

Liquid Viscosity of Binary Mixtures of Methanol with Ethanol and 1-Propanol from 273.15 to 333.15 K

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The liquid viscosities and densities of two binary mixtures of methanol with ethanol and 1-propanol were measured in the temperature range from 273.15 to 333.15 K with a capillary viscometer and a glass pycnometer, respectively. The uncertainties in the measured viscosities were estimated to be smaller than 1.3%. The experimental viscosity values could be fitted to the Mertsch and Wolf equation within 2%.

KEY WORDS: ethanol; methanol; mixtures; 1-propanol; viscosity.

1. INTRODUCTION

The thermophysical properties of alcohol mixtures at various temperatures must be accurately determined for the design of cryogenic power generation systems with the use of cryogenic alcohol mixtures as a heat reservoir. While extensive viscosity data have been reported for pure alcohols, few data are available in the literature for the alcohol mixtures.

In the present work, we report viscosities of two binary mixtures of methanol with ethanol and 1-propanol in the temperature range from 273.15 to 333.15 K obtained with a capillary viscometer. The densities of the binary mixtures were also measured with a glass pycnometer in order to obtain the dynamic viscosities. For the methanol + ethanol mixture, Bingham et al. [1] and Bhagwat and Sabnis [2] measured the viscosity at 303 and from 298 to 328 K, respectively. To the best knowledge of the authors, the viscosity for the methanol + 1-propanol mixture has not been reported yet. To correlate the experimental viscosity data, we applied

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the equation of Mertsch and Wolf [3]. The Flory–Huggins interaction parameters in the Mertsch and Wolf viscosity equation were determined from the experimental viscosity values.

2. EXPERIMENTAL

The viscosity was measured with the capillary viscometer described in a previous publication [4], which is applicable to liquids with a wide range of viscosity by replacing the capillary tube with different inner diameters, shown in Fig. 1. The viscosities of mixtures of HFC-134a with glycols have been measured with an accuracy of 1.6% with this viscometer.

The viscosity η of a liquid can be determined from the following equation:

Fig. 1. Details of the capillary viscometer.

where C_1 and C_2 are the apparatus constants, ρ is the density of the liquid sample obtained by the glass pycnometer described earlier [5] within an accuracy of $\pm 0.04\%$, and t is the efflux time determined with a reproducibility of 0.6% . The values of C_1 and C_2 were determined with the use of standard liquids, JS5 and JS10, where the numbers refer to the kinematic viscosities in $10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ at 293 K, calibrated by the National Research Laboratory of Metrology (Japan), and water within 0.4% . Liquid mixtures were made by direct weighing of each component within $\pm 0.002 \text{ g}$. The amount of sample loaded in the viscometer was adjusted to leave about 10 cm^3 of the vapor phase in the viscometer. The correction of the liquid-phase composition due to the vaporization of each component was negligibly small. The measurements were performed at Reynolds numbers of less than 205, which was below the critical value of 2300. The viscometer was located in a water bath whose temperature was regulated to within 30 mK . The uncertainty in the viscosity, resulting from an absolute accuracy of temperature measurement, is estimated to be less than 0.1% . The uncertainties in the measured viscosities are estimated to be smaller than 1.3% .

Samples were provided by Nacalai Tesque, Inc., for methanol, ethanol, and 1-propanol, with purities of better than 99.8, 99.5, and 99.5%, respectively, and dehydrated by molecular sieves, 3 \AA .

3. RESULTS

Comparisons of the present experimental data for the density and viscosity of methanol, ethanol, and 1-propanol with literature values are given in Table I. Density values of methanol, ethanol, and 1-propanol obtained in the present work agree with the literature data [6–10] within 0.11% , which is adequate for the determination of viscosities. Most of the present viscosity values for pure alcohols agreed with the literature data [1, 6–9, 11–16] if we take into account both the experimental errors within 3% , except for those of 1-propanol, with a maximum deviation of 8.8% . The present experimental data for the density and viscosity of binary mixtures of methanol with ethanol and 1-propanol are listed in Tables II and III and shown in Figs. 2 and 3, respectively. It can be seen in Figs. 2 and 3 that the viscosity isotherms of the two mixtures had a positive curvature and decrease with an increase in the mole fraction of methanol.

