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Density, Viscosity, and Thermal Conductivity of Mixtures of 1-Ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (HFE 7200) with Methanol and 1-Ethoxybutane

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ABSTRACT: The density, viscosity, and thermal conductivity of 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (HFE 7200) + methanol and HFE 7200 + 1-ethoxybutane were measured at ambient conditions and correlated using a modified rough hard-sphere model. Rough hard-sphere parameters of pure HFE 7200 and pure 1-ethoxybutane were obtained by fitting measured values of their thermal conductivities at several temperatures. The rough hard-sphere model was able to reproduce the thermal conductivity and viscosity behavior of the HFE 7200 + 1-ethoxybutane system very well (average absolute deviations of about 2 %), but average deviations between calculated and experimental values were about 10 % in the case of the thermal conductivity and viscosity of HFE 7200 + methanol mixtures.

INTRODUCTION

1-Ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane ($C_4F_9OC_2H_5$ or HFE 7200) belongs to a class of Novec fluids that are widely used in industrial cleaning, lubricant deposition, and heat transfer applications.[1] The dielectric and inert nature of HFE 7200 makes it particularly suitable for electronic cooling, and its mixture formulations are being considered for thermal management systems in the electronics industry.[2,3] In the present work, we report measurements of the density, viscosity, and thermal conductivity of HFE 7200 + methanol and HFE 7200 + 1-ethoxybutane mixtures and develop rough hard-sphere (RHS) correlations for the transport properties of these systems. The data and correlations should prove useful in designing thermal management systems for electronics applications involving HFE 7200 and other dielectric coolants.

EXPERIMENTAL SECTION

HFE 7200 (mole fraction ≥ 0.99), methanol (mole fraction ≥ 0.999), and 1-ethoxybutane (mole fraction ≥ 0.98) were purchased from 3M, Fisher Scientific, and Fluka, respectively, and used without further purification.

Viscosities (η) were measured using a factory-calibrated size 25 Cannon-Fenske viscometer (Cannon Instrument Company, PA). The viscometer was calibrated using viscosity standard fluids I.50 and N1.0, and the maximum uncertainty in the viscosity was reported as 0.16 % for fluids having a kinematic viscosity less than $1 \cdot 10^{-5}$ m$^2 \cdot$s^{-1}. Our measured value of $0.913 \cdot 10^{-6}$ m$^2 \cdot$s^{-1} for the viscosity of deionized (DI) water[4] at 296.0 K agreed with the literature value[5] of $0.9122 \cdot 10^{-6}$ m$^2 \cdot$s^{-1} within the experimental uncertainty. Measurements of the viscosity of HFE 7200 + methanol mixtures are listed in Table 1, and those of HFE 7200 + 1-ethoxybutane mixtures are listed in Table 2. Each value represents an average of three measurements.

Densities (ρ) were measured using a pycnometer described elsewhere.[4] We have previously estimated the uncertainty in the measurements to be ± 1 kg$\cdot$m^{-3}. Our measured density of 996.1 kg$\cdot$m^{-3} for DI water at 295.0 K agreed with the literature value[5] of 997 kg$\cdot$m^{-3} within the stated uncertainty. Measured densities of HFE 7200 + methanol and HFE 7200 + 1-ethoxybutane mixtures are listed in Tables 1 and 2.

Table 1. Measured Properties of HFE 7200 + Methanol Mixtures at 297.8 K

	ρ	$\eta \cdot 10^3$	λ
methanol mass fraction	kg$\cdot$m^{-3}	Pa$\cdot$s	W$\cdot$m$^{-1}\cdot$K^{-1}
0.00	1417.0	0.6065	0.0662[a]
0.10	1357.0	0.6034	0.0729
0.20	1294.4	0.6802	0.0794
0.40	1058.4	0.6089	0.0948
0.60	946.5	0.5710	0.1108
0.80	852.6	0.5495	0.1326
1.00	791.8	0.5463	0.1999[a]

[a] Literature value.[5]

Thermal conductivities (λ) were measured using a transient hot-wire method that employed a mercury-filled glass capillary "wire" suspended in the liquid. The liquid was contained in a cell placed in a constant temperature fluidized sand bath (Techne model SBL-2D). Details of the apparatus and method can be found in our previously published papers.[6,7] Each thermal conductivity value listed in Tables 1 to 4 represents an average of five measurements with an estimated uncertainty of ± 2 % as discussed previously.[6,7]

