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Density, Viscosity, and Surface Tension of Liquid Quinoline, Naphthalene, Biphenyl, Decafluorobiphenyl, and 1,2-Diphenylbenzene from 300 to 400 °C

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The liquid density, liquid viscosity, and surface tension of quinoline, naphthalene, biphenyl, decafluorobiphenyl, and 1,2-diphenylbenzene were measured at saturation between 300 and 400 °C. The results were fit to temperature-dependent correlations. The critical temperature of decafluorobiphenyl was also determined.

Introduction

The compounds quinoline, naphthalene, biphenyl, decafluorobiphenyl, and 1,2-diphenylbenzene have been recently investigated as two-phase heat transport fluids for aerospace thermal control applications between 300 and 400 °C (Grzyll, 1991, and Grzyll et al., 1994). These compounds are attractive for these applications because of their high resistance to pyrolysis and their low volatility. In order to design two-phase thermal control components that use these fluids, the density, viscosity, surface tension, and other thermodynamic properties (Back et al., 1996) of these compounds had to be determined in the temperature range of interest. We report here new experimental measurements of the liquid density, liquid viscosity, and surface tension at saturation conditions using techniques that allow for measurement above and below the normal boiling point of the fluid. We also determined the critical temperature of decafluorobiphenyl.

Materials

The materials evaluated in this study were: quinoline (Aldrich, 99%, RN 91-22-5), naphthalene (Aldrich, 99%, RN 91-20-3), biphenyl (Aldrich, 99%, RN 92-52-4), decafluorobiphenyl (Ryan Scientific, 99%, RN 434-90-2), and 1,2-diphenylbenzene (Aldrich, 99%, RN 84-15-1). All materials as received were further purified by fractional distillation at Mainstream. No purity determination was made on the final samples.

Apparatus and Procedures

An agitated constant temperature bath and temperature control system was used for the experimental measurements. The bath was a 12 in. o.d. × 12 in. high Pyrex jar surrounded with ceramic insulation and contained in an aluminum housing having two 3 in. × 8.5 in. openings for visual inspection of the bath interior. The bath fluid was Tempering A heat transfer salt (Heatbath Corp.). The bath was heated by four 1500 W cartridge heaters (Whatlow Electric) and agitated with a mechanical stirrer. Temperature measurements were made using a type-K thermocouple, and the bath was controlled using a PID controller (Whatlow Electric) having a temperature accuracy of ±0.1% of the set point (±0.67 K at 673 K).

The critical temperature of decafluorobiphenyl was determined by the observation of appearance and disappearance of the meniscus of the fluid contained in a heavy walled, sealed glass tube immersed in the constant temperature bath. The glass tube was loaded with fluid, freeze−thawed under vacuum, and sealed. The tube was carefully loaded so that just below the critical temperature approximately equal volumes of liquid and vapor coexisted. The sample was heated and cooled and passed through the critical temperature to detect the appearance and disappearance of the meniscus.

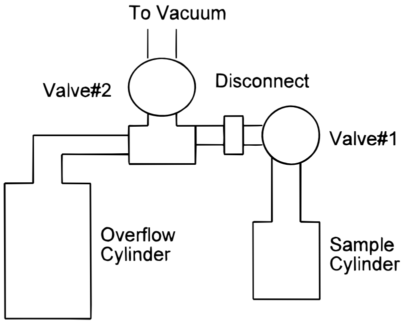

Figure 1. Schematic of liquid density apparatus.

The liquid density measurements were performed using a modified pycnometric technique. A schematic of the experimental apparatus is given in Figure 1. A stainless steel constant-volume sample cylinder is initially disconnected from the apparatus and filled completely in the liquid phase with the compound to be measured. The filled sample cylinder is then reconnected to the apparatus, valve 1 is opened, and the system is freeze−thawed under vacuum. The sample cylinder is then pressurized with nitrogen just above the vapor pressure of the fluid at the test temperature to suppress vaporization, and valve 2 is closed (the effect of nitrogen on the fluid density was neglected). The system is then immersed completely in the constant temperature bath and allowed to reach thermal equilibrium. Since the temperature at which the liquid density measurement will take place is greater than the temperature at which the sample cylinder was filled, an overflow cylinder is present to provide the necessary volume for the fluid expansion at the elevated temperature. After reaching thermal equilibrium, valve no. 1 is closed and the system is removed from the constant temperature bath. The sample cylinder is then cooled, cleaned of excess fluid at the disconnect, and weighed (±0.000 05 g) to determine the mass of the compound in the constant volume sample cylinder. Duplicate measurements for each temperature were made. The density of the liquid is determined by dividing the mass of fluid in the constant volume sample cylinder by the volume of the cylinder.

