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Measurements of the Liquid Viscosities of Mixtures of *n*-Butane, *n*-Hexane, and *n*-Octane with Squalane to 30 MPa

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The viscosities of liquid mixtures of *n*-butane, *n*-hexane, and *n*-octane with squalane that represent model mixtures of refrigerants with refrigeration oil were measured at temperatures between 273.15 and 333.15 K, and at pressures from 0.1 to 30 MPa, by 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 to a Tait-like equation within 2.8%. There are larger deviations between the experimental data and calculated values predicted by the equation of Kanti et al., which is derived from the Flory theory. By introducing an interaction parameter of the energetic mixing rule into the equation, the deviations were significantly reduced.

KEY WORDS: high pressure; liquid mixture; *n*-butane; *n*-hexane; *n*-octane; squalane; viscosity.

1. INTRODUCTION

Accurate viscosity values for mixtures of refrigerants with lubricant oils are essential for the design of refrigeration systems based on natural refrigerants such as *n*-propane 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 model mixtures of refrigerants with refrigeration oil, using a capillary viscometer at temperatures ranging from 273.15 to 333.15 K at the saturated vapor pressure. The present paper extends the viscosity measurements on mixtures of *n*-butane, *n*-hexane, and *n*-octane with squalane to higher pressures, up to 30 MPa.

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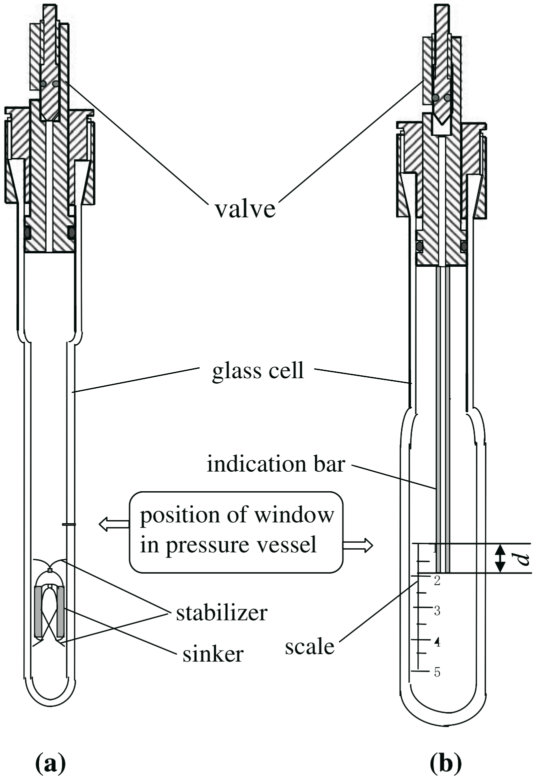
2. EXPERIMENTAL

N-butane, *n*-hexane, and *n*-octane were acquired from Nacalai Tesque Co. Ltd. and squalane from Tokyo Kasei Kogyo Co. Ltd. with minimum purities of 98 mass%. These compounds were used without further purification. The potential effects of these impurities on measured viscosities seem negligible, as impurity contents of *n*-alkanes are probably isomers [3]. The sample mixtures were prepared by directly mixing weighed amounts of the pure liquids at desired ratios. For the mixture of *n*-butane with squalane, the sampling procedure is as follows. The desired amount of squalane was introduced in the glass cell as shown in Fig. 1. Then the valve was mounted to the glass cell. After evacuation of air in the cell, *n*-butane was added through the vacuum line. The amount of *n*-butane charged into the cell was determined by weighing the piezometer before and after loading *n*-butane. The weighing was performed



(a) **(b)**

Fig. 1. Schematic diagram of (a) viscometer and (b) piezometer.