4. DISCUSSION

The experimental excess viscosity $\Delta \ln \eta^{\text{exp}}$ can be expressed as follows:

$$\Delta \ln \eta^{\text{exp}} = \ln \eta^{\text{exp}} - \ln \eta^{\text{id}} \quad (2)$$

Table I. Comparison of the Liquid Density, ρ , and Viscosity, η , of Pure Components from the Present Work with Literature Values

T (K)	ρ ($\text{kg} \cdot \text{m}^{-3}$)			η ($\text{mPa} \cdot \text{s}$)		
	Present work	Literature	Dev. (%) ^a	Present work	Literature	Dev. (%) ^b
Methanol						
273.15	809.7	810.0 [6]	−0.04	0.795	0.803 [7]	−1.0
					0.800 [11]	−0.6
					0.805 [6]	−1.3
293.15	790.9	791.04 [7]	−0.01	0.583	0.586 [12]	−0.5
		791.1 [6]	−0.03		0.5929 [7]	−1.7
					0.588 [11]	−0.9
313.15	772.3	772.7 [6]	−0.05	0.447	0.586 [6]	−0.5
					0.447 [1]	0
					0.446 [12]	0.2
					0.448 [7]	−0.2
					0.451 [11]	−0.9
333.15	753.2	754.0 [6]	−0.11	0.348	0.445 [6]	0.4
					0.348 [7]	0
					0.349 [11]	−0.3
					0.345 [6]	0.9
Ethanol						
273.15	806.1	806.2 [6]	−0.01	1.783	1.735 [7]	2.7
					1.80 [11]	−1.0
					1.807 [6]	−1.3
293.15	789.2	789.20 [7]	0	1.184	1.159 [12]	2.1
		789.5 [6]	−0.04		1.203 [7]	−1.6
					1.19 [11]	−0.5
					1.198 [6]	−1.2
313.15	771.8	772.3 [6]	−0.06	0.819	0.833 [13]	−1.7
		772.1 [8]	−0.04		0.811 [12]	1.0
		772.2 [9]	−0.05		0.823 [7]	−0.5
					0.81 [11]	1.1
					0.822 [6]	−0.4
					0.835 [14]	−2.0
					0.834 [15]	−1.8
333.15	754.0	754.5 [6]	−0.07	0.587	0.826 [8]	−0.9
					0.834 [9]	−1.8
					0.583 [7]	0.7
					0.58 [11]	1.2
					0.590 [6]	−0.5

Table I. (Continued)

T (K)	ρ ($\text{kg} \cdot \text{m}^{-3}$)			η ($\text{mPa} \cdot \text{s}$)		
	Present work	Literature	Dev. (%) ^a	Present work	Literature	Dev. (%) ^b
1-Propanol						
273.15	819.6	820.1 [10]	-0.06	3.68	3.85 [16] 3.63 [7]	-4.6 1.4
293.15	803.9	804.0 [10]	-0.01	2.17	2.09 [12]	3.7
		803.61 [7]	0.04		2.20 [16]	-1.4
313.15	787.4	788.0 [10]	-0.08	1.38	2.36 [7]	-8.8
					1.34 [12]	2.9
					1.38 [16]	0
333.15	770.7	771.3 [10]	-0.08	0.923	1.43 [7]	-3.6
					0.92 [16]	0.3
					0.887 [7]	3.9

^a Dev. = $100[(\rho_{\text{present}} - \rho_{\text{lit.}})/\rho_{\text{present}}]$.

^b Dev. = $100[(\eta_{\text{present}} - \eta_{\text{lit.}})/\eta_{\text{present}}]$.

