Density of Heptacosafluorotributylamine from 303 to 333 K

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During an investigation of the surface tension of liquid mixtures containing heptacosafluorotributylamine, $(C_4F_9)_3N$, a need arose for the density d of the substance at temperatures t between 30 and 60 °C. A pycnometric study was therefore carried out with the results shown in Table I. Koch-Light Laboratories Ltd. supplied the material which was shown, by vapor phase chromatography, to contain only perfluorinated impurities below the 1 mol % level after drying. The temperature was measured using a calibrated platinum resistance thermometer to within ±5 mK. The density values are believed to be accurate to within 0.0006 g cm^{-3}. The data are well represented over this modest range of temperature by the linear equation:

Table I. Densities of Heptacosafluorotributylamine at Different Temperatures

t/°C	d/g cm^{-3}	t/°C	d/g cm^{-3}
29.8	1.874_1	49.0	1.830_5
34.0	1.863_1	54.0	1.819_6
39.0	1.852_3	59.9	1.808_7
44.9	1.841_4		

$$d/\mathrm{g\ cm^{-3}} = 1.9379 - 0.002\,17(t/^\circ\mathrm{C}) \qquad (1)$$

The only literature value for the density of $(C_4F_9)_3N$ is 1.8839 g cm^{-3} at 25 °C (*1*); our extrapolated value using eq 1 is 1.8837 g cm^{-3}.

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Some Physical Properties of Ten Alkanethiols as a Function of Temperature

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Dielectric constants, densities, refractive indices, and viscosities of ten alkanethiols were measured in the temperature range 0–60 °C. The experimental data for density, dielectric constant, and viscosity as a function of temperature were fitted to appropriate equations. The Kirkwood correlation factor (g) and the activation energy for viscous flow (ΔF_η) were calculated using the experimentally measured data. The value of g has been found to vary between 0.88 and 1.2 for these compounds and it decreases with decreasing temperature indicating antiparallel arrangement of dipoles at lower temperature. The value of activation energy for viscous flow (ΔF_η) increases with increasing chain length of the alkanethiols.

Physical properties of alkanethiols (RSH) are of interest as they are similar in structure to alcohols (ROH), which have been extensively studied in order to investigate the effect of hydrogen bonding. Krishnaji et al. (*6–8*) have studied dielectric relaxation behavior of alkanethiols and found that the hydrogen bonding is almost absent or too small to be detected by dielectric measurements in these compounds. The present study was undertaken to measure low frequency dielectric constants, viscosities, densities, and refractive indices of ten alkanethiols, namely, propane-1-thiol, butane-1-thiol, butane-2-thiol, 2-methylpropane-2-thiol, pentane-1-thiol, 2-methylbutane-2-thiol, hexane-1-thiol, heptane-1-thiol, octane-1-thiol, and 2-methyloctane-2-thiol in the temperature range 0–60 °C. The Kirkwood correlation factor (g) and activation energy of viscous flow (ΔF_η) were calculated using these data. The variation of these parameters with temperature and structure of alkanethiols will help understand molecular arrangement and their motion in the liquid state.

Experimental Section

The alkanethiols (97–98%) were procured from M/S Fluka AG, Switzerland, and were fractionally distilled before use. The values of refractive index reported in literature (*10*) are about 0.3% higher than measured values except for propane-1-thiol and butane-2-thiol. This may be due to hydrocarbon contamination.

The static value of dielectric constant (ϵ) was measured at 100 kHz using hetrodyne beat apparatus. A silver-plated cylindrical cell for the measurement of capacitance was used, which was calibrated with dry benzene and carbon tetrachloride (AR grade). The accuracy of measurement of ϵ was 0.5%.

Viscosities were measured by Ostwald viscometer which was calibrated with the help of doubly distilled water. The accuracy of measurement was 0.5%. Refractive indices were measured using Abbe's refractometer and the accuracy of measurement was 0.1%. Densities were measured by pycnometer which was calibrated with doubly distilled water at 30 °C. The accuracy of measurement was 0.1%.

The temperature of the sample was controlled within ±0.5 °C by circulating water from a temperature-controlled bath.

Results and Discussion

Table I contains the experimentally measured values of density, viscosity, dielectric constant, and refractive index for these alkanethiols at different temperatures. The experimental data for density, dielectric constant, and viscosity as functions of temperature were fitted to the following equations 1 through 3 by least-squares analysis performed with the help of an IBM 360 computer

$$\rho = a + bt + ct^2 \tag{1}$$

$$\epsilon = A + B/T + C/T^2 \tag{2}$$

$$\eta = e^{(\alpha + \beta/T + \gamma/T^2 + \delta/T^3)} \tag{3}$$

The values of various constants (a, b, c, A, B, C, α, β, γ, and δ) and the average and the maximum deviations between experimental and calculated values are given in Tables II–IV. The deviations are nearly of the same order of magnitude as the experimental error. Casteel and Sears (*2*) have also used these equations to fit their experimental data for sulfones and sulfoxides.

The Kirkwood–Frohlich equation (*4, 5*) in the form

$$g = \frac{[(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)9MKT]}{[\epsilon(2 + \epsilon_\infty)^2 4\pi N\rho\mu^2]} \tag{4}$$

has been used to calculate the correlation factor (g), which gives an indication of the type of dipole–dipole alignment taking place. Positive deviations of g from unity result when short range hindering torque favors parallel orientation of the dipoles of the neighboring molecules, and negative deviations result when the hindering torque favors antiparallel orientation. If the values of g are nearly equal to unity, the compound is nonassociative and the intermolecular forces are random. The values of g are given in Table V. These values have been calculated using values of dipole moment measured in dilute solution of benzene (*1, 9*). There is only slight deviation in the value of g from unity, which further supports the earlier results that these compounds are nonassociative (*6–8*). For all the compounds studied, g decreases with the decrease in temperature indicating antiparallel arrangement of the dipoles at lower temperature.

