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Viscosity of Aqueous Solutions of CO_2 at High Pressures

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Experimental viscosity measurements of aqueous solutions of CO_2 along three isotherms at 273, 276, and 278 K for pressures up to 30 MPa are reported. The measurements have been carried out in a falling capillary viscometer and have an estimated uncertainty of ±1.5%. The experimental values were compared with the correlation proposed by Kanti et al. derived from Flory's theory. The equation is in poor agreement with the experimental values, but the equations of Kanti et al. and of Grunberg and Nissan with one adjustable parameter yield good agreement with the experimental data.

KEY WORDS: carbon dioxide; Flory's theory; viscosity; water.

1. INTRODUCTION

Viscosity data of aqueous solutions of CO_2 at high pressures (up to 30 MPa) are required for simulation of proposed deep-sea storage of waste CO_2 [1–3]. However, no studies have been reported in the literature which present viscosity data for the solutions. In the present work, the viscosity of the solutions was measured along three isotherms at 273, 276, and 278 K at pressures up to 30 MPa. The measurements have been carried out with a falling capillary viscometer described previously [4], and they have an estimated uncertainty of ±1.5%. The experimental values are compared with a correlation proposed by Kanti et al. based on Flory's theory [5–7].

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2. EXPERIMENTAL

2.1. Materials

Distilled H_2O for liquid chromatographic analysis was purchased from Wako Pure Chem. Ltd. (Osaka, Japan). 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.

2.2. Apparatus and Experimental Method

The viscosity was measured by means of a falling capillary viscometer shown in Fig. 1. A detailed description of the viscometer and the experimental procedure have been presented in an earlier paper [4]. At fixed pressure, temperature, and composition, the viscosity of a fluid, η, can be calculated from the measurement of the fall time, t, of the falling body over a constant length (20 mm) and the pressure difference, Δp, as:

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

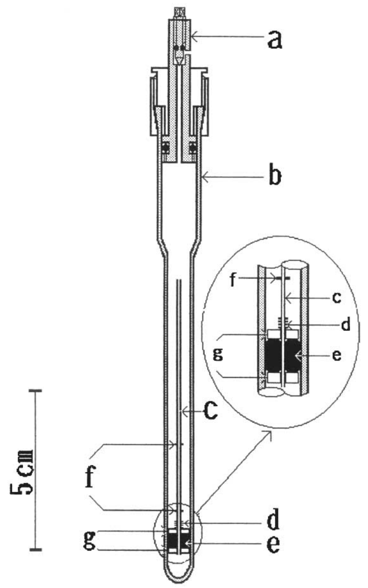

Fig. 1. Falling capillary type viscometer. (a) valve; (b) glass tube; (c) capillary tube; (d) disk stopper; (e) mercury pellet; (f) marks; and (g) steel disks.

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. In this study, we selected water as the standard liquid, since the viscosity of water is known accurately and was 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 standard liquid at the reference temperature and pressure are $\eta_s = 1.002\ \mathrm{mPa \cdot s}$ [8], $t_s = 34.0\ \mathrm{s}$, and $\rho_s = 0.9982\ \mathrm{g \cdot cm^{-3}}$ [9]. The ratio of the pressure difference Δp for the sample and Δp_s for the standard liquid is defined as [4]:

$$\Delta p/\Delta p_s = (\rho_f - \rho)/(\rho_f - \rho_s) \tag{2}$$

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 induced effect of the density of the sample liquid is usually small for the viscosity, since $\rho(1.02\ \mathrm{g \cdot cm^{-3}}$ at 0.1 MPa and 273.15 K) $\ll \rho_f(11.06\ \mathrm{g \cdot cm^{-3}}$ at 273.15 K). The induced change in the viscosity is about 0.2% for a change of 3% in the density of the sample. Therefore, precise density data of the sample are not necessarily required 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 [8] for the viscosity of water from Eq. (1). The viscosity data of water adapted were at 0.1 MPa and in the temperature range from 278 into 333 K. The δ values for the viscometer used in this study can be represented by

$$\delta = 0.088\rho/t^2 - 0.0075 \tag{3}$$

2.3. Accuracy of Measurements

The temperature was measured with a quartz thermometer (DMT-610, Tokyo Denpa, Tokyo, Japan) with an accuracy of ±30 mK, and the pressure was measured with a Heise gauge (Dresser Industries, Newtown CT., USA) with an accuracy of ±0.2 MPa. The falling time, ranging from 51 to 68 s, was measured with a reproducibility of 0.8%. The viscosity measurements have an uncertainty of 1.5% at Reynolds numbers less than 360, which is well within the laminar flow region.