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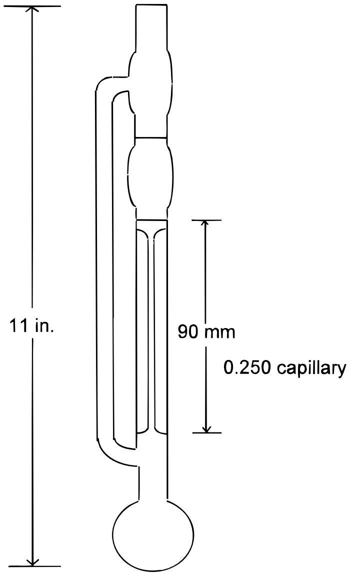

Figure 2. Schematic of viscometer.

The volume of the constant volume cylinder was determined at (30 ± 0.1) °C with deionized water in a constant temperature bath. Due to the significant difference in the measurement temperature compared to the calibration temperature (ranging from 231 to 371 K), a correction for expansion of the constant volume cylinder was included. This correction is

$$V = V_0(1 + \alpha)^3 \tag{1}$$

$$\alpha = \alpha_o \Delta T \tag{2}$$

where α_o is the thermal expansion coefficient of the sample cylinder (1.7×10^{-5} K^{-1}), V_o is the volume of the constant volume cylinder at the calibration temperature, V is the volume of the constant volume cylinder at the test temperature, and ΔT is the test temperature minus the calibration temperature. The magnitude of the correction was from 0.39% to 0.63% of the cylinder volume.

The liquid kinematic viscosity was measured using a closed, modified Cannon−Fenske, capillary glass viscometer (see Figure 2). This method has been used by others (Phillips and Murphy, 1970, and Burns et al., 1958) and is a modification of an ASTM method. Each viscometer was calibrated at (40 ± 0.1) °C using Cannon viscosity standard N1.0. The working equation for this type of viscometer includes a correction for regions where the vapor density becomes significant and may buoy up the liquid (Manning, 1993). The working equation is

$$\upsilon = \mathrm{C}(1.0 - \rho_v/\rho_l)t \tag{3}$$

where ρ is the kinematic viscosity, C is the viscometer constant, ρ_l is the liquid density, ρ_v is the vapor density, and t is the flow time.

The viscometer was filled with molten working fluid, freeze−thawed under vacuum to remove noncondensables, evacuated, and sealed with a torch so that the fluid was at its vapor pressure at all times (no air is in the viscometer). A stopwatch was used to determine the flow time in the viscometer (±0.005 s). Once the apparatus was filled and sealed, it was fastened to its holding fixture and immersed in the lab bath where it was allowed to reach thermal equilibrium at the test temperature. The viscometer holding fixture was then used to invert the viscometer, which allowed liquid to flow into the upper portion above the top timing mark. The viscometer was then re-inverted to its initial position, and the flow time was recorded. This procedure was repeated three times for each temperature, and the average flow time was calculated. Liquid density was calculated using the experimental data fit to a polynomial, and vapor density was calculated using a corresponding states equation of state (Lee and Kesler, 1975). Absolute viscosity was determined by multiplying the kinematic viscosity by the liquid density.

The surface tension was measured using the differential capillary rise technique in a closed glass vessel. This technique has been used on recent alternative refrigerant characterizations (Chae et al., 1990). In this method, surface tension is determined directly from the capillary length parameter through

$$\sigma = \alpha^2(\rho_l - \rho_v)g/2 \tag{4}$$

where σ is the surface tension, α is the capillary length parameter, ρ_l is the liquid density, ρ_v is the vapor density, and g is the acceleration due to gravity.

