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Viscosity Measurements and Correlation of the Squalane + CO_2 Mixture

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Experimental results for the viscosity of squalane + CO_2 mixtures are reported. The viscosities were measured using a rolling ball viscometer. The experimental temperatures were 293.15, 313.15, 333.15, and 353.15 K, and pressures were 10.0, 15.0, and 20.0 MPa. The CO_2 mole fraction of the mixtures varied from 0 to 0.417. The experimental uncertainties in viscosity were estimated to be within ±3.0%. The viscosity of the mixtures decreased with an increase in the CO_2 mole fraction. The experimental data were compared with predictions from the Grunberg–Nissan and McAllister equations, which correlated the experimental data with maximum deviations of 10 and 8.7%, respectively.

KEY WORDS: CO_2; Grunberg–Nissan equation; McAllister equation; mixtures; rolling ball; squalane; viscosity.

1. INTRODUCTION

Natural refrigerants such as CO_2 have attracted much attention as replacements for hydrochlorofluorocarbons (HCFCs) and/or hydrofluorocarbons (HFCs). CO_2 has low ozone depletion and global warning potentials compared to those of HCFCs and HFCs. Furthermore, CO_2 is nontoxic and incombustible. When it is used as a refrigerant, the refrigeration system must be operated at higher pressures than those of HCFC and/or HFC systems. As CO_2 gives high performance based on its thermal properties, the system could be scaled down. Mixtures of lubricating oil and CO_2 must be circulated in the CO_2 refrigeration system. Therefore,

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thermophysical properties of these mixtures over a wide range of composition, temperature, and pressure are essential for optimum design of a CO_2 refrigeration system. Viscosity is one of the most important thermophysical properties used to design the system because of its strong dependence on temperature, pressure, and composition. Additionally, correlation and prediction of properties are very important since the required data often do not exist.

Squalane ($C_{30}H_{62}$) and glycol can serve as suitable model substances for the lubricating oil. In our previous study, we measured the viscosity of squalane + hydrocarbon [1,2] and glycol + HFC-134a [3] systems. The present paper describes continuing work on the experimental determination of the viscosity of liquid mixtures consisting of a lubricating oil and refrigerants. In this study, the viscosity of the squalane + CO_2 mixtures was measured at temperatures ranging from 293.15 to 353.15 K, pressures range from 10.0 to 20.0 MPa, and CO_2 mole fractions ranging from 0 to 0.417.

2. EXPERIMENTAL

The squalane and toluene samples which had stated purities of 98.0 and 99.5%, were purchased from Wako Pure Chemical Industries. The CO_2 were supplied by Nippon Sanso Co., Ltd. The purity was 99.99%. The samples were used without any further purification.

The viscosities were measured using a rolling ball viscometer. A schematic diagram of the viscometer used in this study is shown in Fig. 1. The glass tube was approximately 10 cm in length with an internal diameter of 7.09 mm (±0.01 mm), and the diameter of the stainless steel ball was 7.00 mm (±0.01 mm). The upper part of the glass tube is open to provide equal pressure inside and outside the glass tube. The pressure was regulated by moving a piston at the lower end of the viscometer with the use of a pressure medium. An angle of the glass tube is estimated to be about 44.5°, calculated with the Hubbard–Brown equation [4]. It was constant for all runs except for measuring toluene. At these conditions, laminar flow is obtained during the measurements at different temperatures and pressures. A schematic diagram of the experimental apparatus is shown in Fig. 2. The temperature of the thermostat was measured with a quartz thermometer. The pressure was measured with a Bourdon tube pressure gauge which was periodically calibrated against a dead-weight gauge. The mixture was prepared as follows. Squalane was introduced into the viscometer. After evacuation of air in the viscometer, CO_2 was introduced into the viscometer. The amount of CO_2 charged in the viscometer was determined by weighing the viscometer with the use of an electrical bal-

