Int J Thermophys (2007) 28:1111–1119
DOI 10.1007/s10765-007-0259-y

Measurements of the Liquid Viscosities of Mixtures of Isobutane with Squalane to 30 MPa

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Received: 11 October 2006 / Accepted: 15 August 2007 / Published online: 12 September 2007

Abstract The viscosities of liquid mixtures of isobutane with squalane, which seem to be representative of mixtures of refrigerants with refrigeration oil, were measured from 273.15 to 333.15 K at pressures to 30 MPa using a falling-body viscometer. The uncertainty of the measurements was estimated to be no larger than 2.9%. The experimental viscosity values were fitted with a Tait-like equation within 2.8%. There are large deviations between the experimental data and calculated values predicted by the equation of Kanti et al., which is derived from Flory's theory. By introducing two index numbers of the energetic mixing rule into the equation, the predictions could be improved considerably.

Keywords High pressure · Isobutane · Liquid mixture · Squalane · Viscosity

1 Introduction

Accurate viscosity values for mixtures of refrigerants with lubricant oils are essential for the design of refrigeration systems based on refrigerants such as isobutane and *n*-butane. In previous papers [1,2], we have reported viscosity data for mixtures of *n*-butane, *n*-hexane, and *n*-octane with squalane, which represented mixtures of refrigerants with refrigeration oil, using a capillary viscometer and a falling-body viscometer at temperatures from 273.15 to 333.15 K at pressures up to 30 MPa. The present paper extends the viscosity measurements to mixtures of isobutane with squalane.

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2 Experimental

Isobutane was acquired from Seitetsukagaku Co. Ltd. with a minimum purity of 99.9 mass% and squalane from Tokyo Kasei Kogyo Co. Ltd. with a minimum purity of 98 mass%. These compounds were used without further purification.

The viscosity was measured with a falling-body viscometer, in which the viscometer is mounted in a pressure vessel with windows. The falling-body viscometer has been described elsewhere [2]. The choice of the sinker is determined by considering the magnitude of the viscosity of the measured sample.

The viscosity, η, was calculated from the fall time of the sinker, t, by the following equation:

$$\eta = K\left(\rho_{\mathrm{s}} - \rho_{\mathrm{l}}\right)t \tag{1}$$

where K is the viscometer constant, and ρ_{s} and ρ_l are densities of the sinker and sample liquid, respectively. The fall time was measured with a reproducibility of 0.8%. The density of the sample liquid was obtained by using a piezometer [2].

The temperature was regulated to within 30 mK, the pressure to within 0.2 MPa, and the mole fraction to within 0.001. The uncertainty in the measured viscosity is estimated to be no larger than 2.9%, and the density to be no larger than 0.4%.

3 Results

The experimental viscosity data are given in Table 1 together with values for density at the same temperatures and pressures, which are interpolated from the experimental density values. The present viscosity data for mixtures of isobutane with squalane at low pressures (~2 MPa) agree with previous results [1] within 3.0% in spite of the different experimental techniques. The pressure dependences of viscosities for isobutane in the present work are similar to those presented by Sage et al. [3], but are different from those presented by Gonzalez et al. [4] and Diller et al. [5] as shown in Fig. 1.

Figure 2 shows the typical composition dependence of the viscosity of mixtures of isobutane, together with n-butane, n-hexane, and n-octane, with squalane at 30 MPa and 273.15 K. The logarithmic viscosity isotherm of the mixtures at high pressures was convex upward, and the viscosity increased with increasing squalane mole fraction, x_1. The swell of the convexity for isobutane mixtures was more notable than other n-alkane mixtures in the squalane-rich region. Viscosity isotherms at other pressures showed similar behavior. At constant temperature and composition, the viscosity of mixtures increased monotonically with pressure with a small positive curvature, as shown in Fig. 3.

The experimental viscosity data at high pressures were fitted with a Tait-like equation in terms of viscosity [6,7],

$$\ln\left(\eta_{\mathrm{p}}/\eta_0\right) = E\ln\left[\left(D+P\right)/\left(D+P_0\right)\right] \tag{2}$$