Thermal conductivities of HFE 7200 + methanol mixtures are listed in Table 1 and of HFE 7200 + 1-ethoxybutane mixtures in

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Table 2. Measured Properties of HFE 7200 + 1-Ethoxybutane Mixtures at 298.2 K

	ρ	$\eta \cdot 10^3$	λ
1-ethoxybutane mass fraction	kg·m^{-3}	Pa·s	W·m^{-1}·K^{-1}
0.00	1417.0	0.6065	0.0662[a]
0.10	1293.4	0.5458	0.0664
0.20	1187.4	0.5042	0.0707
0.40	1024.9	0.4379	0.0774
0.60	907.4	0.4077	0.0921
0.80	813.7	0.3970	0.1085
1.00	743.0	0.3868	0.1258

[a] Literature value.[5]

Table 3. Thermal Conductivity of 1-Ethoxybutane

T	λ	
K	W·m^{-1}·K^{-1}	standard deviation in measurement
299.62	0.1250	0.00651
312.17	0.1229	0.00586
333.39	0.1017	0.00324
354.63	0.0949	0.00300

Table 4. Thermal Conductivity of HFE 7200

T	λ	
K	W·m^{-1}·K^{-1}	standard deviation in measurement
278.8	0.0712	0.0001
300.6	0.0644	0.0009
314.1	0.0616	0.0001
328.3	0.0590	0.0001
344.1	0.0563	0.0001

Table 2. Thermal conductivities of pure 1-ethoxybutane and pure HFE 7200 at several temperatures are listed in Tables 3 and 4, respectively. Thermal conductivity values reported in Tables 1, 2, and 4 were obtained using pure HFE 7200 and dimethylphthalate to calibrate our instrument. Thermal conductivities of HFE 7200 were obtained from the literature.[8,9] The thermal conductivity of 1-ethoxybutane was measured by us and differs by about 7 % from the values reported by Sakiadis and Coates[10] who used a steady-state method.

MODIFIED ROUGH HARD-SPHERE CORRELATION

The rough hard sphere expressions for the reduced viscosity (η^*) and reduced thermal conductivity (λ^*) as functions of the reduced molar volume ($V_r = V/V_0$) are as follows:[11−17]

$$\log(\eta^*/R_\eta) = 1.0945 - 9.26324V_r^{-1} + 71.0385V_r^{-2} - 301.9012V_r^{-3} + 797.69V_r^{-4} - 1221.977V_r^{-5} + 987.5574V_r^{-6} - 319.4636V_r^{-7} \quad (1)$$

$$\log(\lambda^*/R_\lambda) = 1.0655 - 3.538V_r^{-1} + 12.120V_r^{-2} - 12.469V_r^{-3} + 4.562V_r^{-4} \quad (2)$$

These equations were used to correlate the viscosity and thermal conductivity of *n*-alkanes, alkanols, aromatic hydrocarbons, and refrigerants, using empirical expressions for the parameters (V_0, R_η, and R_λ). Teja et al.[18,19] showed that the viscosity and thermal conductivity of 58 polar liquids could be correlated using eqs 1 and 2 if V_0, R_η, and R_λ are expressed as follows:

$$R_\eta = A_0 \quad (3)$$

$$V_0 = B_0 + B_1/T \quad (4)$$

$$R_\lambda = C_0 + C_1 T \quad (5)$$

The five coefficients (A_0, B_0, B_1, C_0, C_1) in eqs 3 to 5 were obtained by simultaneously fitting viscosity and thermal conductivity data for the 58 polar liquids. The liquids studied included diols, disulfides, amines, carboxylic acids, alcohol-ethers, pyridines, ethanolates, and polyethylene glycols. Transport properties of these 58 liquids were correlated within experimental error at temperatures between T = (293 to 423) K. The parameters were found to exhibit regular trends for series of diols, carboxylic acids, ethanolates, and polyethylene glycols. Recently, Sun and Teja[20] proposed further generalizations for the RHS parameters to correlate the viscosity and thermal conductivity of *n*-alkanes, 1-alkanols, alkanediols, benzene, toluene, and refrigerants.