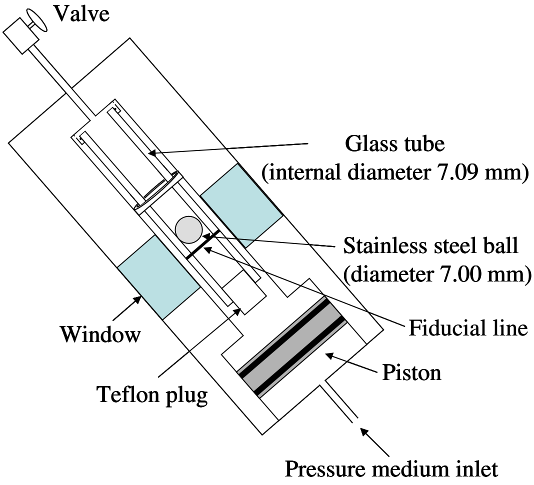

Fig. 1. Rolling ball viscometer.

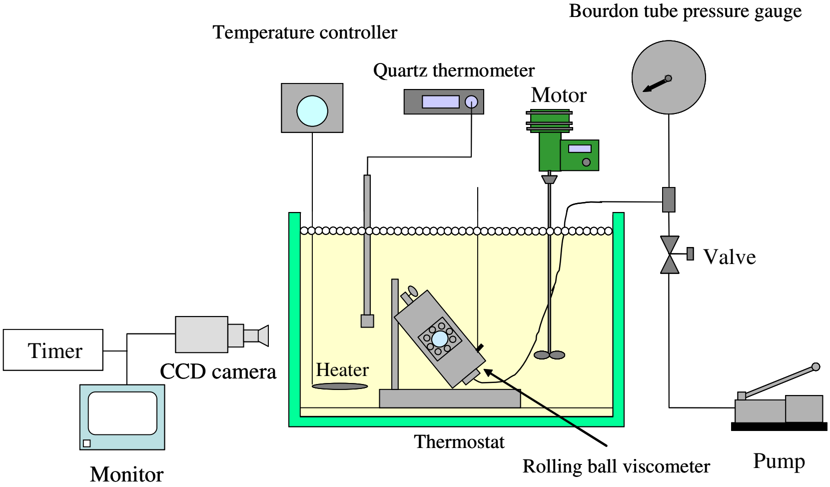

Fig. 2. Schematic diagram of the apparatus.

ance, accurate to within 0.01 g, before and after loading CO_2. After introducing CO_2 and weighing the viscometer, the viscometer is connected to a pressure pump and set into a thermostat. The ball was rolled more than 10 times at 293.15 K and 10 MPa in order to obtain homogeneous conditions before commencing the viscosity measurements.

The density of the sample fluid was obtained by using a glass piezometer which was from a previous study [2]. The viscosity, η, was calculated from the fall time of the ball, t, by the following equation

$$\eta = K(\rho_\mathrm{s} - \rho)t, \tag{1}$$

where K is the viscometer constant, and ρ_s and ρ are densities of the stainless steel ball and sample fluid, respectively. Since the viscometer constant shows temperature and pressure dependences, it should be determined at each temperature and pressure. Estrada-Baltazar et al. expressed K as a polynomial equation on temperature and pressure [5]. However, this method needs many experiments over a wide range of temperature and pressure. In many cases, there is no standard liquid which has similar viscosities of the liquid of interest, especially in the high viscosity range at high pressure. Therefore, we determined K with another method. Based on the Hubbard–Brown [4] and Lewis [6] equations, Izuchi et al. [7] proposed the following equations

$$\begin{aligned}(K/l)/(K_0/l_0) = 1 &+ \left\{\beta_\mathrm{b} + \left(\frac{r}{1+r} - \frac{5}{2}\frac{r}{1-r}\right)(\beta_\mathrm{b} - \beta_\mathrm{t})\right\}(T - T_0) \\ &- \left\{\kappa_\mathrm{b} + \left(\frac{r}{1+r} - \frac{5}{2}\frac{r}{1-r}\right)(\kappa_\mathrm{b} - \kappa_\mathrm{t})\right\}P,\end{aligned} \tag{2}$$

where β_b and β_t are the thermal expansion coefficients of the ball and tube materials, κ_b and κ_t are the linear compressibilities of those materials, l is the distance for measuring the fall time of the ball, $r(=d_0/D_0)$ is the ratio of the diameter of the ball to that of the tube at the reference conditions (293.15 K, 0.1 MPa), T and T_0 are the temperatures of the viscometer at the measuring and reference conditions, and P is the pressure. The viscometer constant K_0 at 293.15 K, 0.1 MPa was determined by using standard liquids for calibration of the viscometer, that is, JS10, JS20, and JS50 reference fluids calibrated by the National Metrology Institute of Japan (NMIJ). The precision of the viscosity values of fluids calibrated by NMIJ is ±0.1%. The estimated uncertainty of the K values was ±0.78%.