with an analytical balance with an uncertainty of ±0.1 mg. The viscosity was measured with a falling body viscometer (Fig. 1a), in which the viscometer is mounted in a pressure vessel attached to windows. The details of the experimental apparatus, except for the viscometer and piezometer, are the same as described in our previous studies [4,5]. The principle involves measurements of the fall time of a sinker over a constant length (20 mm) inside a borosilicate glass tube with a 6.60 mm inside diameter. Three different cylindrical sinkers with diameters of 6.50 (borosilicate glass), 6.45, and 6.35 mm (stainless steel), and with a 20 mm cylindrical section were employed in our experiments. The choice of the sinker is determined by considering the magnitude of the viscosity of the measured sample. Two γ-shaped stabilizers, made from a stainless steel wire with 0.3 mm diameter and carefully adjusted at its ends to meet the requirements of the viscosity measurement in terms of maintaining a symmetric shape, fitting the inside diameter of the glass tube, and ensuring a point contact, were fixed to the sinker at both the top and bottom positions with polymer adhesive.

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

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

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 viscometer constant was obtained by measuring the fall time at temperatures between 278 and 333 K, and at 0.1 MPa in liquids of *n*-octane [1], squalane [1], water [6], and standard liquids, that is, JS10 and JS100 calibrated by the National Metrology Institute of Japan, to within an uncertainty of 1.0%. The viscometer constant was applied even for high-pressure ranges on the basis of a fit between literature data at high pressure and the present values determined with the use of the constant at 0.1 MPa. The agreement was within 2.3% for *n*-octane [7–10] at temperatures between 298 and 333 K, and up to 30 MPa. The density of the sample liquid was obtained by using a piezometer as shown in Fig. 1b. The piezometer had a volume of 13 cm^3 and was fixed to the pressure vessel. As can be seen, both the viscometer and piezometer have the same type of valve, which also functions as a piston [4]. By pressurization, the valve stem can move into the glass tube of the viscometer or piezometer. The displacement of the valve and the indicator bar caused by the applied pressure was read directly with a scale through an optical window attached to the pressure vessel. The density of the sample, ρ_{l}, was calculated from the displacement, d, at each pressure and temperature by the following equation:

$$\rho_1 = W/(V_0 - ad) \tag{2}$$

where W is the mass of sample, V_0 is the volume of the glass cell for which the piston of the end of the indication bar is just at the zero position of the scale, and a is the cross-sectional area of the glass tube in Fig. 1b.

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 Ia,b,c together with values for the density at the same temperatures and pressures, which are interpolated from the experimental density values. The present viscosity data for mixtures of *n*-butane and *n*-hexane with squalane at 0.1 MPa agree with previous results [2] within 3.0% independent of the different experimental techniques. The present viscosity data at temperatures between 298 and 333 K, and up to 30 MPa agreed with literature data for *n*-hexane [7–9] and *n*-butane [7,11,12] to within 1.7%, and 3.8%, respectively.

Figure 2 shows the typical composition dependence of the viscosity of mixtures of *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. Viscosity isotherms at other pressures showed similar behavior. At constant temperature and composition, the viscosity of mixtures increased monotonically with increasing pressure with a small positive curvature, as shown in Fig. 3.

The experimental viscosity data at high pressures were fitted to a Tait-form equation in terms of viscosity [9,13],

$$\ln\left(\eta_p/\eta_0\right) = E \ln[(D + P)/(D + P_0)] \tag{3}$$

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 IIa,b,c show the values of the parameters determined from the present data. The E values of mixtures were given by a linear function of the mole fraction of squalane. The equation represents the present viscosity data with a maximum deviation of 2.8%. Solid lines in Fig. 3 represent the values calculated from Eq. (3).