The capillary length parameter is determined by measuring the differential height of the liquid menisci in two different capillaries with larger and smaller radii, r_L and r_S, respectively. Determination of the capillary length parameter is an iterative process using polynomial functions (Lane, 1973). The first approximation (α_1) to the capillary length parameter α is

$$\alpha_1^{\,2} = \Delta h r_S \tag{5}$$

where Δh is the differential height (mm) and r_S is the smaller radii.

This first approximation of the capillary length parameter is then used to determine the capillary rise in the larger tube h_L

$$h_L = \frac{\alpha_i^{\,2}}{r_L}\frac{1}{F(r_L/\alpha_i)} \qquad \text{for } \frac{r_L}{\alpha_i} < 2$$

$$h_L = \frac{\alpha_i^{\,2}}{r_L}\Phi(r_L/\alpha_i) \qquad \text{for } \frac{r_L}{\alpha_i} > 2 \tag{6}$$

where α_i is the capillary length parameter for the ith iteration ($i = 1$ for the first approximation), r_L is the larger radii, and

$$F\left(X = \frac{r}{\alpha}\right) = 1 + a_2X^2 + a_3X^3 - a_4X^4 + a_5X^5 - a_6X^6 + a_7X^7 - a_8X^8 \tag{7}$$

$$\Phi\left(X = \frac{r}{\alpha}\right) = X^{3/2}\exp(b_1X + b_2 - b_3X^{-1} + b_4X^{-2}) \tag{8}$$

This value of h_L is then used to obtain a better estimate of α^2

$$\alpha_i^{\,2} = r_S(h_L + \Delta h)F(r_S/\alpha_i) \qquad \text{for } \frac{r_S}{\alpha_i} < 2$$

$$\alpha_i^{\,2} = r_S(h_L + \Delta h)\frac{1}{\Phi(r_S/\alpha_i)} \qquad \text{for } \frac{r_S}{\alpha_i} > 2 \tag{9}$$

This procedure is iterated until the solution converges. The final value of α^2 is then used to determine σ. A computer program was used to perform the calculation of α^2.

The differential height of the fluids was measured with a capillary glass apparatus consisting of three capillary tubes of different radii: 0.276, 0.320, and 0.574 mm (Tudor

biphenyl	$\rho/\mathrm{g{\cdot}cm^{-3}} = 1.721 - 0.002051(T/\mathrm{K}) + 7.395e^{-7}(T/\mathrm{K})^2$	$574.15 < T/\mathrm{K} < 673.15$	
naphthalene	$\rho/\mathrm{g{\cdot}cm^{-3}} = -0.7018 + 0.00591(T/\mathrm{K}) - 5.842e^{-6}(T/\mathrm{K})^2$	$574.15 < T/\mathrm{K} < 674.15$	
quinoline	$\rho/\mathrm{g{\cdot}cm^{-3}} = 2.755 - 0.004885(T/\mathrm{K}) + 2.739e^{-6}(T/\mathrm{K})^2$	$574.15 < T/\mathrm{K} < 674.15$	(10)
o-terphenyl	$\rho/\mathrm{g{\cdot}cm^{-3}} = -0.1711 + 0.003956(T/\mathrm{K}) - 3.833e^{-6}(T/\mathrm{K})^2$	$574.15 < T/\mathrm{K} < 673.15$	
decafluorobiphenyl	$\rho/\mathrm{g{\cdot}cm^{-3}} = -1.480 + 0.01248(T/\mathrm{K}) - 1.383e^{-5}(T/\mathrm{K})^2$	$534.15 < T/\mathrm{K} < 614.15$	
naphthalene	$\ln(\eta/\mathrm{mPa{\cdot}s}) = -6.220 + 2663.3/(T/\mathrm{K})$	$574.15 < T/\mathrm{K} < 673.15$	
biphenyl	$\ln(\eta/\mathrm{mPa{\cdot}s}) = -6.120 + 2.772.6/(T/\mathrm{K})$	$574.15 < T/\mathrm{K} < 673.15$	
o-terphenyl	$\ln(\eta/\mathrm{mPa{\cdot}s}) = -4.534 + 2010.5/(T/\mathrm{K})$	$574.15 < T/\mathrm{K} < 673.15$	(11)
quinoline	$\ln(\eta/\mathrm{mPa{\cdot}s}) = -5.486 + 2296.4(T/\mathrm{K})$	$574.15 < T/\mathrm{K} < 674.15$	
decafluorobiphenyl	$\ln(\eta/\mathrm{mPa{\cdot}s}) = -5.616 + 2279.0/(T/\mathrm{K})$	$524.15 < T/\mathrm{K} < 594.15$	
biphenyl	$\sigma/(\mathrm{N{\cdot}m^{-1}}) = 0.05611(1 - T_\mathrm{r})^{1.14}$	$573.15 < T/\mathrm{K} < 673.15$	
o-terphenyl	$\sigma/(\mathrm{N{\cdot}m^{-1}}) = 0.07577(1 - T_\mathrm{r})^{1.43}$	$574.15 < T/\mathrm{K} < 673.15$	
naphthalene	$\sigma/(\mathrm{N{\cdot}m^{-1}}) = 0.06866(1 - T_\mathrm{r})^{1.15}$	$574.15 < T/\mathrm{K} < 673.15$	(12)
quinoline	$\sigma/(\mathrm{N{\cdot}m^{-1}}) = 0.08698(1 - T_\mathrm{r})^{1.32}$	$574.15 < T/\mathrm{K} < 673.15$	
decafluorobiphenyl	$\sigma/(\mathrm{N{\cdot}m^{-1}}) = 0.06494(1 - T_\mathrm{r})^{1.3_9}$	$524.15 < T/\mathrm{K} < 594.15$	