A fiducial line was stained on the glass tube by colloidal particles of silver. By monitoring the fiducial line and the ball with the use of a CCD camera through an optical window equipped in the viscometer body, the fall time was measured. The fall time was defined as a time interval that the ball passes through the fiducial line. Therefore, the distance for the fall-time measurement is the same as the diameter of the ball. At each experimental condition, the falling time measurements were repeated at least 10 times to obtain an average. Reproducibility of the fall-time measurement was better than ±1.30%.

The experimental uncertainties in temperature, pressure, and mole fraction are estimated to be ±4 mK, ±0.2 MPa, and ±0.001, respectively. By considering the experimental uncertainties of the viscometer constant, density, and fall time, the uncertainty of the reported viscosity data is estimated to be ±3.0%.

3. RESULTS

In order to elucidate the reliability of Eq. (2), we compared the K values obtained from Eq. (2) and those determined from the measurement of the fall time and literature viscosity and density values. Table I shows the comparison of the K values at 0.1 MPa for the standard liquid (JS20) at 293.15 and 313.15 K, and for ethylene glycol at 333.15 and 353.15 K. Table II shows a comparison of the pressure dependence of the K values at 293.15 K obtained from Eq. (2) and determined from the experiment with toluene. The experimental data for ethylene glycol and toluene were taken from Yang et al. [8] and Assael et al. [9], respectively. As shown in Tables I and II, fairly good agreement was obtained for both cases. Therefore, we decided to use Eq. (2) over the present experimental temperature and pressure ranges. Table III shows comparisons between the present viscosity values for toluene and literature data [9]. Good agreement was obtained.

The experimental viscosity data of the squalane + CO_2 mixture are given in Table IV together with values for the density under the same conditions, which are interpolated from the experimental density values.

Table I. Temperature Dependence of Viscometer Constant at 0.1 MPa

T (K)	$K_{\mathrm{exp}} \times 10^8$ ($m^2 \cdot s^{-2}$)	$K_{\mathrm{calc}} \times 10^8$ ($m^2 \cdot s^{-2}$)	Dev. (%)
293.15	5.805	5.809	−0.1
313.15	5.602	5.541	1.1
333.15	5.259	5.275	−0.3
353.15	4.892	5.008	−2.3

Table II. Pressure Dependence of Viscometer Constant at 293.15 K

P (MPa)	$K_{\mathrm{exp}} \times 10^9$ ($m^2 \cdot s^{-2}$)	$K_{\mathrm{calc}} \times 10^9$ ($m^2 \cdot s^{-2}$)	Dev. (%)
0.1	5.747	5.773	−0.5
10.2	5.584	5.555	0.5
20.2	5.346	5.340	0.1

Table III. Comparison of the Present Viscosity Data for Toluene with Literature Results

T (K)	P (MPa)	η (μPa·s) Measured	Literature [9]	Dev. (%)
293.15	0.1	587	584	0.5
293.15	10.2	628	631	−0.5
293.15	20.2	678	679	−0.1
313.15	0.1	451	466	−3.2
333.15	0.1	374	380	−1.6
353.15	0.1	305	317	−3.8

The density values have an estimated uncertainty of ±0.2%. No literature viscosity data have been found for the mixtures studied here. For comparison purposes, the present viscosity data for squalane at high pressure are shown in Table V together with our previous results which were measured using a falling body viscometer [2]. The agreement between both sets of data is satisfactory.