Table I(a). Viscosity and Density for *n*-Butane (2) + Squalane (1) Mixtures

Temperature (K)	x_1	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($mPa \cdot s$)
273.15	0.000	0.1	601	0.203
		10.0	612	0.225
		20.0	622	0.247
		30.0	631	0.269
	0.154	1.0	719	1.34
		10.0	726	1.50
		20.0	733	1.66
		30.0	739	1.87
	0.290	1.0	758	4.14
		10.0	765	4.73
		20.0	771	5.42
		30.0	775	6.27
	0.518	1.0	792	16.6
		10.0	798	19.4
		20.0	804	23.2
		30.0	808	27.7
	0.741	1.0	808	46.2
		10.0	815	57.0
		20.0	820	72.2
		30.0	825	91.5
293.15	0.000	0.2	578	0.170
		10.0	592	0.184
		20.0	605	0.209
		30.0	614	0.232
	0.154	1.0	702	0.973
		10.0	710	1.06
		20.0	717	1.19
		30.0	724	1.33
	0.290	1.0	742	2.60
		10.0	750	2.86
		20.0	757	3.33
		30.0	762	3.74
	0.518	1.0	778	7.84
		10.0	784	9.03
		20.0	790	10.7
		30.0	795	12.9
	0.741	1.0	795	17.9
		10.0	802	21.8
		20.0	807	26.1
		30.0	812	31.1
313.15	0.000	0.4	555	0.143
		10.0	572	0.160
		20.0	586	0.184

Table I(a). *(Continued)*

Temperature (K)	x_1	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($mPa \cdot s$)
		30.0	598	0.202
	0.154	1.0	686	0.757
		10.0	695	0.821
		20.0	702	0.905
		30.0	710	1.01
	0.290	1.0	727	1.75
		10.0	736	1.97
		20.0	744	2.20
		30.0	750	2.50
	0.544	1.0	765	5.08
		10.0	771	5.87
		20.0	777	6.84
		30.0	783	8.07
	0.753	1.0	784	8.53
		10.0	791	10.1
		20.0	798	12.1
		30.0	802	14.3
333.15	0.000	0.6	529	0.118
		10.0	550	0.133
		20.0	567	0.153
		30.0	580	0.172
	0.154	1.0	671	0.580
		10.0	681	0.614
		20.0	688	0.680
		30.0	697	0.744
	0.290	1.0	713	1.30
		10.0	722	1.40
		20.0	732	1.54
		30.0	738	1.73
	0.544	1.0	752	3.18
		10.0	758	3.56
		20.0	765	4.12
		30.0	772	4.80
	0.753	1.0	773	5.18
		10.0	779	5.81
		20.0	785	6.74
		30.0	791	8.00

The experimental viscosity values were next fitted with the model proposed by Kanti et al. [14], which was derived from Bloomfield and Dewan [15] and Flory theory [16–18]. The equation without an adjustable parameter proposed by Kanti et al. can be applied in the high-pressure

Table I(b). Viscosity and Density for *n*-Hexane (2) + Squalane (1) Mixtures

Temperature (K)	x_1	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($mPa \cdot s$)
273.15	0.000	0.1	678	0.382
		10.0	686	0.421
		20.0	693	0.456
		30.0	700	0.492
	0.235	0.1	745	3.34
		10.0	751	3.88
		20.0	755	4.43
		30.0	761	5.16
	0.511	0.1	792	16.9
		10.0	797	20.9
		20.0	799	26.0
		30.0	804	33.1
	0.743	0.1	810	45.3
		10.0	816	58.5
		20.0	818	77.0
		30.0	824	97.1
293.15	0.000	0.1	660	0.310
		10.0	670	0.340
		20.0	678	0.375
		30.0	685	0.407
	0.235	0.1	731	1.91
		10.0	738	2.26
		20.0	743	2.66
		30.0	749	3.09
	0.511	0.1	778	7.76
		10.0	783	9.51
		20.0	787	11.6
		30.0	792	14.2
	0.743	0.1	797	17.5
		10.0	803	21.2
		20.0	807	25.8
		30.0	813	31.1
313.15	0.000	0.1	642	0.257
		10.0	653	0.287
		20.0	662	0.317
		30.0	671	0.351
	0.235	0.1	717	1.36
		10.0	725	1.58
		20.0	731	1.83
		30.0	737	2.09
	0.511	0.1	764	4.15
		10.0	770	5.09