Equations 1 and 2 can be extended to mixtures using mole fraction averaged mixture parameters[18] (V_0, R_η, and R_λ). These mixing rules have been shown to work well for thermal conductivity, although they were less satisfactory for viscosity.[18] Sun and Teja[21] incorporated binary interaction parameters in these mixing rules and were able to successfully correlate the thermal conductivity and viscosity of aqueous solutions of glycols. In the present work, we have used modified versions of their mixing rules as follows:

$$V_{0,\mathrm{mix}} = x_1^2 V_{0,1} + 2x_1x_2V_{0,12} + x_2^2V_{0,2} \quad (6)$$

$$V_{0,12} = \frac{(V_{0,1}^{1/3} + V_{0,2}^{1/3})^3}{8} \quad (7)$$

$$R_{\eta,\mathrm{mix}} = x_1^2 R_{\eta 1} + 2x_1x_2R_{\eta 12} + x_2^2R_{\eta 2} \quad (8)$$

$$R_{\eta 12} = (R_{\eta 1}R_{\eta 2})^{1/2}(1 - K_\eta) \quad (9)$$

$$R_{\lambda,\mathrm{mix}} = x_1^2 R_{\lambda 1} + 2x_1x_2R_{\lambda 12} + x_2^2R_{\lambda 2} \quad (10)$$

$$R_{\lambda 12} = (R_{\lambda 1}R_{\lambda 2})^{1/2}(1 - K_\lambda) \quad (11)$$

Here, K_η and K_λ are adjustable parameters that account for any nonlinear dependence of the viscosity and thermal conductivity, respectively.

RHS parameters for pure fluids required in eqs 6 to 11 were calculated from the density, viscosity, and thermal conductivity versus temperature data obtained from literature[5,8,9] or measured in this work. Literature correlations are given below:

Methanol[5]

$$\rho/\mathrm{kmol\cdot m^{-3}} = \frac{2.3267}{0.27073^{[1 + (1 - (T/\mathrm{K})/512.4)]^{0.24713}}} \quad (12)$$

$$\eta/\mathrm{Pa\cdot s} = \exp[-25.317 + 1789.2/(T/\mathrm{K}) + 2.069\ln(T/\mathrm{K})] \quad (13)$$

$$\lambda/\mathrm{W\cdot m^{-1}\cdot K^{-1}} = 0.2837 - 0.000281(T/\mathrm{K}) \quad (14)$$

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Table 5. Coefficients for the RHS Parameters for Pure Fluids[a]

	$B_0 \cdot 10^5$	$B_1 \cdot 10^3$	R_η	C_0	$C_1 \cdot 10^3$	AAD, η	AAD, λ
1-ethoxybutane	6.3041	6.4810	1.5151	3.4823	−3.4476	1.07	2.26
methanol	0.0326	5.9965	3.3976	−0.9370	7.9504	1.01	0.26
HFE 7200	4.9303	17.3975	2.3055	0.4939	7.8426	0.49	2.57

[a] AAD/% = $\Sigma_{i=1}^{N}|(\text{expt} - \text{calc})/\text{expt}| \cdot 100/N$.

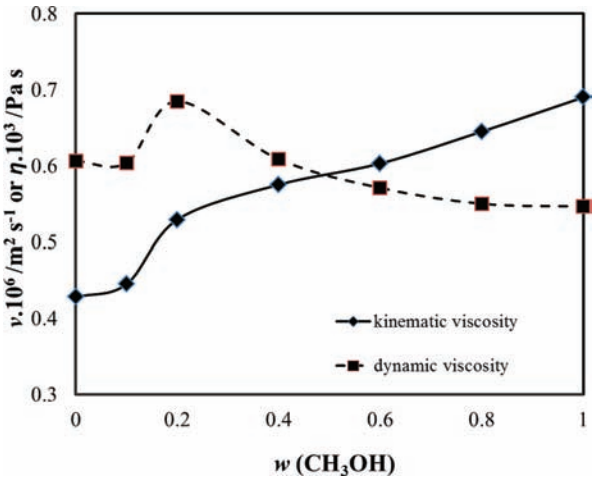

Figure 1. Kinematic viscosity (ν, solid line —) and dynamic viscosity (η, dashed line – –) of HFE 7200−methanol mixtures as a function of methanol mass fraction (w). The lines represent best fits of the data and are drawn to show the unusual behavior of the viscosity in this system.