4. CORRELATION WITH THE GRUNBERG–NISSAN EQUATION

The viscosity of mixtures is often calculated from the viscosity of the pure components at the same temperature and pressure. The Grunberg–Nissan equation is one of the most widely used equations for correlation of the viscosity of liquid mixtures [10]. This simple empirical equation is written as

$$\ln\eta = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1 x_2 G, \tag{3}$$

where η is the viscosity of the mixture and η_i is the viscosity of pure component i at the measurement temperature and pressure. x_i is the mole fraction of component i, and G is the interaction parameter. Subscripts 1 and 2 represent CO_2 and squalane, respectively. While the squalane + CO_2 mixture in some experimental regions measured in this study is consistent with CO_2 as a liquid and in a supercritical state (except for the experimental conditions at 293.15 K), we tested the Grunberg–Nissan equation straightforwardly. When $G$is calculated by using the experimental data of η, η_1, and η_2, literature values were used for the viscosity of pure CO_2 (η_1) [11]. Figure 3 shows the composition dependence of G at 10.0 MPa. It was found that G shows a dependence on mole fraction, temperature, and pressure. G increases linearly with the CO_2 mole fraction. However, we did not succeed in expressing G as a simple function of temperature and pressure. Therefore, the experimental data for each experimental temperature

Table IV. Viscosity of Squalane (2) + CO_2 (1) Mixtures

T (K)	x_1	P (MPa)	ρ (kg·m^{-3})	η (mPa·s)	T (K)	x_1	P (MPa)	ρ (kg·m^{-3})	η (mPa·s)
293.15	0.000	10.0	812	43.4	333.15	0.000	10.0	792	9.18
		15.0	815	48.3			15.0	795	10.4
		20.0	817	53.3			20.0	798	11.0
	0.095	10.0	814	33.1		0.095	10.0	792	8.32
		15.0	817	37.2			15.0	795	8.95
		20.0	820	40.6			20.0	798	9.68
	0.201	10.0	817	28.5		0.201	10.0	793	7.22
		15.0	820	30.8			15.0	796	7.56
		20.0	822	34.4			20.0	799	8.48
	0.280	10.0	819	19.3		0.280	10.0	794	5.83
		15.0	821	21.8			15.0	797	6.24
		20.0	824	23.9			20.0	800	6.84
	0.362	10.0	821	16.6		0.362	10.0	795	5.39
		15.0	824	19.5			15.0	798	5.65
		20.0	826	21.3			20.0	801	6.17
	0.417	10.0	822	13.0		0.417	10.0	795	4.50
		15.0	825	14.4			15.0	798	4.77
		20.0	828	15.6			20.0	801	5.01
313.15	0.000	10.0	803	18.0	353.15	0.000	10.0	783	5.38
		15.0	806	20.1			15.0	786	5.79
		20.0	808	22.1			20.0	789	6.44
	0.095	10.0	803	15.7		0.095	10.0	782	4.91
		15.0	806	17.3			15.0	784	5.44
		20.0	809	18.4			20.0	786	5.70
	0.201	10.0	805	13.1		0.201	10.0	782	4.36
		15.0	808	14.8			15.0	784	4.62
		20.0	811	16.1			20.0	786	5.25
	0.280	10.0	806	10.3		0.280	10.0	782	3.70
		15.0	809	11.4			15.0	784	4.02
		20.0	812	12.0			20.0	787	4.37
	0.362	10.0	808	8.85		0.362	10.0	782	3.33
		15.0	810	9.79			15.0	784	3.61
		20.0	813	10.4			20.0	788	3.89
	0.417	10.0	808	7.20		0.417	10.0	782	2.97
		15.0	811	7.63			15.0	785	3.13
		20.0	814	8.06			20.0	789	3.28

and pressure were correlated with G expressed as a linear function of the CO_2 mole fraction. The equations for G are listed in Table VI. Figure 4 shows comparisons of experimental measurements at 10.0 MPa and correlated results from the Grunberg–Nissan equation. Figure 5 shows deviations of the experimental values of the viscosity of the squalane + CO_2