Table 1 Viscosity and Density Data for Isobutane (2) + Squalane (1) Mixtures

Temperature (K)	x_1	Pressure (MPa)	Density ($\mathrm{kg \cdot m^{-3}}$)	Viscosity ($\mathrm{mPa \cdot s}$)
273.15	0.000	2.0	586	0.197
		10.0	598	0.217
		20.0	609	0.241
		30.0	618	0.261
	0.169	2.0	714	1.69
		10.0	721	1.94
		20.0	728	2.22
		30.0	735	2.56
	0.288	2.0	751	4.22
		10.0	756	4.91
		20.0	763	5.87
		30.0	768	7.06
	0.513	2.0	788	21.6
		10.0	792	26.4
		20.0	798	33.2
		30.0	804	40.2
	0.777	2.0	809	75.8
		10.0	813	93.3
		20.0	818	119.2
		30.0	822	150.5
293.15	0.000	2.0	563	0.162
		10.0	576	0.179
		20.0	589	0.200
		30.0	601	0.219
	0.169	2.0	698	1.20
		10.0	706	1.34
		20.0	713	1.53
		30.0	721	1.74
	0.288	2.0	736	2.49
		10.0	744	2.88
		20.0	750	3.37
		30.0	755	3.92
	0.513	2.0	774	10.2
		10.0	780	11.9
		20.0	787	14.5
		30.0	790	17.5
	0.777	2.0	795	26.7
		10.0	801	31.3
		20.0	806	38.4
		30.0	810	48.6

Table 1 continued

Temperature (K)	x_1	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($mPa \cdot s$)
313.15	0.000	2.0	537	0.132
		10.0	554	0.149
		20.0	571	0.167
		30.0	584	0.186
	0.169	2.0	681	0.900
		10.0	691	1.03
		20.0	698	1.18
		30.0	708	1.33
	0.288	2.0	721	1.68
		10.0	730	1.89
		20.0	737	2.17
		30.0	743	2.54
	0.509	2.0	760	4.30
		10.0	765	5.01
		20.0	773	5.96
		30.0	778	7.01
	0.763	2.0	781	8.77
		10.0	786	10.4
		20.0	792	12.9
		30.0	798	15.5
333.15	0.000	2.0	509	0.109
		10.0	532	0.126
		20.0	552	0.145
		30.0	567	0.161
	0.169	2.0	664	0.622
		10.0	676	0.705
		20.0	684	0.820
		30.0	695	0.941
	0.288	2.0	706	1.17
		10.0	715	1.34
		20.0	724	1.57
		30.0	732	1.78
	0.509	2.0	745	2.73
		10.0	752	3.17
		20.0	760	3.75
		30.0	766	4.34
	0.763	2.0	767	5.56
		10.0	774	6.40
		20.0	780	7.56
		30.0	787	8.96

where η_p and η_0 are the viscosities at P and P_0 (reference pressure), respectively, and E and D are adjustable parameters. Table 2 shows the values of the parameters determined from the present data. The Evalues of mixtures were given by a linear function of the mole fraction of squalane, x_1. The equation represents the present viscosity data with a maximum deviation of 2.7%. Solid lines in Fig. 3 represent the values calculated from Eq. (2).

The experimental viscosity values were next fitted with the model proposed by Kanti et al. [8], which was derived from Bloomfield and Dewan [9] and from the Flory theory [10–12]. The equation without an adjustable parameter proposed by Kanti et al. can be applied in the high-pressure region. $\Delta^E \ln \eta$ is defined as:

$$\Delta^{\mathrm{E}} \ln \eta = \ln \eta - [x_1 \ln \eta_1 + (1 - x_1) \ln \eta_2] \tag{3}$$

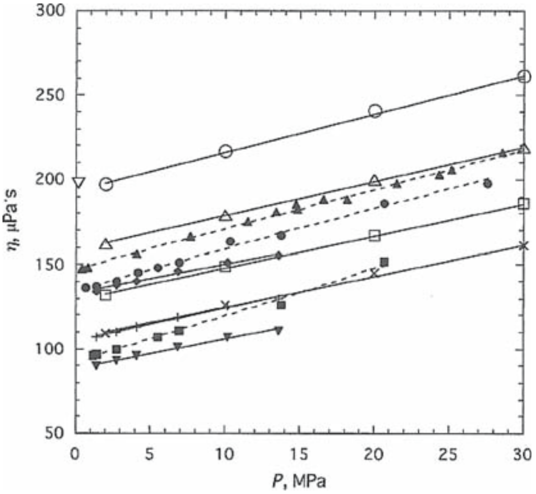

Fig. 1 Comparison of viscosity values of isobutane with literature data at high pressure. Present work: 273.15 K (○), 293.15 K (△), 313.15 K (□), 333.15 K (×); Diller et al. [5]: 300 K (▲), 273.15 K (interpolated) (▽); Gonzalez et al. [4]: 100°F (●), 160°F (■); Sage et al. [3]: 100°F (◆), 130°F (+), 160°F (▼)

