J. Chem. Eng. Data **1999,** *44,* 227−229

Viscosities of Aqueous NaCl Solutions Containing CO_2 at High Pressures

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Viscosity measurements of aqueous NaCl solutions containing CO_2 along three isotherms at 273 K, 276 K, and 278 K at pressures up to 30 MPa are reported. The measurements have been carried out within a falling capillary type viscometer and have an estimated uncertainty of ±0.8%. The experimental values were correlated in terms of pressure, temperature, and concentrations of NaCl and CO_2. The correlation reproduces the experimental values to within ±1.3%.

Introduction

There are no data in the literature on viscosities of aqueous NaCl solutions containing CO_2 at high pressures except for earlier works on aqueous NaCl solutions (Kestin et al., 1978; Out and Los, 1980) and on aqueous solutions containing CO_2 (Kumagai and Yokoyama, 1998). Such information is required for simulation of the proposed deep-sea storage of waste CO_2 (Liro et al., 1992; Lund et al., 1994; Haugen et al., 1995; Hirai et al., 1997). Under a continuing program to establish a database for thermophysical properties required for this simulation, we report here the viscosities of aqueous NaCl solutions containing CO_2 measured along three isotherms at 273 K, 276 K, and 278 K at pressures up to 30 MPa. The measurements have been carried out with a falling capillary type viscometer developed and described in detail previously (Kumagai et al., 1998). The measurements have an estimated uncertainty of ±0.8%. The experimental values were presented as a function of the temperature, pressure, and molalities of CO_2 and NaCl.

Experimental Section

Materials. Distilled H_2O for liquid chromatograph analysis and NaCl with a purity of 99.5% were purchased from Wako Pure Chem. Ltd. (Osaka, Japan) and Kanto Chemical Co. Inc. (Tokyo, Japan), respectively. The CO_2, the purity of which was certified to be 99.99%, was provided by the Nihon Sanso Co. (Tokyo, Japan) and used without further purification.

Table 1. Accuracy of Measurements at Each Observation Point and Responsible Error for Viscosity

	exptl value	responsible error for viscosity/%
falling time/s		
for standard liquid	33.1 ± 0.1	0.3
for sample liquid	(50−60) ± 0.1	0.2
temp/K	(273−278) ± 0.03	0.1
pressure/MPa	(10−30) ± 0.2	<0.01
density/(g cm^{-3})		
for falling body	11.06 ± 0.01	0.05
for sample liquid	(1.01−1.04) ± 0.006	0.06
concn/(g/(100 g of H_2O))		
of NaCl	(0−5.0) ± 0.001	<0.01
of CO_2	(0−4.0) ± 0.05	0.1

Table 2. Comparison of Viscosity, η, of Aqueous NaCl Solutions from the Present Work with Literature Values at 0.1 MPa

		η/(mPa s)		
T/K	M/(mol kg^{-1})	present work	lit.	$100((\eta_{\text{present}} - \eta_{\text{lit.}})/\eta_{\text{present}})$
278.15	0.342	1.539	1.546^{a,b}	−0.5
298.15		1.033	1.030^{c}	+0.3
278.15	0.599	1.569	1.569^{a,b}	0
293.15		1.053	1.052^{c}	+0.1
278.15	0.856	1.580	1.589^{a,b}	−0.4
293.15		1.076	1.076^{c}	0

[a] Interpolated value. [b] Kestin et al. (1978). [c] Out and Ros (1980).

Apparatus and Experimental Method. The viscosity was measured by a falling capillary type viscometer. A detailed description of the viscometer and the experimental procedure have been presented in an earlier paper (Kumagai et al., 1998). At fixed pressure, temperature, and compositions, the viscosity of a fluid, η, can be calculated from the measurement of the fall time, t, of the falling body, measured in an apparatus that consists of a capillary tube, mercury pellet, two stainless steel disks, and a disk stopper, over a constant length (20 mm) and of the pressure difference, Δp, as

$$\eta/\eta_s = (t/t_s)(\Delta p/\Delta p_s)(1 - \delta) \tag{1}$$

where the subscript s refers to a standard liquid at a reference temperature and pressure, which can be defined arbitrarily, and where δ is a correction factor which becomes equal to zero for the standard liquid at the reference temperature and pressure. The determination of δ was described in detail previously (Kumagai et al., 1998). In this study, we selected water as the standard liquid, since the viscosity of H_2O is known accurately and is close to those of the sample mixtures; we defined arbitrarily the reference temperature and pressure as 293.15 K and 0.1 MPa, respectively. The thermophysical properties of the

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10.1021/je980178p CCC: $18.00