Table V. Comparison of Present Viscosity Data for Squalane with Previous Results

T (K)	P (MPa)	η_{present} (mPa·s)	η_{previous} (mPa·s) [2]	Dev. (%)
293.15	10.0	43.4	43.6	−0.5
	20.0	53.3	54.0	−1.3
313.15	10.0	18.0	18.3	−1.6
	20.0	22.1	22.7	−2.6
333.15	10.0	9.18	9.43	−2.7
	20.0	11.0	11.0	0.0

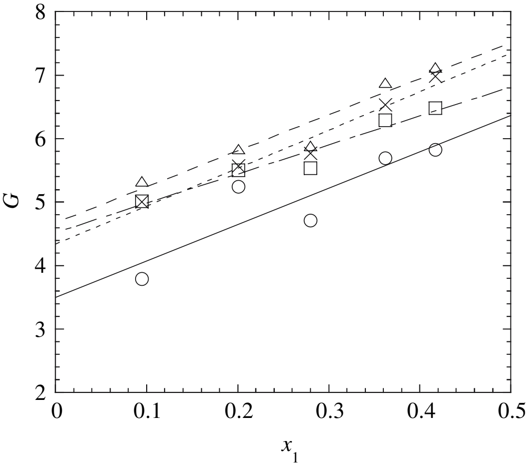

Fig. 3. Dependence of G on mole fraction and temperature for the squalane (2) + CO_2 (1) mixture (at 10.0 MPa) (○) 293.15 K, (□) 313.15 K, (△) 333.15 K, (×) 353.15 K.

mixture from Eq. (3) at each pressure. It was found that the Grunberg–Nissan equation correlated the experimental data with an average absolute deviation (AAD) of 3.2% and a maximum deviation of 10%.

5. CORRELATION WITH THE McALLISTER EQUATION

The McAllister equation is based on Eyring's absolute rate model for viscosity [12]. For a binary mixture, this semi-theoretical equation is written as

Table VI. Parameters of the Grunberg and Nissan Equation (x_1: mole fraction of CO$_2$)

T (K)	P (MPa)	G	T (K)	P (MPa)	G
293.15	10.0	$3.50 + 5.72x_1$	333.15	10.0	$4.68 + 5.67x_1$
	15.0	$3.54 + 6.00x_1$		15.0	$3.61 + 5.87x_1$
	20.0	$3.43 + 5.90x_1$		20.0	$3.86 + 4.53x_1$
313.15	10.0	$4.52 + 4.60x_1$	353.15	10.0	$4.34 + 6.02x_1$
	15.0	$4.25 + 3.87x_1$		15.0	$4.36 + 4.48x_1$
	20.0	$3.87 + 4.27x_1$		20.0	$3.67 + 5.00x_1$

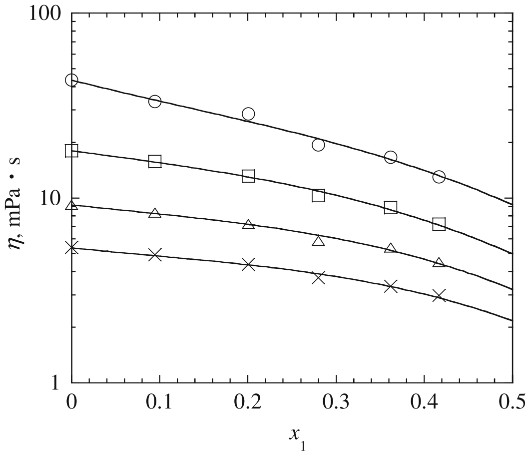

Fig. 4. Comparison of the viscosity data for the squalane (2) + CO$_2$ (1) mixture with results from the Grunberg and Nissan equation (at 10.0 MPa). Symbols are the same as in Fig. 3.

