vessel (28-mm inner diameter and 650 mm long) could be pressurized to a maximum of 70 MPa. A total of three pairs of windows at 200-mm intervals along the test section of the vessel were used to view the particle sedimenting through the solution by using the CCD

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cameras. The vessel and all of the tubes were made of stainless steel. The pure water used in the NaCl solution was filtered by using a water purification system (Milli-Q, Millipore). The purity of CO_2 was 99.99%. Ruby particles (moritex, D-0862), and BK-7 particles (moritex, D-0855) with densities of ρ_b = (3979.90 and 2509.94) kg/m^3, respectively, were used. The particles were 0.5 mm in diameter with a standard deviation of less than 2.5 μm, and their sphericity was less than 0.64 μm.

The viscosity of aqueous NaCl solutions saturated with CO_2, η_{CS}, was measured at temperatures t of 30 °C, 40 °C, 50 °C, and 60 °C, at pressures P of 10 MPa and 20 MPa, and at NaCl mass fractions S of 0, 0.01, and 0.03. The CO_2 mole fraction of the solutions saturated with CO_2, x_{CS}, is calculated by using the following empirical equation[5]

$$x_{CS} = \frac{P/\text{MPa}}{36.1P/\text{MPa} + 3.87(t/°\text{C} + 273.15) - 1097.1 + \{196P/\text{MPa} + 26.9(t/°\text{C} + 273.15) - 8810\}S} \tag{1}$$

where P, t and S denote pressure, temperature, and mass fraction of NaCl, respectively.

First, the test section was filled with the aqueous solution, and then valve 1 was closed. Then, a particle was placed in the test section between the pump and valve 1. At 30 °C and 40 °C, ruby and BK-7 particles were used. At 50 °C and 60 °C, only BK-7 particles were used. The solution was then pressurized, and valve 1 was opened. The velocity of the sedimenting particle was measured by using the CCD cameras. The measurements were repeated for each set of experimental conditions, and then the average viscosity was calculated.

The viscosity of aqueous NaCl solutions containing CO_2, η_C, was also measured at the desaturated concentrations of CO_2.

The viscosity of the liquid, η_l, was calculated from the force balance between the buoyancy and drag force acting on sedimenting particles. At steady state, the drag coefficient of the sedimenting particle, C_D, can be expressed as[6]

$$C_D = \frac{8(\rho_b - \rho_l)gR}{3\rho_l U^2} \tag{2}$$

where U is the velocity of the sedimenting particle, R is the radius of the particle, and ρ is the density and subscripts b and l denote the particle and liquid, respectively.

There are many correlation of drag coefficients. The viscosity of water at 0.1 MPa was measured to determine the best correlation of drag coefficient. By using the empirical equation for the drag coefficient of a rigid sphere,[6]

$$C_D = \frac{24}{Re}(1 + 0.1935Re^{0.6305}) \quad \left(20 \le Re = \frac{2\rho_l UR}{\eta_l} \le 260\right) \tag{3}$$

and eq 2 with measured values of U, we determined η_l.

The density of the aqueous CO_2 solution, ρ_C, was estimated using the following empirical equation:[7]

$$\rho_C/(\text{kg·m}^{-3}) = \rho_W/(\text{kg·m}^{-3}) + 1.96 \times 10^2 x_C + 1.54 \times 10^4 {x_C}^2 \tag{4}$$

Table 1. Accuracy of Measurements and Responsible Error for Viscosity

	measurement accuracy	responsible error for viscosity/%
temperature/°C	±0.2	0.5
pressure/MPa	±0.2	<0.01
sedimenting particle's velocity/(mm·s^{-1})	±0.01	<0.01
ball diameter/mm	±0.0025	1.5
ball density/(kg·m^{-3})	±0.1	<0.01
liquid density/%	±0.15	0.03
drag coefficient/%	±0.6	1.1

Table 2. Viscosity of Pure Water, η_W/(mPa·s), at 0.1 MPa

t/°C	27.2	47.2	60
current study	0.85 ± 0.02	0.56 ± 0.02	0.47 ± 0.02
literature [12]	0.85 ± 0.01	0.58 ± 0.01	0.47 ± 0.01

where ρ and x are the density and CO_2 mole fraction, respectively. Subscripts C and W denote the aqueous solution containing CO_2 and pure water, respectively. This equation is valid for solutions at (278 to 293) K and (6.44 to 29.49) MPa. To estimate the density of an aqueous electrolyte solution containing CO_2, we used the following modified equation.

$$\rho_C/(\text{kg·m}^{-3}) = \rho_S/(\text{kg·m}^{-3}) + 1.96 \times 10^2 x_C + 1.54 \times 10^4 {x_C}^2 \tag{5}$$

where the subscript S denotes the aqueous NaCl solution.