Table 3. Viscosities of Aqueous NaCl Solutions Containing CO_2

		$\eta(0.324M_{NaCl})/(mPa\ s)$			$\eta(0.599M_{NaCl})/(mPa\ s)$			$\eta(0.856M_{NaCl})/(mPa\ s)$		
P/MPa	T/K	0 M_{CO_2}	0.532 M_{CO_2}	0.873 M_{CO_2}	0 M_{CO_2}	0.500 M_{CO_2}	0.913 M_{CO_2}	0 M_{CO_2}	0.450 M_{CO_2}	0.857 M_{CO_2}
0.1	273.15	1.789			1.812			1.829		
	276.15	1.615			1.651			1.674		
	278.15	1.539			1.569			1.589		
10	273.15	1.760	1.815	1.863	1.788	1.852	1.909	1.805	1.878	1.933
	276.15	1.592	1.632	1.672	1.627	1.682	1.736	1.647	1.696	1.750
	278.15	1.516	1.528	1.580	1.554	1.573	1.633	1.571	1.586	1.653
20	273.15	1.745	1.799	1.842	1.776	1.840	1.894	1.793	1.866	1.917
	276.15	1.580	1.617	1.656	1.612	1.667	1.724	1.635	1.680	1.735
	278.15	1.504	1.513	1.562	1.542	1.560	1.621	1.556	1.571	1.635
30	273.15	1.728	1.782	1.819	1.762	1.823	1.874	1.781	1.852	1.900
	276.15	1.570	1.600	1.639	1.598	1.647	1.710	1.621	1.664	1.721
	278.15	1.490	1.500	1.542	1.528	1.547	1.610	1.539	1.554	1.618

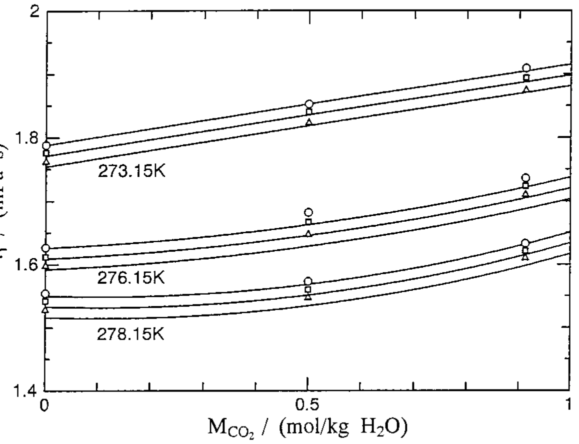

Figure 1. Experimental viscosity data for aqueous NaCl solutions containing CO_2 at 0.599 M_{NaCl}: (○) 10 MPa; (□) 20 MPa; (△) 30 MPa; (—) eq 4.

standard liquid at the reference temperature and pressure are $\eta_s = 1.002$ mPa s (JIS Z8803, 1978), $t_s = 33.1$ s, and $\rho_s = 0.9982$ g cm^{-3} (Kell and Whalley, 1965). The ratio of the pressure difference Δp for the sample and Δp_s for the standard liquid is defined as

$$\Delta p/\Delta p_s = (\rho_f - \rho)/(\rho_f - \rho_s) \quad (2)$$

where ρ_f denotes the density of the falling body and ρ the density of the fluid. As can be seen from eqs 1 and 2, the variation effect of the density of the sample liquid on viscosity is usually small, since ρ(1.02 g cm^{-3} at 0.1 MPa and 273.15 K) $\ll$ ρ_f(11.06 g cm^{-3} at 273.15 K). Therefore, precise density data of the sample are not necessary for the calculation of the viscosity of the sample, which is an advantage over other capillary viscometers.

The values of δ were determined experimentally from the measurements of the falling time and from the literature data for the viscosity of water (JIS Z8803, 1978) from eq 1. The viscosity data of water that were adopted were at 0.1 MPa and in the temperature range from 278 K to 333 K. The δ values for the viscometer used in this study can be represented by

$$\delta = 0.088\rho/t^2 - 0.0075 \quad (3)$$

where the units of ρ and t are kg m^{-3} and s, respectively. The application of eq 3 to a higher pressure region was confirmed by the agreement between the literature and experimental values obtained by this equation for H_2O in the pressure range from 20 MPa to 40 MPa and the temperature range from 273.15 K to 323.15 K (Kumagai et al., 1998).