Table I(b). *(Continued)*

Temperature (K)	x_1	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($mPa \cdot s$)
		20.0	775	5.96
		30.0	781	6.95
	0.743	0.1	784	8.25
		10.0	790	10.1
		20.0	796	12.3
		30.0	802	14.7
333.15	0.000	0.1	623	0.218
		10.0	636	0.241
		20.0	647	0.266
		30.0	656	0.291
	0.235	0.1	703	0.996
		10.0	712	1.18
		20.0	719	1.32
		30.0	725	1.50
	0.511	0.1	750	2.62
		10.0	757	3.12
		20.0	763	3.60
		30.0	770	4.18
	0.743	0.1	771	4.64
		10.0	778	5.63
		20.0	785	6.66
		30.0	791	7.82

Table I(c). Viscosity and Density for *n*-Octane (2) + Squalane (1) Mixtures

Temperature (K)	x_1	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($mPa \cdot s$)
273.15	0.000	0.1	719	0.705
		10.0	726	0.793
		20.0	733	0.871
		30.0	739	0.971
	0.238	0.1	770	4.17
		10.0	777	4.80
		20.0	783	5.55
		30.0	788	6.37
	0.543	0.1	800	22.0
		10.0	809	27.6
		20.0	811	33.9
		30.0	817	41.4
	0.709	0.1	809	42.0
		10.0	817	54.2
		20.0	820	67.7
		30.0	824	84.5

Table I(c). *(Continued)*

Temperature (K)	x_1	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($mPa \cdot s$)
	1.000	0.1	819	116.6
		10.0	824	152.4
		20.0	830	199.4
		30.0	835	261.4
293.15	0.000	0.1	703	0.544
		10.0	711	0.596
		20.0	718	0.659
		30.0	725	0.717
	0.238	0.1	755	2.43
		10.0	761	2.82
		20.0	768	3.21
		30.0	774	3.64
	0.492	0.1	782	7.43
		10.0	790	8.82
		20.0	796	10.4
		30.0	800	12.3
	0.709	0.1	798	15.6
		10.0	802	19.1
		20.0	808	23.8
		30.0	814	29.5
	1.000	0.1	809	35.3
		10.0	814	43.6
		20.0	819	54.0
		30.0	823	65.6
313.15	0.000	0.1	687	0.429
		10.0	696	0.483
		20.0	704	0.536
		30.0	712	0.593
	0.238	0.1	743	1.60
		10.0	749	1.86
		20.0	756	2.16
		30.0	762	2.44
	0.492	0.1	770	4.27
		10.0	778	4.83
		20.0	783	5.56
		30.0	789	6.49
	0.709	0.1	788	7.68
		10.0	792	9.55
		20.0	797	11.6
		30.0	803	13.5
	1.000	0.1	795	15.4
		10.0	800	18.3
		20.0	806	22.7
		30.0	812	27.5

Table I(c). *(Continued)*

Temperature (K)	x_1	Pressure (MPa)	Density ($\mathrm{kg \cdot m^{-3}}$)	Viscosity ($\mathrm{mPa \cdot s}$)
333.15	0.000	0.1	670	0.351
		10.0	681	0.388
		20.0	690	0.441
		30.0	698	0.482
	0.238	0.1	731	1.25
		10.0	739	1.45
		20.0	747	1.65
		30.0	754	1.85
	0.492	0.1	754	2.78
		10.0	763	3.18
		20.0	771	3.62
		30.0	779	4.07
	0.709	0.1	770	4.45
		10.0	780	5.43
		20.0	787	6.31
		30.0	792	7.38
	1.000	0.1	782	7.85
		10.0	789	9.43
		20.0	795	11.0
		30.0	802	13.1

region. The excess viscosity of a binary mixture, $\Delta^E \ln\eta$, can be defined as:

$$\Delta^E \ln \eta = \ln \eta - [x_1 \ln \eta_1 + (1 - x_1) \ln \eta_2] \tag{4}$$

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 a hydrocarbon (*n*-butane, *n*-hexane, or *n*-octane), respectively.