By comparing with the experimental data obtained by Song et al., [8] eq 5 can be used to estimate the density data of an aqueous solution containing electrolytes and CO_2, ρ_C, with an uncertainty of ±0.15%.

Therefore we estimated the density of an aqueous NaCl solution containing CO_2, ρ_C, using this equation and the values of ρ_S[9] and x_C.

The accuracies of the measurements together with the responsible error for viscosity are listed in Table 1. The viscosity measurements have an uncertainty of 2% when using a standard technique.[10]

Results and Discussion

Tables 2 and 3 list the measured viscosity of water, η_W, and of an aqueous NaCl solution, η_S. The measured values agreed well with reference values, indicating good reliability for the results obtained by the experimental method used here.

Figure 2 shows the measured viscosity of the aqueous solution saturated with CO_2, η_{CS}, and Table 4 lists the data. The results show that (a) for the same values of pressure and mass fraction of NaCl the viscosity of the aqueous solution saturated with CO_2 decreased as temperature increased, (b) the viscosity of the aqueous solution saturated with CO_2 was relatively independent of pressure, and (c) the viscosity of the aqueous solution saturated with CO_2 increased with increasing mass fraction of NaCl.

Table 5 lists the measured viscosities for aqueous NaCl solutions containing CO_2. The results show that the viscosity was proportional to the mole fraction of CO_2.

By regressing the experimental data in Tables 4 and 5, a prediction equation was derived for the viscosity of aqueous NaCl solutions containing CO_2, η_C, at P from (10 to 20) MPa, t from (30 to 60) °C, and S from (0 to 0.03).

Table 3. Viscosity of Pure Water, η_W/(mPa·s), and an Aqueous NaCl Solution, η_S/(mPa·s)

t/°C		30		40		50		60	
P/MPa		10	20	10	20	10	20	10	20
S		η/mPa·s							
0	current study	0.80 ± 0.02		0.66 ± 0.02		0.56 ± 0.02		0.47 ± 0.02	
	literature[12]	0.80 ± 0.02		0.65 ± 0.02		0.55 ± 0.01		0.47 ± 0.01	
0.03	current study	0.84 ± 0.02	0.83 ± 0.02	0.68 ± 0.02	0.69 ± 0.02	0.59 ± 0.02	0.59± 0.02	0.49 ± 0.02	0.50 ± 0.02
	literature calculation value[11]	0.83 ± 0.02	0.83 ± 0.02	0.68 ± 0.02	0.69 ± 0.02	0.58 ± 0.02	0.58± 0.02	0.50 ± 0.02	0.50 ± 0.02

Table 4. Viscosity of an Aqueous NaCl Solution Saturated with CO_2, η_{CS}, at NaCl Mass Fractions S = 0, 0.01, and 0.03

t/°C	30		40		50		60	
P/MPa	10	20	10	20	10	20	10	20
S	η/mPa·s							
0	0.89 ± 0.03	0.88 ± 0.03	0.70 ± 0.03	0.71 ± 0.03	0.57 ± 0.02	0.57 ± 0.02	0.47 ± 0.02	0.48 ± 0.02
0.01	0.90 ± 0.03	0.90 ± 0.02	0.72 ± 0.02	0.72 ± 0.02	0.58 ± 0.02	0.58 ± 0.02	0.49 ± 0.02	0.48 ± 0.02
0.03	0.93 ± 0.03	0.95 ± 0.02	0.75 ± 0.02	0.75 ± 0.02	0.61 ± 0.02	0.60 ± 0.02	0.51 ± 0.02	0.51 ± 0.02

Table 5. Viscosity of an Aqueous NaCl Solution Containing CO_2, η_C, at 10 MPa for NaCl Mass Fractions of S = 0, 0.01, and 0.03

t/°C S		30				40		
0	10^2x_C	0	0.73 ± 0.01	1.48 ± 0.02	2.38 ± 0.07[5]	0	1.07 ± 0.01	2.07 ± 0.02[5]
	η_C/(mPa·s)	0.80[12] ± 0.02	0.81 ± 0.02	0.86 ± 0.02	0.89 ± 0.03	0.65[12] ± 0.02	0.68 ± 0.02	0.70 ± 0.03
0.01	10^2x_C	0	0.73 ± 0.01	1.48 ± 0.02	2.27 ± 0.07 [5]	0	1.06 ± 0.01	2.03 ± 0.02[5]
	η_C/(mPa·s)	0.81[12] ± 0.02	0.85 ± 0.02	0.86 ± 0.02	0.90 ± 0.02	0.68[12] ± 0.02	0.70 ± 0.02	0.72 ± 0.02
0.03	10^2x_C	0	1.08 ± 0.01	2.09 ± 0.04[5]				
	η_C/(mPa·s)	0.83[12] ± 0.02	0.86 ± 0.02	0.93 ± 0.02				