3. RESULTS AND CORRELATION

The experimental results for the viscosity of aqueous solutions of CO_2 are listed in Table I and shown in Fig. 2 at four concentrations from 0 to 3.95 g CO_2/100 g water at temperatures from 273 to 278 K and pressures up to 30 MPa. The density data needed for the determination of the viscosity were calculated from the COSTALD correlation developed by Thomson et al. [10]. At constant temperature and pressure, the viscosity of the aqueous solutions increases with an increase in CO_2 content as shown in Fig. 2. The viscosity at the same temperature can be reasonably extrapolated to the value of pure water for each pressure, and decreases with pressure for the same CO_2 concentration.

The experimental values were fitted to the viscosity correlation proposed by Kanti et al. [11], which was derived from the Bloomfield–Dewan equation [12] and Flory's theory [5–7]. The equation without an adjustable parameter deduced by Kanti et al. can be applied in the high-pressure region. An excess viscosity of a binary mixture, $\Delta^E \ln \eta$, can be defined as:

$$\Delta^E \ln \eta = \ln \eta - [x \ln \eta_1 + (1-x) \ln \eta_2] \tag{4}$$

Table I. Viscosity of Aqueous Solutions of CO_2

			Viscosity (mPa · s)		
m ($gCO_2/100gH_2O$)	mole fraction	p (MPa)	273.15 K	276.15 K	278.1 K
0	0	0.1	1.785		
			1.792^a	$1.610^{a,c}$	1.520^a
		10.0	1.769^b	$1.603^{b,c}$	$1.507^{b,c}$
		20.0	1.739		
			1.749^b	$1.590^{b,c}$	$1.479^{b,c}$
		30.0	1.731^b	$1.579^{b,c}$	$1.488^{b,c}$
1.18	4.82×10^{-3}	10.0	1.844	1.681	1.572
		20.0	1.805	1.639	1.538
		30.0	1.771	1.623	1.517
2.49	1.01×10^{-2}	10.0	1.953	1.779	1.658
		20.0	1.926	1.760	1.642
		30.0	1.895	1.742	1.621
3.95	1.59×10^{-2}	10.0	2.016	1.829	1.711
		20.0	1.994	1.808	1.695
		30.0	1.975	1.786	1.677

[a] Ref. 8.

[b] Ref. 13.

[c] interpolated.

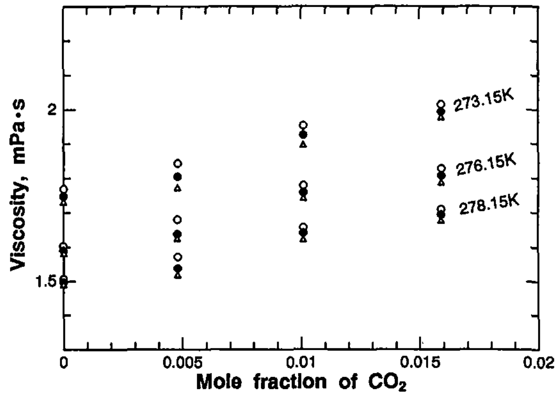

Fig. 2. Experimental viscosity data for aqueous solutions of CO_2 at high pressures. ○: 10 MPa, ●: 20 MPa, △: 30 MPa. Viscosities of pure H_2O are literature data [13].

where η is the viscosity of the mixture, η_1 and η_2 are the viscosities of the two pure constituents, and x is the mole fraction of constituent 1.

By following Bloomfield and Dewan [9], the excess viscosity can be expressed as:

$$\Delta^E \ln \eta = -\Delta G^R/RT + f(\tilde{V}) \tag{5}$$

where

$$f(\tilde{V}) = 1/(\tilde{V}-1) - x/(\tilde{V}_1 - 1) - (1-x)/(\tilde{V}_2 - 1) \tag{6}$$

$$\begin{aligned}\Delta G^R = {} & xP_1^* V_1^* [1/\tilde{V}_1 - 1/\tilde{V} + 3\tilde{T}_1 \ln[(\tilde{V}_1^{1/3} - 1)/(\tilde{V}^{1/3} - 1)] \\ & + (1-x)\, P_2^* V_2^* [1/\tilde{V}_2 - 1/\tilde{V} + 3\tilde{T}_2 \ln[(\tilde{V}_2^{1/3} - 1)/(\tilde{V}^{1/3} - 1)] \\ & + x\theta V_1^* X_{12}/\tilde{V}\end{aligned} \tag{7}$$