From Bloomfield and Dewan [15], the excess viscosity can be expressed as

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

where

$$f(\tilde{V}) = 1/(\tilde{V} - 1) - x_1/(\tilde{V}_1 - 1) - (1 - x_1)/(\tilde{V}_2 - 1) \tag{6}$$

$$\begin{aligned} \Delta G^{\mathrm{R}} = {} & x_1 P_1^* V_1^* [1/\tilde{V}_1 - 1/\tilde{V} + 3\tilde{T}_1 \ln[(\tilde{V}_1^{1/3} - 1)/(\tilde{V}^{1/3} - 1)]] \\ & + (1 - x_1) P_2^* V_2^* [1/\tilde{V}_2 - 1/V + 3\tilde{T}_2 \ln[(\tilde{V}_2^{1/3} - 1)/(\tilde{V}^{1/3} - 1)]] \\ & + x_1 \vartheta V_1^* X_{12}/\tilde{V} \end{aligned} \tag{7}$$

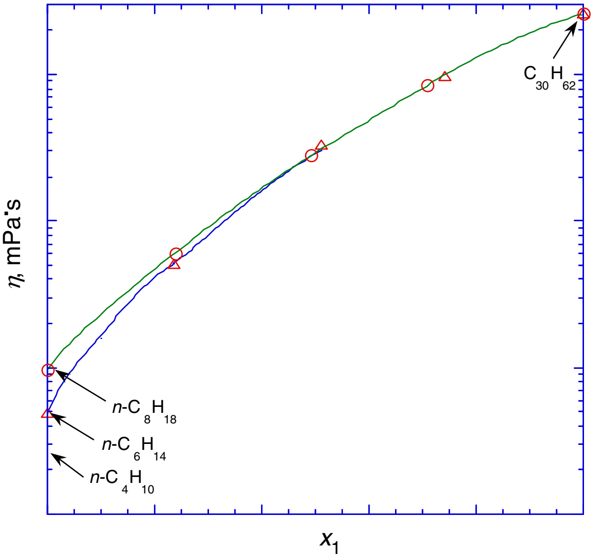


Fig. 2. Composition dependence of experimental viscosity for mixtures of n-butane (2), n-hexane (2), and n-octane (2) with squalane (1) at 30 MPa and 273.15 K.

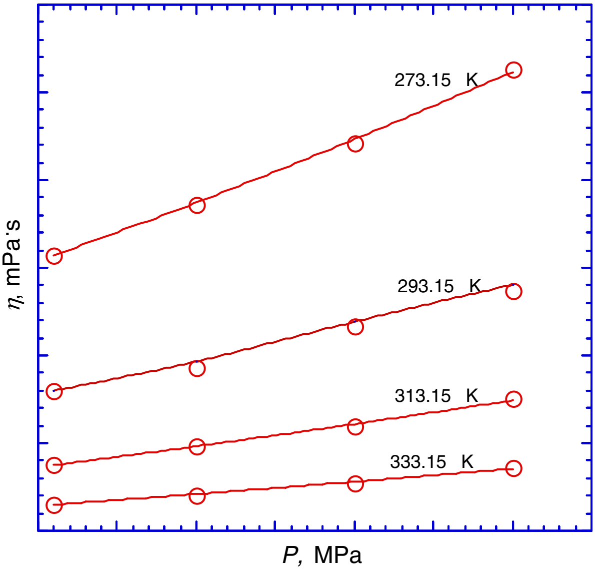


Fig. 3. Pressure dependence of viscosity for mixtures of n-butane (2) with squalane (1) at $x_1 = 0.290$; solid lines -Tait-like equation.