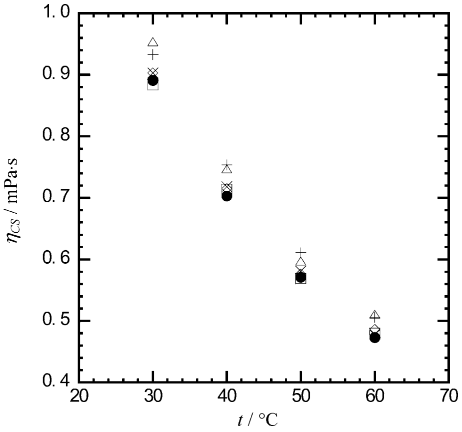

Figure 2. Viscosity of an aqueous NaCl solution saturated with CO_2, η_{CS}, vs temperature, t, for various pressures and NaCl mass fractions: ●, 0% NaCl, 10 MPa; □, 0% NaCl, 20 MPa; ◇, 1% NaCl, 10 MPa; ×, 1% NaCl, 20 MPa; +, 3% NaCl, 10 MPa; △, 3% NaCl, 20 MPa.

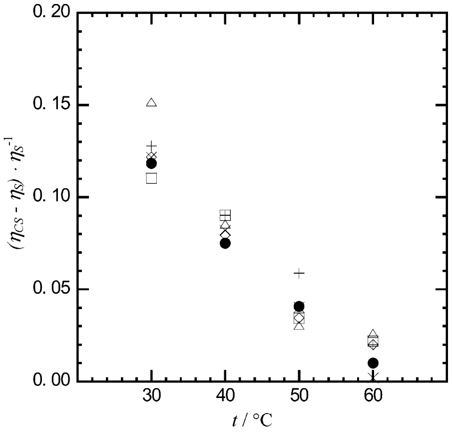

Figure 3. Relative ratio between the viscosity of an aqueous NaCl solution saturated with CO_2, η_{CS}, and that of an NaCl solution without CO_2, η_S, vs temperature, t, for various pressures and mass fractions of NaCl: ●, 0% NaCl, 10 MPa; □, 0% NaCl, 20 MPa; ◇, 1% NaCl, 10 MPa; ×, 1% NaCl, 20 MPa; +, 3% NaCl, 10 MPa; △, 3% NaCl, 20 MPa.

Figure 3 shows the relative ratio of viscosity, $\gamma = \eta_{CS} - \eta_S/\eta_S$, as a function temperature, t. As temperature increased, γ decreased, indicating that CO_2 molecules have little effect on the viscosity of the solution at high temperature. This Figure also shows that the relative ratio, γ, can be expressed as a linear function of temperature, t, by regression of the data:

$$\gamma(t) = \frac{\eta_{CS} - \eta_S}{\eta_S} = -4.069 \times 10^{-3} t/°\mathrm{C} + 0.2531 \qquad (6)$$

$\gamma(t)$ values are large at low temperature, so the viscosity of the solution containing CO_2, η_C, is measured only at 30 °C and 40 °C. Figure 4 shows η_C as a function of x_C. Regression of the data in this Figure yields η_C expressed as a linear function of x_C:

$$\frac{\eta_C}{\eta_S} = 1 + \gamma(t)\frac{x_C}{x_{CS}} \qquad (7)$$

where g(t) is a function of temperature. Here, η_S is determined from the empirical equations (eqs 8−18) proposed by Kestin et al.[11]

$$\eta_S(P, t, c) = \eta^0(t, c)[1 + \beta(t, c)P/\mathrm{MPa}] \qquad (8)$$

where c, η^0, and β denote the concentration of NaCl, the

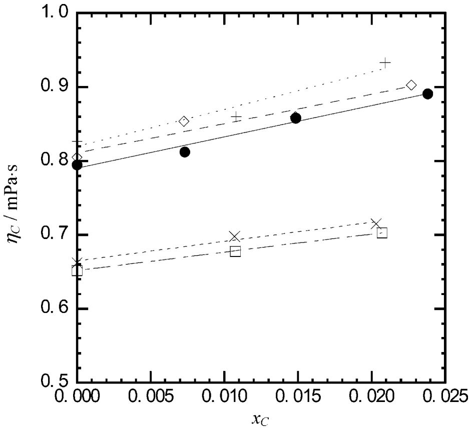

Figure 4. Viscosity of aqueous NaCl solution containing CO_2, η_C, vs CO_2 mole fraction, x_C at 10 MPa: ●, 0% NaCl, 30 °C; □, 0% NaCl, 40 °C; ◇, 1% NaCl, 30 °C; ×, 1% NaCl, 40 °C; +, 3% NaCl, 30 °C.