Table 1. Liquid Density Measurements

T/°C	exptl $\varrho_\mathrm{l}/\mathrm{g{\cdot}cm^{-3}}$	curve fit $\varrho_\mathrm{l}/\mathrm{g{\cdot}cm^{-3}}$	curve fit % error
	Biphenyl		
301	0.788	0.787	0.032
311	0.777	0.775	0.149
321	0.767	0.764	0.380
331	0.748	0.752	0.500
341	0.737	0.740	0.428
351	0.726	0.729	0.400
361	0.719	0.718	0.166
371	0.710	0.707	0.444
381	0.701	0.696	0.724
400	0.672	0.676	0.565
	Naphthalene		
301	0.768	0.766	0.260
321	0.744	0.747	0.415
341	0.723	0.724	0.153
361	0.699	0.697	0.289
380	0.668	0.666	0.252
401	0.626	0.627	0.235
	Quinoline		
301	0.848	0.853	0.569
321	0.829	0.819	1.187
341	0.784	0.788	0.407
361	0.758	0.758	0.025
381	0.727	0.731	0.632
401	0.709	0.706	0.446
	1,2-Diphenylbenzene		
301	0.838	0.836	0.133
321	0.823	0.826	0.331
341	0.814	0.812	0.213
361	0.796	0.796	0.011
381	0.776	0.776	0.003
400	0.754	0.755	0.029
	Decafluorobiphenyl		
261	1.24	1.239	0.068
281	1.19	1.188	0.026
301	1.12	1.125	0.364
321	1.06	1.052	0.549
341	0.96	0.967	0.228

Scientific Glass). This apparatus is shown in Figure 3. The apparatus was filled with fluid, freeze−thawed under vacuum, evacuated, and sealed with a torch so that the fluid is at its own vapor pressure at all times. Therefore, the surface tension determined was the liquid/vapor interfacial tension of the fluid (no air is in the apparatus). The laboratory bath described above was used with an appropriate fixture to hold the apparatus. A cathetometer was used to measure Δh (±0.013 mm).

Once the apparatus was filled and sealed, it was immersed in the bath and allowed to reach thermal equilibrium at the temperature. The differential height between each of the capillaries was then measured with the cathetometer and the computer program was run to determine the capillary length parameter.