Table II(a). Parameters of the Tait-like Equation for *n*-Butane (2) + Squalane (1)

Temperature (K)	x_1	η_0^a (mPa · s)	E	D (MPa)
273.15	0.000	0.205	1.30	123
293.15		0.171		111
313.15		0.144		96
333.15		0.118		86
273.15	0.154	1.34	1.62	129
293.15		0.973		138
313.15		0.757		153
333.15		0.580		179
273.15	0.290	4.14	1.91	120
293.15		2.60		138
313.15		1.75		143
333.15		1.30		188
273.15	0.518	16.6	2.38	121
293.15		7.84		126
313.15	0.544	5.08	2.44	140
333.15		3.17		159
273.15	0.741	46.2	2.85	108
293.15		17.9		134
313.15	0.753	8.53	2.87	146
333.15		5.18		183

Table II(b). Parameters of the Tait-like Equation for *n*-Hexane (2) + Squalane (1)

Temperature (K)	x_1	η_0^a (mPa · s)	E	D (MPa)
273.15	0.000	0.382	1.56	168
293.15		0.310		157
313.15		0.257		136
333.15		0.218		146
273.15	0.235	3.34	1.99	125
293.15		1.91		110
313.15		1.36		124
333.15		0.996		129
273.15	0.511	16.9	2.50	100
293.15		7.76		111
313.15		4.15		129
333.15		2.62		145
273.15	0.743	45.3	2.92	100
293.15		17.5		137
313.15		8.25		136
333.15		4.64		152

Table II(c). Parameters of the Tait-like Equation for *n*-Octane (2) + Squalane (1)

Temperature (K)	x_1	η_0^a (mPa·s)	E	D (MPa)
273.15	0.000	0.705	2.04	177
293.15		0.544		210
313.15		0.429		173
333.15		0.351		176
273.15	0.238	4.17	2.36	153
293.15		2.43		162
313.15		1.60		153
333.15		1.25		164
273.15	0.543	22.0	2.77	117
293.15	0.492	7.43	2.70	149
313.15		4.27		186
333.15		2.78		199
273.15	0.709	42.0	3.00	115
293.15		15.6		129
313.15		7.68		138
333.15		4.45		162
273.15	1.00	116.6	3.39	113
293.15		35.3		150
313.15		15.4		163
333.15		7.85		187

[a] Viscosity at reference pressure (1 MPa for Table IIa, and 0.1 MPa for Table IIb,c)

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

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

$$\phi_1=1-\phi_2=x_1V_1^*/[x_1V_1^*+(1-x_1)V_2^*] \tag{10}$$

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

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 volume defined by Eq. (6). The interaction coefficient, X_{12}, the site fraction, ϑ, and the volume fraction, ϕ_1, depend on characteristic parameters, P^* and V^*, presented by Flory et al. [16–18] according to Eqs (8)–(10). Kanti et al. [14] 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 isothermal compressibility, β, using Flory's theory as follows:

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

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

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

Table III. Physicochemical Parameters, α, β, and V_{Bondi} for *n*-Butane, *n*-Hexane, *n*-Octane, and Squalane