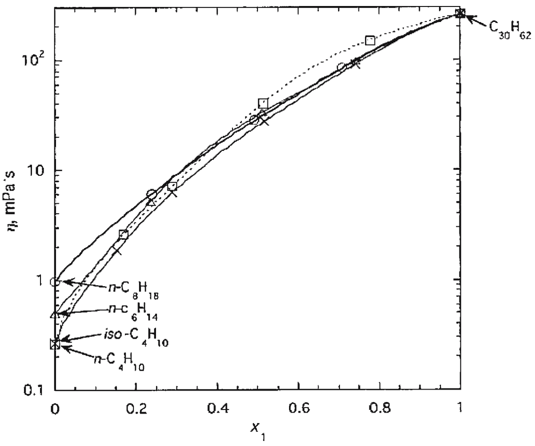

Fig. 2 Composition dependence of experimental viscosity for mixtures of isobutane(□), n-butane(×), n-hexane(△), and n-octane(○) with squalane at 30 MPa and 273.15 K

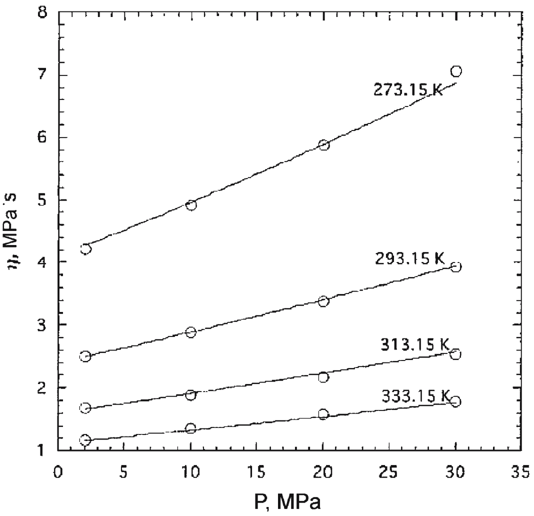

Fig. 3 Pressure dependence of viscosity for mixtures of isobutane with squalane at $x_1 = 0.288$. Solid lines; Tait-like equation

where η is the viscosity of the mixture, η_i is the viscosity of component i, and x_1 is the mole fraction of component 1. Components 1 and 2 represent squalane and isobutane, respectively.

In the calculation of the viscosity from the predictive model of Kanti et al., we shall assume that the input parameters, α, β, ρ, and η are only known for the pure components. The isothermal compressibility β can be calculated from the Tait equation,

$$(\rho - \rho_0)/\rho = C \ln[(B + P)/(B + P_0)] \tag{4}$$

$$\beta = \rho/\rho_0[C/(B + P)] \tag{5}$$

where ρ and ρ_0 are the densities at P and P_0 (reference pressure), respectively, and B and C are adjustable parameters. The values of B and C were determined from the present experimental density data.

For calculation of the thermal expansion coefficient, α, the following equation was used:

$$\rho_{(T,P)} = \rho_{(T_0,P)}\,[1 + \kappa(T - T_0)] \tag{6}$$

$$\alpha = -\kappa/\,[1 + \kappa(T - T_0)] \tag{7}$$

where $\rho_{(T,P)}$ and $\rho_{(T_0,P)}$ are the densities at $(T,\ P)$ and $(T_0,\ P)$ respectively, and T_0 is 273.15 K. κ is the coefficient in Eq. (7). The values of κ and α were determined from the present experimental density data. The values for the parameters in the equation of Kanti et al. are listed in Table 3. The predicted viscosities showed large deviations from

Table 2 Parameters of the Tait-like Equation for Isobutane (2) + Squalane (1) Mixtures

Temperature (K)	x_1	η_0 (mPa · s)	E	D (MPa)
273.15	0.000	0.191	0.68	50
293.15		0.158		46
313.15		0.129		40
333.15		0.104		35
273.15	0.169	1.63	1.14	66
293.15		1.14		66
313.15		0.880		67
333.15		0.602		67
273.15	0.288	4.08	1.46	70
293.15		2.40		74
313.15		1.60		78
333.15		1.12		82
273.15	0.513	20.9	2.07	82
293.15		9.84		91
313.15	0.509	4.13	2.05	100
333.15		2.62		110
273.15	0.777	72.0	2.79	98
293.15		25.0		114
313.15	0.763	8.60	2.75	131
333.15		5.39		147
273.15	1.000	116.6	3.39	113
293.15		35.3		150
313.15		15.4		163
333.15		7.85		187

the experimental data with a maximum deviation of 66.9%, and average deviations of 54.9% for mixtures of isobutane with squalane.