viscosity of the solution at 0.1 MPa, and the pressure coefficient, respectively.

$$\log\left[\frac{\eta^0(t, c)}{\eta^0_W(t)}\right] = A(c) + B(c) \log\left[\frac{\eta^0_W(t)}{\eta^0_W(20\ °C)}\right] \tag{9}$$

$$\log\left[\frac{\eta^0_W(t)}{\eta^0_W(20\ °C)}\right] = \frac{20 - t/°C}{96 + t/°C}\left[\begin{array}{l}1.2378 - 1.303 \times 10^{-3}(20 - t/°C) + 3.06 \times \\ \quad 10^{-6}(20 - t/°C)^2 \\ + 2.55 \times 10^{-8}(20 - t/°C)^3\end{array}\right] \tag{10}$$

with

$$\eta^0_W(20\ °C) = 1.002(\text{mPa·s})$$

Subscript W denotes pure water, and c is expressed as a molality (M = mol of NaCl/kg of H_2O):

$$c/[M] = \frac{1000S}{58.44(1 - S)} \tag{11}$$

$$A(c) = 0.3324 \times 10^{-1}(c/M) + 0.3624 \times 10^{-2}(c/M)^2 - 0.1879 \times 10^{-3}(c/M)^3 \tag{12}$$

$$B(c) = -0.396 \times 10^{-1}(c/M) + 0.102 \times 10^{-1}(c/M)^2 - 0.702 \times 10^{-3}(c/M)^3 \tag{13}$$

$$\beta(t, c)/\text{MPa}^{-1} = (\beta^E_S(t)/\text{MPa}^{-1})\beta^*\left(\frac{c}{c_S}\right) + \beta_W(t)/\text{MPa}^{-1} \tag{14}$$

where β^E and β^* denote the excess pressure coefficient and the reduced coefficient, respectively. Subscripts S and SS denote aqueous the NaCl solution and the aqueous solution saturated with NaCl, respectively.

$$\beta_W(t)/\text{MPa}^{-1} = -1.297 \times 10^{-3} + 0.574 \times 10^{-4}(t/°C) - 0.697 \times 10^{-6}(t/°C)^2 + 0.447 \times 10^{-8}(t/°C)^3 - 0.105 \times 10^{-10}(t/°C)^4 \tag{15}$$

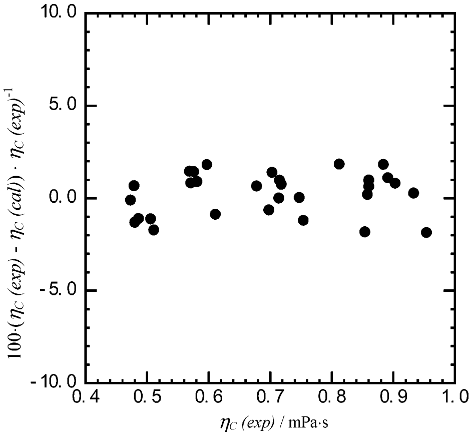

Figure 5. Deviation of measured viscosity η_C(exp) from η_C(cal) calculated using the prediction equation.

$$\beta^E_S(t)/\text{MPa}^{-1} = 0.545 \times 10^{-3} + 0.28 \times 10^{-5}(t/°C) - \beta_W(t)/\text{MPa}^{-1} \tag{16}$$

$$c_S(t)/[M] = 6.044 + 0.28 \times 10^{-2}(t/°C) + 0.36 \times 10^{-4}(t/°C)^2 \tag{17}$$

$$\beta^*\left(\frac{c}{c_S}\right) = 2.5 \times 10^{-3}\left(\frac{c}{c_S}\right) - 2.0 \times 10^{-3}\left(\frac{c}{c_S}\right)^2 + 0.5 \times 10^{-3}\left(\frac{c}{c_S}\right)^3 \tag{18}$$

In the above equations, all viscosities are expressed in mPa·s, pressure is expressed in MPa, and temperature is expressed in °C

By combining eqs 6 and 7, the viscosity of the solution containing CO_2, η_C, can be expressed as

$$\eta_C = \eta_S\left\{1 + (-4.069 \times 10^{-3} t/°C + 0.2531)\frac{x_C}{x_{CS}}\right\} \tag{19}$$

Figure 5 shows the viscosity of the aqueous solution saturated with CO_2, η_{CS}, calculated from this prediction equation normalized by the corresponding measured η_{CS}. These results show that η_{CS} can be predicted within 2% of the measured η_{CS}.

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