$$\begin{aligned}\ln\nu = {} & x_1^4\ln\nu_1 + 4x_1^3x_2\ln\nu_{1112} + 6x_1^2x_2^2\ln\nu_{1122} + 4x_1x_2^3\ln\nu_{2221} + x_2^4\ln\nu_2 \\ & -\ln\left[x_1 + x_2\frac{M_2}{M_1}\right] + 4x_1^3x_2\ln\left[\frac{3+M_2/M_1}{4}\right] + 6x_1^2x_2^2\ln\left[\frac{1+M_2/M_1}{2}\right] \quad (4) \\ & +4x_1x_2^3\ln\left[\frac{1+3M_2/M_1}{4}\right] + x_2^4\ln\left[\frac{M_2}{M_1}\right],\end{aligned}$$

where ν is the kinematic viscosity of the mixture, ν_i is the kinematic viscosity of pure component i at the same temperature and pressure as those of the mixture, x is the mole fraction, and M is the molar mass. ν_{1112}, ν_{1122}, and ν_{2221} are adjustable parameters calculated by using a least-squares method along with experimental data. Subscripts 1 and 2 repre-

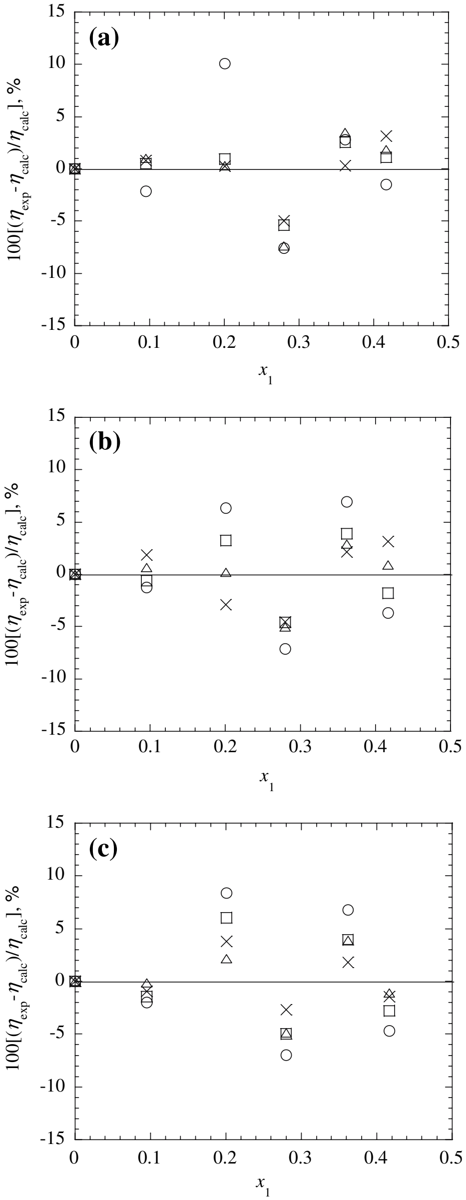

Fig. 5. Deviations of the experimental values of the viscosity of the squalane (2)+ CO_2 (1) mixture from Eq. (3): (a) 10.0 MPa, (b) 15.0 MPa, (c) 20.0 MPa. Symbols are the same as in Fig. 3.

Table VII. Parameters of the McAllister Equation

T (K)	P (MPa)	$\ln\nu_{1112}$	$\ln\nu_{1122}$	$\ln\nu_{2221}$	$\ln\nu_1$ [11]	$\ln\nu_2$
293.15	10.0	−11.814	−10.992	−10.422	−16.176	−9.837
	15.0	−12.146	−10.536	−10.419	−16.173	−9.733
	20.0	−12.503	−10.248	−10.367	−16.040	−9.638
313.15	10.0	−11.572	−11.934	−10.924	−16.440	−10.706
	15.0	−12.552	−11.358	−10.919	−16.265	−10.599
	20.0	−12.804	−11.124	−10.931	−16.191	−10.507
333.15	10.0	−11.497	−12.529	−11.470	−16.222	−11.366
	15.0	−11.672	−12.238	−11.565	−16.395	−11.245
	20.0	−12.405	−11.875	−11.461	−16.306	−11.192
353.15	10.0	−11.847	−12.891	−11.979	−16.120	−11.888
	15.0	−11.618	−12.966	−11.838	−16.391	−11.818
	20.0	−13.261	−11.981	−11.989	−16.372	−11.716