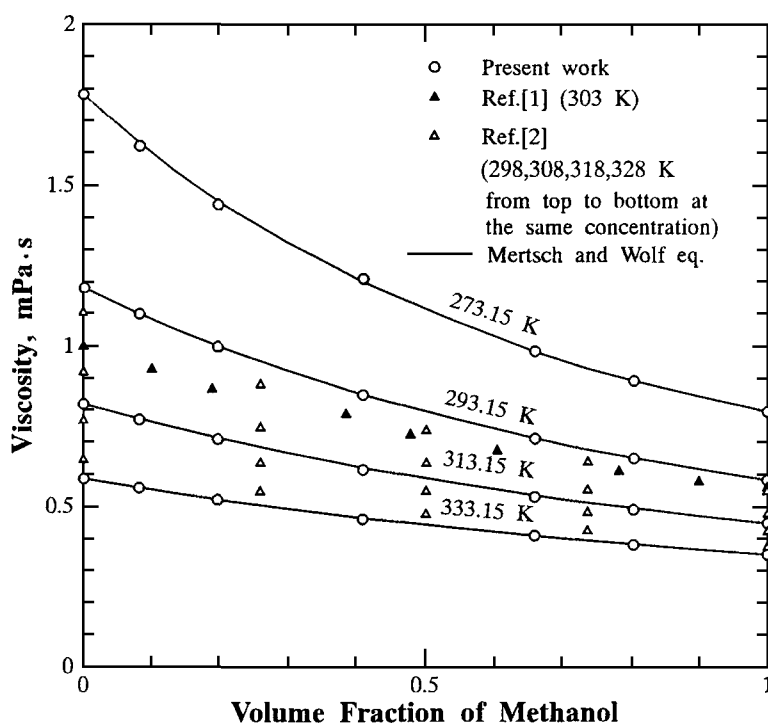


Fig. 2. Viscosity of the methanol + ethanol mixture.

Table II. Densities ($\text{kg} \cdot \text{m}^{-3}$) of Methanol + Ethanol and Methanol + 1-Propanol Mixtures

X^a	T (K)			
	273.15	293.15	313.15	333.15
Methanol + ethanol				
0	806.1	789.2	771.8	754.0
0.273	806.5	789.5	771.5	753.4
0.481	807.8	790.0	772.0	753.5
0.755	808.7	790.5	771.9	753.0
1	809.7	790.9	772.3	753.2
Methanol + 1-propanol				
0	819.6	803.9	787.4	770.7
0.223	817.6	801.6	785.0	767.8
0.520	815.0	798.1	780.9	763.1
0.708	812.5	795.0	777.2	759.0

^a Mole fraction of methanol.**Table III.** Viscosities ($\text{mPa} \cdot \text{s}$) of Methanol + Ethanol and Methanol + 1-Propanol Mixtures

X^a	T (K)			
	273.15	293.15	313.15	333.15
Methanol + ethanol				
0	1.78	1.18	0.819	0.587
0.114	1.62	1.10	0.770	0.558
0.263	1.44	0.997	0.709	0.521
0.501	1.21	0.849	0.615	0.461
0.738	0.984	0.712	0.531	0.408
0.856	0.892	0.651	0.491	0.379
1	0.795	0.583	0.447	0.348
Methanol + 1-propanol				
0	3.68	2.17	1.38	0.923
0.174	2.86	1.78	1.17	0.799
0.339	2.23	1.45	0.986	0.697
0.510	1.73	1.16	0.822	0.597
0.741	1.21	0.857	0.624	0.471
0.873	0.980	0.711	0.530	0.410

^a Mole fraction of methanol.