In our previous study [2], we applied an energetic mixing rule for U by introducing an interaction parameter in order to obtain good correlations. It was found that the interaction parameter can be expressed by a simple equation as a function of temperature and molar volumes evaluated from the group contribution method of Bondi [13]. This equation was found to be very effective for mixtures of n-alkanes (n-butane, n-hexane, and n-octane) with squalane. As described previously, however, the composition dependence of the viscosity of the isobutane + squalane mixture is significantly different from that of the n-butane + squalane mixture in the squalane-rich region. Since the Bondi method provides almost similar molar-volume values for isobutane and n-butane, the energetic mixing rule with the interaction parameter can not represent correctly the experimental viscosity values of the isobutane + squalane

Table 3 Physicochemical Parameters, α and β for Isobutane and Squalane in the Equation of Kanti et al. [8]

	P (MPa)	273.15 K	293.15 K	313.15 K	333.15 K
		α (10^4 K^{-1})			
Isobutane	2.0	21.9	22.9	24.0	25.2
	10.0	18.4	19.1	19.9	20.7
	20.0	15.5	16.0	16.6	17.1
	30.0	13.8	14.1	14.6	15.0
Squalane	0.1	7.29	7.50	7.74	7.99
	10.0	7.18	7.38	7.62	7.86
	20.0	7.07	7.27	7.50	7.73
	30.0	6.97	7.17	7.38	7.59
		β (10^9 Pa^{-1})			
Isobutane	2.0	2.57	3.16	4.70	6.70
	10.0	2.18	2.58	3.53	4.58
	20.0	1.83	2.11	2.72	3.31
	30.0	1.58	1.79	2.22	2.61
Squalane	0.1	0.692	0.726	0.769	0.812
	10.0	0.658	0.689	0.727	0.766
	20.0	0.628	0.655	0.689	0.724
	30.0	0.600	0.624	0.656	0.689

mixture. In this study, therefore, we tried to develop another mixing rule applicable to both the isobutane + squalane and n-alkane + squalane mixtures.

To improve the calculated results, an energetic mixing rule introducing two index numbers, n and m, was used as follows:

$$U_m^* = x_1^n U_1^* + (1 - x_1)^m \, U_2^* \tag{8}$$

By analyzing experimental results for mixtures of isobutane, n-butane, n-hexane, and n-octane with squalane, it was found that n and m values may be expressed as

$$n = 0.937 + 2.5 \times 10^{-4} T \tag{9}$$

$$m = 1.17\,(T_c - 399.5)^{-0.113} + 15 \times 10^{-3} T \tag{10}$$

where T_c is the critical temperature, 408.1, 425.2, 507.9, and 569.9 K for isobutane, n-butane, n-hexane, and n-octane, respectively. The values of n and m were close to unity ($n = 1.005$ to 1.020, $m = 1.06$ to 1.42). It was possible to reproduce the experimental viscosity for mixtures of isobutane with squalane at 333.15 K, as shown in Fig. 4, where the solid lines represent the viscosity from the correlation obtained by Kanti et al. in conjunction with Eqs. (8)–(10).

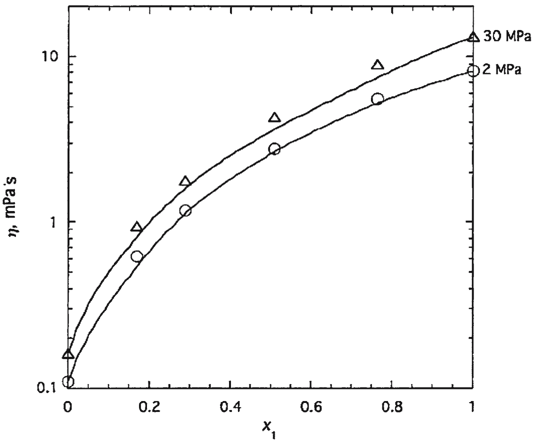

Fig. 4 Viscosity values calculated by the improved Flory et al. equation for mixtures of isobutane with squalane at 2 and 30 MPa, and 333.15 K

The correlated viscosities by Kanti et al. with Eqs. (8)–(10) can approximate more closely the experimental data with maximum deviations of 24.2, 23.8, 23.8, and 20.6% and average deviations of 1.7, 3.9, 4.4, and 1.0% for mixtures of *n*-butane, isobutane, *n*-hexane, and *n*-octane with squalane, respectively.

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