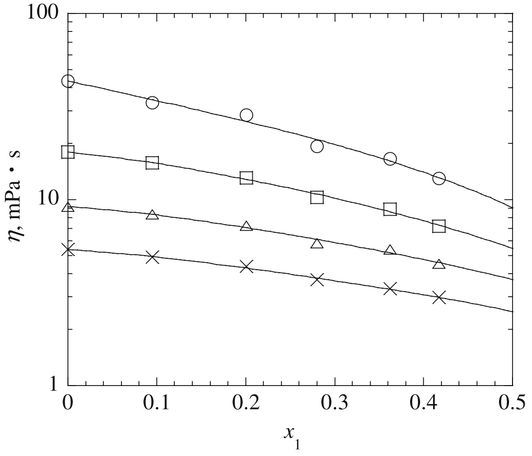

Fig. 6. Comparison of the viscosity data for the squalane (2) + CO_2 (1) mixture with results from the McAllister equation (at 10.0 MPa). Symbols are the same as in Fig. 3.

sent CO_2 and squalane, respectively. The obtained parameters are listed in Table VII. Comparisons of the experimental results at 10.0 MPa with results from the McAllister equation are shown in Fig. 6. Figure 7 shows deviations of the experimental values of the viscosity of the squalane + CO_2 mixture from Eq. (4) at each pressure. This equation correlated the experimental data with an AAD of 2.9% and a maximum deviation of 8.7%.

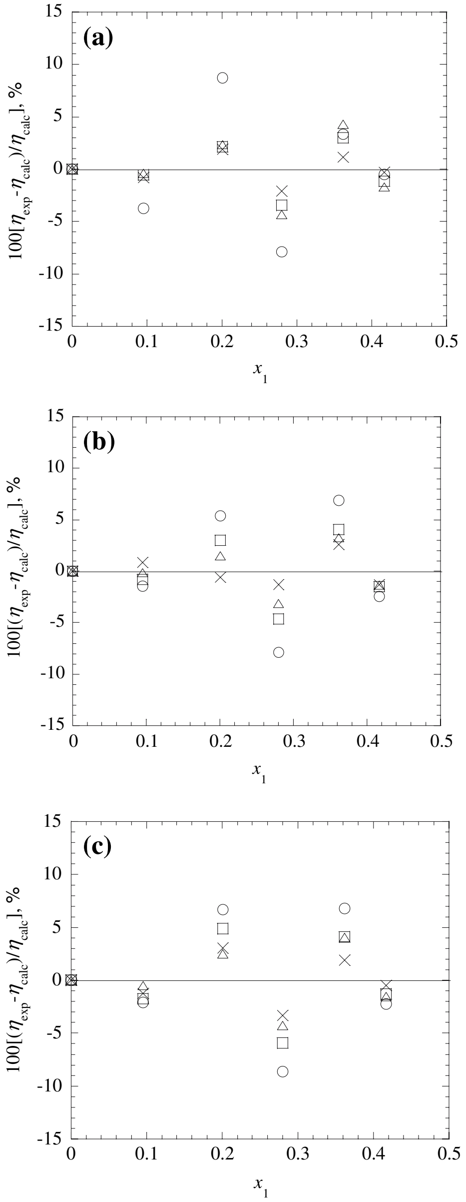

Fig. 7. Deviations of the experimental values of the viscosity of the squalane (2) + CO_2 (1) mixture from Eq. (4): (a) 10.0 MPa, (b) 15.0 MPa, (c) 20.0 MPa. Symbols are the same as in Fig. 3.

The deviations between experimental and correlated values at 293.15 K were relatively large compared to other temperatures. The reason may be a result of the large difference in the viscosities of squalane and CO_2.

6. CONCLUSION

The viscosities of squalane + CO_2 mixtures were measured with a rolling ball viscometer to within an uncertainty of ±3.0%. The experimental data for each experimental temperature and pressure were correlated with the Grunberg–Nissan equation. It was found that this equation can correlate the experimental data with a maximum deviation of 10% and an AAD of 3.2% with the adjustable parameter expressed as a linear function of composition at each temperature and pressure. The McAllister three-parameter equation correlated the experimental data within a maximum deviation of 8.7%, and an AAD of 2.9%.

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