Ethoxybutane[5]

$$\rho/\text{g}\cdot\text{cm}^{-3} = 0.26107/0.26506^{[1-(T/\text{K})/531]^{0.28570}} \quad (15)$$

$$\eta/\text{Pa}\cdot\text{s} = \exp[-25.317 + 1789.2/(T/\text{K}) + 2.069\ln(T/\text{K})] \quad (16)$$

HFE 7200[8,9]

$$\rho/\text{g}\cdot\text{cm}^{-3} = 1.4811 - 0.0023026[(T/\text{K}) - 273.15] \quad (17)$$

$$\eta/\text{cP} = -1.363\cdot10^{-5}(T/\text{K})^3 + 1.226\cdot10^{-2}(T/\text{K})^2 - 3.685(T/\text{K}) + 370.25 \quad (18)$$

RHS coefficients and regression statistics are presented in Table 5.

Mixture data were correlated using RHS parameters from Table 5 and mixing rules given in eqs 6 to 11. HFE 7200 + 1-ethoxybutane data could be correlated reasonably well without any adjustable parameters (K_λ and $K_\eta = 0$). Average absolute deviations between calculated and experimental values were 7.72 % for thermal conductivity and 4.55 % for viscosity. The deviations could be reduced to 1.46 % for thermal conductivity and 2.19 % in the case of viscosity using $K_\lambda = 0.1755$ and $K_\eta = 0.0937$ in the calculations. HFE 7200 + methanol mixtures, on the other hand, required the use of adjustable parameters to obtain reasonable fits of the data. This is not surprising because of the significant difference in polarities between the two compounds. Highly nonlinear viscosity−composition behavior has also been reported for

Table 6. RHS Correlations for HFE 7200−1-Ethoxybutane Mixtures

	$\lvert(\lambda_{\text{expt}} - \lambda_{\text{calc}}/\lambda_{\text{expt}})\rvert \cdot 100$		$\lvert(\eta_{\text{expt}} - \eta_{\text{calc}}/\eta_{\text{expt}})\rvert \cdot 100$	
1-ethoxybutane mass fraction	$K_\lambda = 0$	$K_\lambda = 0.1755$	$K_\eta = 0$	$K_\eta = 0.0937$
0.10	6.20	0.00	2.60	0.34
0.20	7.57	1.29	1.71	2.58
0.40	13.15	3.75	4.78	0.00
0.60	8.66	2.17	7.43	3.74
0.80	2.99	0.09	6.22	4.32
average	7.72	1.46	4.55	2.19

Table 7. RHS Correlations for HFE 7200−Methanol Mixtures

	$\lvert(\lambda_{\text{expt}} - \lambda_{\text{calc}}/\lambda_{\text{expt}})\rvert \cdot 100$		$\lvert(\eta_{\text{expt}} - \eta_{\text{calc}}/\eta_{\text{expt}})\rvert \cdot 100$	
methanol mass fraction	$K_\lambda = 0$	$K_\lambda = 0.3146$	$K_\eta = 0$	$K_\eta = -0.2451$
0.10	3.28	12.25	3.11	8.74
0.20	17.89	0.00	9.09	0.00
0.40	11.92	0.49	21.55	17.19
0.60	22.52	15.44	13.91	11.43
0.80	23.56	20.51	9.67	8.61
average	15.83	9.74	11.46	9.19

mixtures of methanol with toluene and benzene.[22] In addition, the dynamic and kinematic viscosities of HFE 7200 + methanol mixtures exhibit unusual behavior as can be seen in Figure 1. The sudden increase in viscosity at low mass fractions could be due to a change of phase, as has been observed in mixtures of methanol with hexane and cyclohexane.[23] We did not, however, observe phase separation in HFE 7200 + methanol mixtures at 298 ± 2 K over a period of one week. Assuming no phase separation, average absolute deviations between calculated and experimental were 15.83 % in the case of thermal conductivity and 11.46 % in the case of without the use of adjustable parameters. The best fit was obtained with $K_\lambda = 0.3146$ and $K_\eta = -0.2451$ as shown in Tables 6 and 7. However, average absolute deviations were still about 10 %, suggesting that further investigation of phase separation in this system may be warranted.

SUMMARY

The density, viscosity, and thermal conductivity of HFE 7200 + methanol and HFE 7200 + 1-ethoxybutane mixtures were measured at 298 K, and the data were correlated using a modified rough hard-sphere theory. HFE 7200 + 1-ethoxybutane mixtures could be correlated reasonably well without the use of adjustable parameters. However, adjustable parameters were required to

correlate the highly nonlinear behavior of the viscosity of HFE 7200 + methanol mixtures. Even with the use of adjustable parameters, average absolute deviations between calculated and experimental thermal conductivities and viscosities were of the order of 10 % for HFE 7200 + methanol mixtures.

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