	V_{Bondi} ($\mathrm{cm^3 \cdot mol^{-1}}$)	P (MPa)	α ($10^4\mathrm{K^{-1}}$)			
			273.15 K	293.15 K	313.15 K	333.15 K
n-Butane	47.80	1.0	19.5	21.1	23.0	25.5
		10.0	17.2	18.4	19.8	21.5
		20.0	15.0	15.9	16.9	18.2
		30.0	13.0	13.7	14.5	15.4
n-Hexane	68.26	0.1	13.5	13.9	14.3	14.7
		10.0	12.2	12.5	12.8	13.1
		20.0	11.1	11.4	11.6	11.9
		30.0	10.4	10.7	10.9	11.1
n-Octane	88.72	0.1	11.4	11.7	11.9	12.2
		10.0	10.3	10.5	10.8	11.0
		20.0	9.76	9.95	10.2	10.4
		30.0	9.20	9.38	9.55	9.74
Squalane	306.82	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
		P (MPa)	β ($10^9\mathrm{Pa^{-1}}$)			
			273.15 K	293.15 K	313.15 K	333.15 K
n-Butane		1.0	1.98	2.67	3.41	4.54
		10.0	1.74	2.26	2.77	3.48
		20.0	1.54	1.93	2.30	2.77
		30.0	1.38	1.69	1.97	2.31
n-Hexane		0.1	1.24	1.52	1.83	2.26
		10.0	1.12	1.35	1.58	1.90
		20.0	1.03	1.21	1.40	1.64
		30.0	0.947	1.10	1.26	1.45
n-Octane		0.1	1.06	1.21	1.52	1.72
		10.0	0.967	1.09	1.33	1.49
		20.0	0.888	0.985	1.18	1.31
		30.0	0.821	0.904	1.07	1.17
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

Delmas et al. [19] used the following mixing rule, since only $\tilde{V}$ for the mixture is needed to calculate the excess viscosity from Eq. (5):

$$\tilde{V}^{-1} = x_1 \tilde{V}_1^{-1} (U_1^*/U_m^*) + (1 - x_1) \tilde{V}_2^{-1} (U_2^*/U_m^*) \tag{15}$$

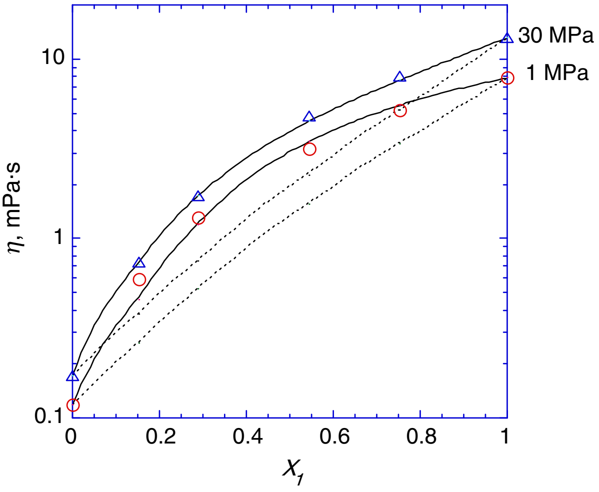


Fig. 4. Comparison of experimental viscosity with prediction and correlation for mixtures of *n*-butane (2) with squalane (1) at 333.15 K. ……, prediction obtained with Kanti et al. model; ——, correlation obtained with Kanti et al. model in conjunction with Eq. (22).

where

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

$$U_m^* = x_1 U_1^* + (1 - x_1) U_2^* \tag{17}$$

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;

$$(\rho - \rho_0)/\rho = C \ln[(B + P)/(B + P_0)] \tag{18}$$

$$\beta = \rho/\rho_0 [C/(B + P)] \tag{19}$$

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 equations were used:

$$\rho_{(T,P)} = \rho_{(T_0,P)}[1 + \kappa(T - T_0)] \tag{20}$$

$$\alpha = -\kappa/[1 + \kappa(T - T_0)] \tag{21}$$

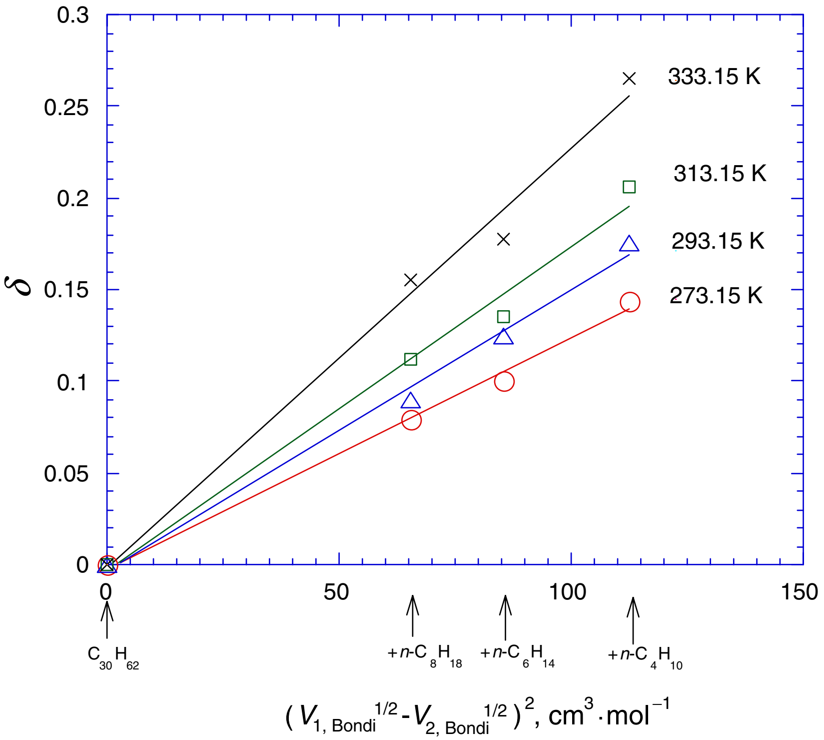


Fig. 5. Interaction parameter, δ, versus difference in molar volumes of components, $\left(V_{1,\mathrm{Bondi}}{}^{1/2} - V_{2,\mathrm{Bondi}}{}^{1/2}\right)^2$. Components 1 and 2 represents squalane and hydrocarbon, respectively.

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. (20). 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 III. The predicted viscosities were very different from the experimental data with maximum deviations of 59.9, 56.2, and 52.6%, and average deviations of 46.8, 43.1, and 39.1% for mixtures of *n*-butane, *n*-hexane, and *n*-octane with squalane, respectively. One of the examples of comparisons of the experimental viscosities with predictions is shown in Fig. 4 for mixtures of *n*-butane with squalane at 333.15 K, where dashed lines represent the viscosity from the predictive model of Kanti et al. To improve the calculated results, an energetic mixing rule introducing an interaction parameter, δ, was used instead of Eq. (17), as follows:

$$U_m^* = x_1^2 U_1^* + (1-x_1)^2 U_2^* - \delta x_1(1-x_1)(U_1^* U_2^*)^{1/2} \tag{22}$$

Parterson and Delmas [20] show that this interaction parameter reflects the large molecular size differences of components. From the analogy to the excess Gibbs energy demonstrated by Oswal and Patel [21], the optimum δvalues are plotted against the difference in molar volumes of components, $\left(V_{1,\text{Bondi}}^{1/2} - V_{2,\text{Bondi}}^{1/2}\right)^2$ in Fig. 5, where $V_{1,\text{Bondi}}$ and $V_{2,\text{Bondi}}$ are the molar volumes of component 1 (squalane) and 2 (hydrocarbon) evaluated from the group contribution method by Bondi [22]. The values are listed in Table III. The δvalues may be expressed mathematically as follows since the isotherms give straight lines through the origin:

$$\delta = 7.7 \times 10^{-5} \exp(T/100) \left(V_{1,\text{Bondi}}^{1/2} - V_{2,\text{Bondi}}^{1/2}\right)^2 \tag{23}$$

It was possible to reproduce the experimental viscosities for mixtures of n-butane with squalane at 333.15 K, as shown in Fig. 4, where solid lines represent the viscosities from the correlation with the use of the viscosity model of Kanti et al. in conjunction with Eqs (22) and (23). The correlated viscosities can approximate more closely to the experimental data with maximum deviations of 23.6, −22.7, and −17.1%, and average deviations of 1.4, 2.2, and 1.2% for mixtures of n-butane, n-hexane, and n-octane, respectively, with squalane.

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