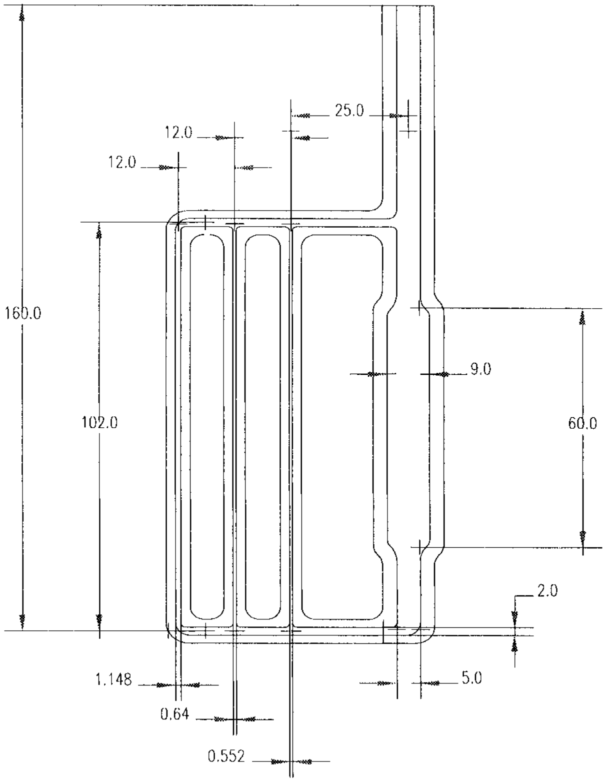

Figure 3. Schematic of surface tension apparatus.

Table 2. Comparison of Measured Density with Literature

T/°C	exptl $\varrho_\mathrm{l}/\mathrm{g{\cdot}cm^{-3}}$	curve fit $\varrho_\mathrm{l}/\mathrm{g{\cdot}cm^{-3}}$	Montillon et al. $\varrho_\mathrm{l}/\mathrm{g{\cdot}cm^{-3}}$
311	0.777	0.775	
315.6		0.770	0.785 545
321	0.767	0.764	
341	0.737	0.740	
343.3		0.738	0.757 673
351	0.726	0.729	
371	0.710	0.707	
371.1		0.707	0.726 918
381	0.701	0.696	
398.9		0.677	0.693 279
400	0.672	0.676	

Results

The critical temperature of decafluorobiphenyl was determined to be (367 ± 1) °C by the repeated appearance and disappearance of the meniscus as the fluid passed through this temperature. No evidence of thermal decomposition was seen.

The average measured liquid densities are given in Table 1. The uncertainty in the density measurements was determined to be ±0.001 g·cm^{-3}. Table 2 compares the

Table 3. Liquid Viscosity Measurements

	exptl		curve fit	
T/°C	$10^6\nu^2$·s^{-1}	μ/mPa·s	μ/mPa·s	% error
		Naphthalene		
301	0.266	0.204	0.206	0.961
311	0.251	0.190	0.190	0.144
321	0.236	0.177	0.176	0.380
331	0.221	0.163	0.163	0.340
341	0.210	0.152	0.152	0.093
351	0.200	0.142	0.142	0.422
361	0.192	0.134	0.133	0.771
371	0.182	0.124	0.124	0.169
381	0.176	0.117	0.117	0.380
391	0.169	0.109	0.110	0.500
400	0.162	0.102	0.104	2.19
		Biphenyl		
301	0.359	0.282	0.275	2.64
311	0.336	0.261	0.253	2.82
321	0.301	0.230	0.234	1.60
331	0.286	0.215	0.216	0.671
341	0.268	0.199	0.201	1.10
351	0.256	0.187	0.187	0.122
361	0.240	0.172	0.174	1.07
371	0.224	0.158	0.163	2.91
381	0.217	0.151	0.152	0.971
391	0.207	0.142	0.143	0.935
400	0.198	0.134	0.135	0.999
		1,2-Diphenylbenzene		
301	0.426	0.357	0.356	0.162
311	0.408	0.339	0.335	1.15
321	0.389	0.321	0.317	1.42
331	0.367	0.301	0.299	0.477
341	0.349	0.284	0.284	0.003
351	0.333	0.268	0.269	0.521
361	0.316	0.251	0.256	1.71
371	0.307	0.242	0.243	0.703
381	0.294	0.229	0.232	1.57
391	0.288	0.220	0.222	0.612
400	0.278	0.210	0.213	1.55
		Quinoline		
301	0.264	0.225	0.216	0.402
311	0.253	0.212	0.211	0.254
321	0.243	0.199	0.198	0.567
331	0.232	0.187	0.185	0.616
341	0.222	0.175	0.174	0.264
351	0.213	0.164	0.164	0.180
361	0.205	0.155	0.155	0.277
371	0.196	0.146	0.146	0.205
380	0.190	0.139	0.139	0.003
391	0.183	0.132	0.132	0.143
401	0.177	0.125	0.125	0.204
		Decafluorobiphenyl		
251	0.229	0.289	0.282	2.54
261	0.216	0.267	0.260	2.94
271	0.202	0.146	0.240	2.51
281	0.184	0.219	0.223	1.67
291	0.175	0.203	0.207	1.70
301	0.166	0.187	0.193	3.32
311	0.151	0.164	0.180	9.60