$$X_{12} = P_1^* [1 - (V_1^*/V_2^*)^{-1/6} (P_2^*/P_1^*)^{1/2}]^2 \tag{8}$$

$$\theta = \phi_2 V_1^{*1/3}/(\phi_1 V_1^{*1/3} + \phi_2 V_2^{*1/3}) \tag{9}$$

$$\phi_1 = 1 - \phi_2 = xV_1^*/(xV_1^* + (1-x)\, V_2^*) \tag{10}$$

$$\tilde{P} = P/P^*,\ \tilde{V} = V/V^*,\ \tilde{T} = T/T^* \tag{11}$$

Here, ΔG^R is the residual free energy of mixing, R is the universal gas constant, and $f(\tilde{V})$ is a characteristic function of free volumes defined by Eq. (6). The interaction coefficient, X_{12}, the site fraction, θ, and the volume fraction, ϕ, depend on characteristic parameters, P^* and V^*, presented by Flory et al. [5–7] according to Eqs. (8)–(10).

Kanti et al. [11] related the reduced variables ($\tilde{P}$, $\tilde{V}$, and $\tilde{T}$) of pressure, P, volume, V, and temperature, T, to the coefficient of thermal expansion, α, and the isothermal compressibility, β, using Flory's theory [5–7] as follows:

$$\tilde{V} = [\alpha T/(3(1+\alpha T-2\beta P)+1]^3 \tag{12}$$

$$\tilde{P} = \beta P[3(1+\alpha T-2\beta P)]^6/[(\alpha T-\beta P)(3+4\alpha T-6\beta P)^6] \tag{13}$$

$$\tilde{T} = (\alpha T)^2\,[3(1+\alpha T-2\beta P)]^3/[(\alpha T-\beta P)(3+4\alpha T-6\beta P)^4] \tag{14}$$

In the calculation of the viscosity from the correlation of Kanti et al., we shall assume that the input parameters, α, β, ρ ($=1/V$), and η are only known for the pure components. Estimates of α and β were obtained from the COSTALD correlation [10]. The viscosity and density of water and CO_2 were taken from Refs. [9, 13, 14]. The values for the parameters in the equation of Kanti et al. are listed in Table II. The characteristic

Table II. Physicochemical Parameters for H_2O and CO_2 in Eqs. (4) and (11) to (14)

	H_2O				CO_2			
	α^a ($10^4\,K^{-1}$)	β^a ($10^{11}\,Pa^{-1}$)	η^b (mPa·s)	ρ^c ($g\cdot cm^{-3}$)	α^a ($10^3\,K^{-1}$)	β^a ($10^{10}\,Pa^{-1}$)	η^d (mPa·s)	ρ^d ($g\cdot cm^{-3}$)
273.15 K								
10 MPa	7.1	4.3	1.769	1.005	6.4	6.2	0.1159	0.971
20 MPa	7.1	4.3	1.749	1.010	6.2	5.8	0.1337	1.020
30 MPa	7.1	4.2	1.731	1.015	6.1	5.4	0.1495	1.058
276.15 K								
10 MPa	7.1	4.3	1.603	1.005	6.5	6.6	0.1109	0.955
20 MPa	7.1	4.3	1.590	1.009	6.4	6.1	0.1291	1.008
30 MPa	7.1	4.2	1.579	1.014	6.3	5.7	0.1450	1.048
278.15 K								
10 MPa	7.1	4.3	1.507	1.005	6.6	6.9	0.1075	0.945
20 MPa	7.1	4.3	1.497	1.010	6.4	6.4	0.1261	0.999
30 MPa	7.1	4.3	1.488	1.014	6.3	5.9	0.1421	1.041

[a] Ref. 10.
[b] Ref. 13.
[c] Ref. 9.
[d] Ref. 14.

pressure, P_i^*, and the characteristic volume, V_i^*, for pure component i can be determined from Eqs. (11), (12), and (13).

The following mixing law for $\tilde{V}$ was used by Delmas et al. [15], since only $\tilde{V}$ for the mixture is needed to calculate the excess viscosity from Eq. (5).

$$\tilde{V} = x\tilde{V}_1^{-1}(U_1^*/U_m^*) + (1-x)\,\tilde{V}_2^{-1}(U_2^*/U_m^*) \tag{15}$$

where

$$U_i^* = P_i^* V_i^* \quad (i = 1 \text{ or } 2) \tag{16}$$

$$U_m^* = xU_1^* + (1-x)\,U_2^* \tag{17}$$

The calculated viscosity values for the aqueous CO_2 solutions at 10 and 30 MPa are shown in Figs. 3 and 4, respectively, where the dashed lines represent the viscosities calculated from the equation of Kanti et al. As can be seen, the calculated values decrease with increasing CO_2 concentration, which is different from the experimental data.