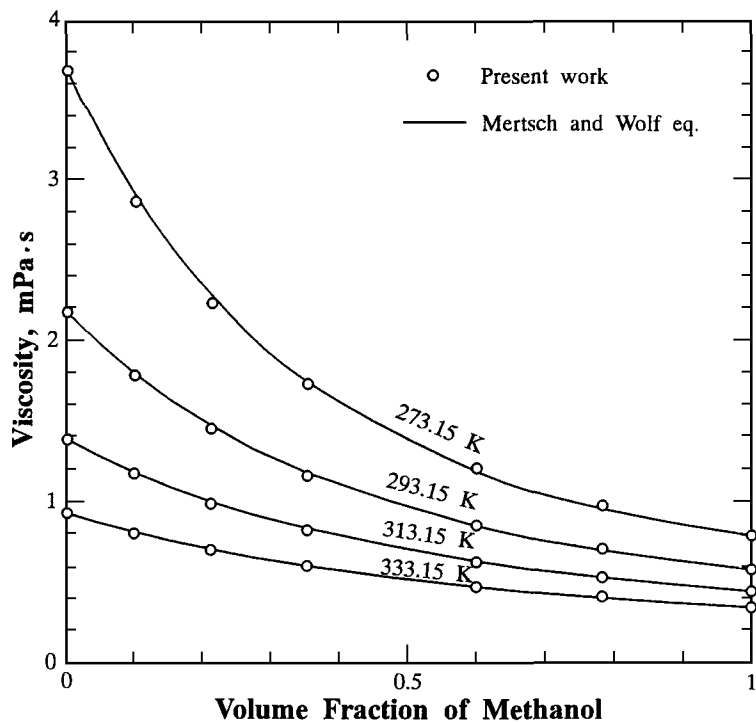


Fig. 3. Viscosity of the methanol + 1-propanol mixture.

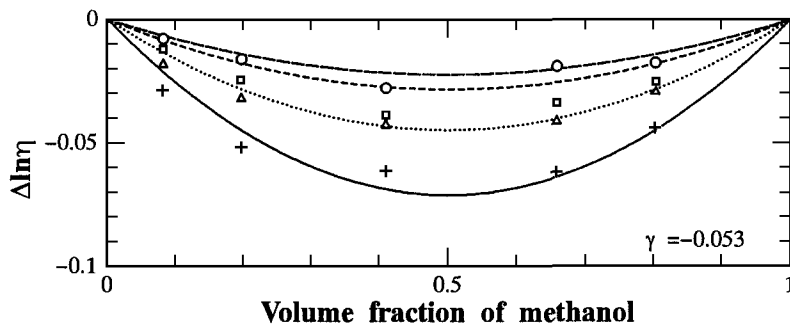


Fig. 4. Comparison of the experimental excess viscosities with those calculated from the Mertsch and Wolf equation for the methanol + ethanol mixture. (+) —, 273.15 K; (Δ) ·····, 293.15 K; (\square) ----, 313.15 K; (\circ) -·-·-, 333.15 K. Symbols, experimental; lines, Mertsch and Wolf equation.

where η^{exp} is the experimental viscosity, and η^{id} is an idealized reference viscosity expressed as

$$\ln \eta^{\text{id}} = \phi_1 \ln \eta_1 + \phi_2 \ln \eta_2 \quad (3)$$

where ϕ_i and η_i are the volume fraction and the viscosity of pure component i ($= 1, 2$), respectively. The plots of the experimental excess viscosities vs. the volume fraction of methanol are shown in Figs. 4 and 5. It can be seen that the excess value is almost symmetric with the volume fraction. The excess viscosity of the methanol + 1-propanol mixture is two to four times higher than that of the methanol + ethanol mixture at the same temperature.

It is instructive to consider the relationship between the excess viscosity and the residual molecular interaction parameter. The viscosity equation of Mertsch and Wolf [3] seems to be appropriate to test this idea. Following Mertsch and Wolf, the theoretical excess viscosity $\Delta \ln \eta_{\text{theo}}$ may be calculated from

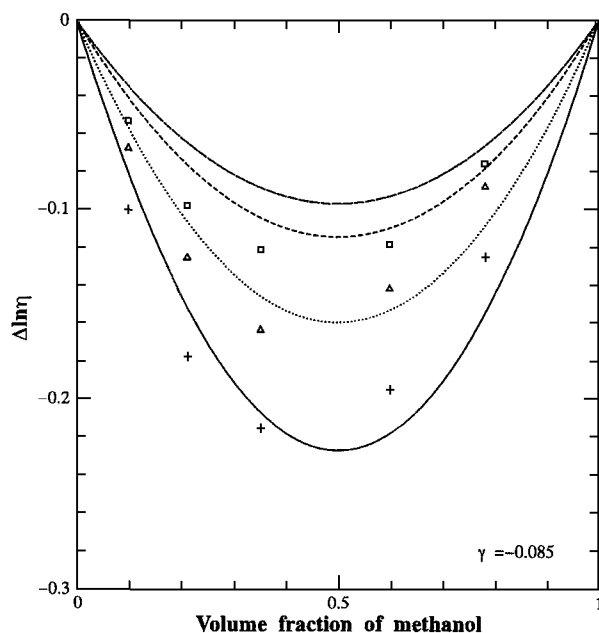


Fig. 5. Comparison of the experimental excess viscosities with those calculated from the Mertsch and Wolf equation for the methanol + 1-propanol mixture. For symbols and lines, refer to the legend to Fig. 4.