Table 4. Surface Tension Measurements

		curve fit	
T/°C	exptl $10^3\sigma$/N·m^{-1}	$10^3\sigma$/N·m^{-1}	% error
	Biphenyl		
300	12.9	12.8	0.869
310	12.2	12.1	0.243
321	11.6	11.4	1.67
331	10.6	10.7	0.941
341	10.0	10.1	0.666
351	9.14	9.42	2.98
361	8.70	8.77	0.757
371	8.10	8.12	0.366
381	7.60	7.49	1.46
391	6.96	6.86	1.45
400	6.42	6.30	1.96
	1,2-Diphenylbenzene		
301	17.3	17.3	0.001
310	16.7	16.6	0.721
321	15.9	15.7	1.17
331	15.2	15.0	1.41
341	14.3	14.2	0.337
351	13.6	13.5	0.521
361	12.9	12.8	1.07
371	12.1	12.1	0.003
381	11.5	11.4	0.612
391	10.8	10.7	0.653
400	10.2	10.1	1.10
	Naphthalene		
301	12.9	12.9	0.184
311	12.0	12.1	0.351
321	11.2	11.2	0.423
331	10.2	10.4	1.565
341	9.43	9.57	1.543
351	8.78	8.76	0.262
361	7.94	7.96	0.264
371	7.10	7.16	0.964
380	6.41	6.46	0.814
390	5.64	5.69	0.812
400	4.92	4.93	0.330
	Decafluorobiphenyl		
251	5.99	6.06	1.27
261	5.49	5.35	2.45
271	4.70	4.66	0.809
281	4.06	4.01	1.33
291	3.18	3.38	6.11
301	2.79	2.78	0.419
311	2.44	2.21	9.35
321	1.54	1.69	9.27
	Quinoline		
301	15.5	15.2	1.75
311	14.4	14.3	0.669
321	13.2	13.3	1.01
331	12.3	12.4	0.889
341	11.3	11.5	1.61
351	10.4	10.6	1.64
361	9.67	9.73	0.536
371	8.86	8.87	0.139
381	8.12	8.03	1.02
391	7.20	7.22	0.209
400	6.81	6.50	4.44

measured density of biphenyl from this work to literature values (Montillon et al., 1931). The data were then fit to a second-order polynomial (eq 10) (Chart 1) to account for the variation of liquid density with temperature. Table 1 also provides a comparison of the measured data to the calculated values using eq 10.

The kinematic viscosities and the absolute viscosities are given in Table 3. The uncertainty in the absolute viscosity was determined to be ±0.0053 mPa·s. The absolute viscosities were then fit to eq 11 (Chart 1) to account for the variation in liquid viscosity with temperature. Table 3also provides a comparison of the measured data to the calculated values using eq 11.

The surface tensions of the fluids are presented in Table 4. The uncertainty in the surface tension measurements was determined to be $\pm 3.42 \times 10^{-4}$ N·m^{-1}. The surface tension data were then fit to eq 12 (Chart 1) which accounts for the variation of surface tension with temperature, where T_r is the reduced temperature ($=T/T_c$) (Reid et al., 1987). Table 4 also provides a comparison of the measured data to the calculated values using eq 12.

Conclusions

The liquid density, liquid viscosity, and surface tension of quinoline, naphthalene, biphenyl, decafluorobiphenyl, and 1,2-diphenylbenzene were measured at saturation conditions from 300 to 400 °C. The critical temperature of decafluorobiphenyl was also determined. A review of the technical literature showed that much of the data presented here had not been determined over this temperature range for the fluids considered. The experimental data will be valuable in the design of two-phase thermal control systems in the 300 to 400 °C temperature range using these heat transport fluids.

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