To improve the calculated results, a new mixing law introducing an interaction parameter, K, was used instead of Eq. (17), as follows:

$$U_m^* = x^2 U_1^* + (1-x)^2\, U_2^* + 2Kx(1-x)(U_1^* U_2^*)^{1/2} \tag{18}$$

It was possible to reproduce the experimental viscosities at 10 and 30 MPa as shown by the solid lines in Figs. 3 and 4 by adding one adjustable

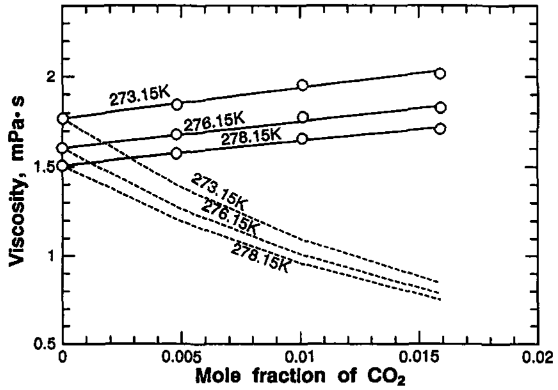

Fig. 3. Comparison of experimental viscosity with correlations for aqueous solutions of CO_2 at 10 MPa. ○: experimental, ····: Eqs. (4) to (17), —; Eqs. (4) to (16) and (18) with $K = 0.63$.

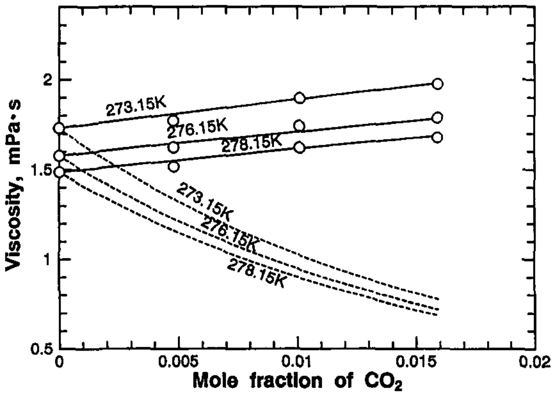

Fig. 4. Comparison of experimental viscosity with correlations for aqueous solutions of CO_2 at 30 MPa. ○: experimental, ···: Eqs. (4) to (17), —; Eqs. (4) to (16) and (18) with $K = 0.63$.

Table III. Deviations of Experimental Data from Correlations for Liquid Viscosity of Aqueous Solutions of CO_2

	Eqs. (4) to (17)		
		only $f(\tilde{V})$ in Eq. (5)	only $-\Delta G^R/RT$ in Eq. (5)
Av. dev. (%)	40.6	29.9	23.4
Max. dev. (%)	60.7	43.9	35.1
	Eqs. (4) to (16) and (18) with $K = 0.63$		
		only $f(\tilde{V})$ in Eq. (5)	only $-\Delta G^R/RT$ in Eq. (5)
Av. dev. (%)	0.9	20.5	24.6
Max. dev. (%)	−2.2	−35.4	37.6
	Eqs. (4) and (19) with $d = 11.0$		
Av. dev. (%)	0.9		
Max. dev. (%)	−2.2		

Ave. dev. = $100\Sigma(|\eta_{exp} - \eta_{calc}|/\eta_{exp})/n$

Max. dev. = Maximum of $100((\eta_{exp} - \eta_{calc})/\eta_{exp})$

parameter ($K = 0.63$), which was independent of temperature and pressure for the present experimental conditions. Table III lists the deviations of the experimental data from the correlations of Kanti et al. in conjunction with the original mixing law, Eqs. (15)–(17), and the new mixing law, Eqs. (15), (16), and (18). The contributions of the two terms in Eq. (5), the residual free energy and free-volume terms, are also listed in Table III. It can be seen that the introduction of K decreases the free-volume term significantly, while the effect of the K on the residual free-energy term is comparatively unimportant. We can also apply the simple viscosity equation of Grunberg and Nissan [16] with one adjustable parameter, d:

$$\Delta^{E} \ln \eta = x(1-x)\,d \tag{19}$$

The deviations of the experimental results from the correlation of Grunberg and Nissan are also shown in Table III. From this table, the correlation of Grunberg and Nissan reproduces the data within 2.2%, which is similar to that of Kanti et al. with one adjustable parameter.

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