$$\Delta \ln \eta_{\text{theo}} = \gamma \delta / (1 + \gamma \phi_2) \phi_2 (1 - \phi_2) + 2g(1 + \gamma) / (1 + \gamma \phi_2)^2 \phi_2 (1 - \phi_2) \quad (4)$$

$$\gamma = (F_2/V_2)/(F_1/V_1) - 1 \quad (5)$$

$$\phi_2 = n_2(V_2/V_1)/(n_1 + n_2(V_2/V_1)) \quad (6)$$

$$\delta = \ln(\eta_2/\eta_1) \quad (7)$$

$$g = \Delta G^R / (RTx_1\phi_2) \quad (8)$$

where n_i is the number of moles of component i ($= 1, 2$), and x_1 is the mole fraction of component 1. The molecular surface F_i and molar volume V_i of component i ($= 1, 2$) can be evaluated from the group-contributions method of Bondi [17]. The parameters F_i and V_i used in the evaluation are listed in Table IV. ΔG^R is the molar residual Gibbs free energy of mixing and g is the interaction parameter defined by ΔG^R from Eq. (8). In principle, ΔG^R can be determined from the activity coefficients obtained from vapor liquid equilibrium (VLE) data. Since, however, the thermodynamic consistent VLE data for the two binary alcohol mixtures are very scarce in the present experimental temperature range [18–20], we determined the values of g by the least-squares method from the experimental viscosity data. The temperature dependence of g for the two binary systems is shown in Fig. 6. As can be seen, the g exhibits a slight variation with temperature for the methanol + ethanol mixture in accordance with the literature [1, 2], and has a relatively large temperature dependence for the methanol + 1-propanol mixture. The error bars in Fig. 6 refer to viscosity errors of 2%. The solid lines represent the g values calculated from the following equations as a function of temperature T in K.

$$g = -2.77 + 1.64 \times 10^{-2}T - 2.46 \times 10^{-5}T^2 \quad (9)$$

(for the methanol + ethanol mixture)

$$g = -6.47 + 3.74 \times 10^{-2}T - 5.54 \times 10^{-5}T^2 \quad (10)$$

(for the methanol + 1-propanol mixture)

Table IV. Molecular Surface F_i and Molar Volume V_i Determined from the Group-Contribution Method of Bondi [17]

	F_i (cm ² · mol ⁻¹)	V_i (cm ³ · mol ⁻¹)
Methanol	3.58	22
Ethanol	4.93	32
1-Propanol	6.28	42

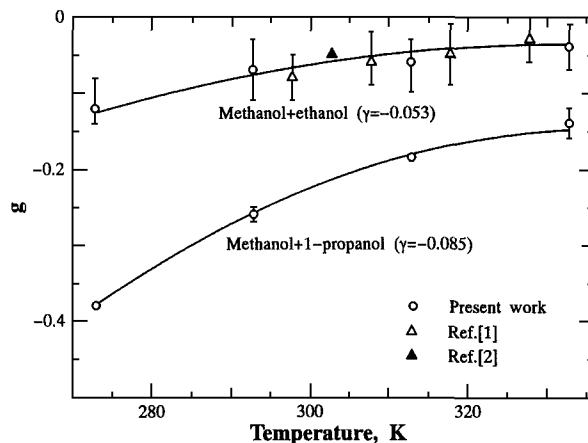


Fig. 6. Temperature dependence of the g parameter.

The curves in Figs. 4 and 5 show the excess viscosities evaluated using the Mertsch and Wolf equation with Eqs. (9) and (10) for the two mixtures, respectively. It was possible to reproduce the experimental viscosities as shown in Figs. 2 and 3 in terms of the Mertsch and Wolf equation with an average deviation of 0.8% and a maximum deviation of 2.1% for the two mixtures. To use the viscosity equation of Mertsch and Wolf as a predictive tool, one would need independent thermodynamic information for g or ΔG^R .

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