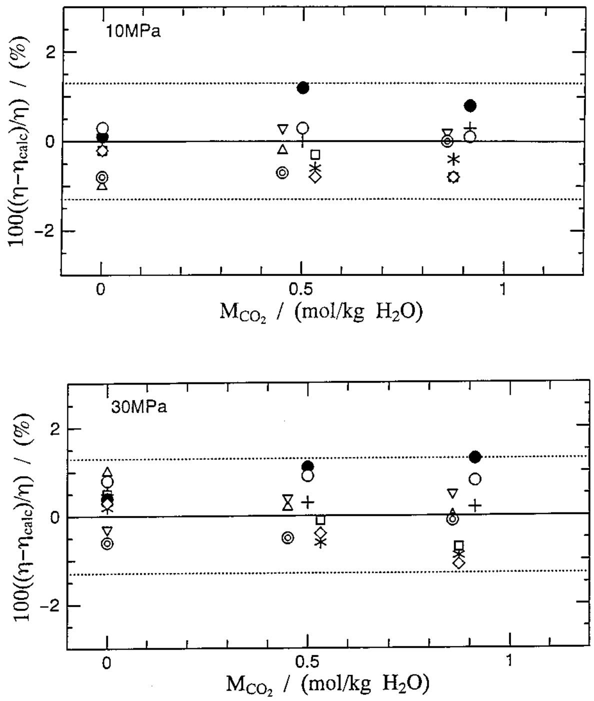

Figure 2. Deviation of measured data from the correlation in eq 4 for aqueous NaCl solutions containing CO_2 at 10 MPa and 30 MPa: (∗) 273.15 K, 0.342 M_{NaCl}; (+) 273.15 K, 0.599 M_{NaCl}; (△) 273.15 K, 0.856 M_{NaCl}; (□) 276.15 K, 0.342 M_{NaCl}; (●) 276.15 K, 0.599 M_{NaCl}; (▽) 276.15 K, 0.856 M_{NaCl}; (◇) 278.15 K, 0.342 M_{NaCl}; (○) 278.15 K, 0.599 M_{NaCl}; (◎) 278.15 K, 0.856 M_{NaCl}.

Accuracy of Measurements. The temperature was measured with a quartz thermometer (DMT-610, Tokyo Denpa, Tokyo, Japan), and the pressure was measured with a Bourdon tube gauge (Nagano Keiki Ltd., Nagano, Japan). The falling time was measured with a electric timer (VTG-33, FOR-A Co. Ltd., Tokyo, Japan). The accuracy of measurement at each observation point together with the responsible error for viscosity are listed in Table 1. The viscosity measurements have an uncertainty of 0.8% at Reynolds numbers less than 58, which is well within the laminar flow region.

Results and Correlation

Comparison of the present experimental data for the viscosity of aqueous NaCl solutions with literature values (Kestin et al., 1978; Out and Los, 1980) is given in Table 2. The present viscosity values agree with the literature data if we take into account both the experimental errors within ±0.5%. The experimental results for the viscosity of aqueous NaCl solutions containing CO_2 are listed in Table 3 and shown in Figure 1 (only at 0.599 M NaCl) along

Table 4. Adjustable Parameters in Equation 4

a	3.859 71	d	$1.906\ 21 \times 10^{-2}$	g	−7.227 69
b	$-1.325\ 61 \times 10^{-2}$	e	8.795 52	h	$2.644\ 98 \times 10^{-2}$
c	−5.375 39	f	$-3.172\ 29 \times 10^{-2}$	i	$-1.699\ 56 \times 10^{-3}$

three concentrations of NaCl up to 0.856 M at temperatures from 273 K to 278 K, concentrations of CO_2 up to 0.913 M, and pressures up to 30 MPa. Since the experimental density values for the aqueous NaCl solutions containing CO_2 have not been reported, the literature values of the density of aqueous NaCl solutions under high pressures (Rowe and Chou, 1970) were substituted for ρ in eq 2. From the experimental density data for the aqueous CO_2 solutions (Parkinson and Nevers, 1969), it can be assumed that the probable maximum variation of the density values of the aqueous NaCl solutions with the addition of CO_2 was at most 0.6% in the present experimental conditions. Therefore, the responsible error for viscosity was to be 0.06% by this substitution, which is much smaller than the uncertainty of the viscosity measurement. At fixed temperature and pressure, the viscosity of the solutions increases with an increase in NaCl and CO_2 concentrations. The viscosity at the same temperature and for the same NaCl and CO_2 concentrations decreases with increasing pressure.

The experimental data in Table 3 are presented as a function of temperature, pressure, and molalities of NaCl and CO_2 by the following equation:

$$\eta = (a + bT)M_{\mathrm{NaCl}} + (c + dT){M_{\mathrm{NaCl}}}^{1/2} + (e + fT)M_{\mathrm{CO_2}} + (g + hT){M_{\mathrm{CO_2}}}^{2} + i(P - 0.1) + \eta_{\mathrm{H_2O}}(T,P{=}0.1) \quad (4)$$

where η is in mPa s, T is in K, P is in MPa, a−i are adjustable parameters, M_{NaCl}, $M_{\mathrm{CO_2}}$ are molarities of NaCl and CO_2 in mol kg^{-1}, respectively, and $\eta_{\mathrm{H_2O}}(T,P{=}0.1)$ is the viscosity of H_2O at T and $P = 0.1$ MPa. Table 4 gives the values of the parameters. The solid lines in Figure 1 show the calculated values with eq 4. It was found that eq 4 reproduces the present results with the maximum deviation of 1.3%, as shown Figure 2.

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Received for review August 8, 1998. Accepted November 27, 1998.

JE980178P