The free energy of activation (ΔF_η) of viscous flow has been calculated using Eyring rate equation (3):

$$\eta = \left(\frac{Nh}{V}\right) e^{\Delta F_\eta/RT} \tag{5}$$

The values of ΔF_η for the different compounds are given in Table V.

The graph between ΔF_η vs. number of carbon atoms in alkanethiols at 30 °C (Figure 1) indicates that the free energy of activation for viscous flow increases with the increase in chain length.

Table I. Experimental Values of Viscosity, Density, Dielectric Constant (100 kHz), and Refractive Index

Temp, °C	Viscosity, cP	Density, g cm^{-3}	Temp, °C	Dielectric constant, 100 kHz	Refractive index
Propane-1-thiol					
10	0.517	0.850	0	6.260	1.448
20	0.468	0.840	15	5.934	1.439
30	0.423	0.829	30	5.685	1.431
40	0.392	0.819	45	5.365	1.423
50	0.353	0.808			
60					
Butane-1-thiol					
10	0.597	0.850	0	5.538	1.450
20	0.535	0.841	20	5.204	1.439
30	0.479	0.831	40	4.900	1.428
40	0.440	0.821	60	4.601	1.418
50	0.394	0.812			
60	0.355	0.802			
Butane-2-thiol					
10	0.570	0.838	0	5.978	1.445
20	0.509	0.828	15	5.645	1.436
30	0.457	0.819	30	5.400	1.427
40	0.419	0.809	45	5.160	1.419
50	0.376	0.799			
60					
2-Methylpropane-2-thiol					
10	0.744	0.810	10	5.629	1.425
20	0.629	0.799	20	5.475	1.419
30	0.538	0.789	30	5.309	1.414
40	0.475	0.778	40	5.101	1.407
Pentane-1-thiol					
10	0.725	0.850	0	5.052	1.454
20	0.639	0.840	20	4.847	1.444
30	0.564	0.829	40	4.539	1.433
40	0.511	0.819	60	4.293	1.423
50	0.453	0.808			
60	0.405				
2-Methylbutane-2-thiol					
10	0.772	0.833	0	5.463	1.445
20	0.665	0.824	20	5.087	1.435
30	0.575	0.814	40	4.754	1.424
40	0.515	0.805	60	4.468	1.413
50	0.452	0.796			
60	0.399	0.786			
Hexane-1-thiol					
10	0.898	0.850	0	4.711	1.455
20	0.773	0.842	20	4.436	1.446
30	0.672	0.834	40	4.203	1.436
40	0.599	0.826	60	3.995	1.427
50	0.524	0.817			
60	0.463	0.809			
Heptane-1-thiol					
10	1.135	0.850	0	4.374	1.458
20	0.955	0.843	20	4.194	1.448
30	0.815	0.836	40	3.941	1.439
40	0.713	0.828	60	3.759	1.430
50	0.616	0.820			
60	0.536	0.811			
Octane-1-thiol					
10	1.447	0.850	0	4.105	1.458
20	1.184	0.842	20	3.949	1.450
30	0.987	0.834	40	3.798	1.441
40	0.851	0.827	60	3.645	1.433
50		0.819			
60	0.625	0.811			
2-Methyloctane-2-thiol					
10	1.616	0.854	0	4.272	1.462
20	1.308	0.846	20	4.069	1.453
30	1.070	0.838	40	3.922	1.444
40	0.914	0.830	60	3.708	1.435
50	0.767	0.823			
60		0.815			

Table II. Results for Density Data Fitted to Equation 1

Compound	a	$-b \times 10^3$	$-c \times 10^6$	% deviation $\times 10^3$ [a]	
				Mean	Max
Propane-1-thiol	0.860 20	0.010 07	0.714 29	22	41
Butane-1-thiol	0.859 70	0.950 36	0.178 57	26	48
Butane-2-thiol	0.847 21	0.927 14	0.714 29	21	45
2-Methylpropane-2-thiol	0.820 49	0.010 59	0.015 43	25	38
Pentane-1-thiol	0.860 20	0.010 07	0.714 29	22	41
2-Methylbutane-2-thiol	0.842 30	0.924 64	0.178 57	26	49
Hexane-1-thiol	0.857 80	0.772 86	0.714 29	17	45
Heptane-1-thiol	0.856 20	0.602 14	0.025 00	33	137
Octane-1-thiol	0.857 60	0.774 53	0.003 27	90	433
2-Methyloctane-2-thiol	0.862 20	0.827 14	−0.714 29	17	45

[a] % deviation = $100|\rho_{\text{exptl}} - \rho_{\text{calcd}}|/\rho_{\text{exptl}}$.

Table III. Results for Dielectric Constant Data Fitted to Equation 2

Compound	$-A$	$B \times 10^{-4}$	$-C \times 10^{-6}$	% deviation $\times 10^2$ [a]	
				Mean	Max
Propane-1-thiol	5.312 37	0.483 01	0.456 50	26	42
Butane-1-thiol	2.295 82	0.301 98	0.240 63	5	8
Butane-2-thiol	−4.889 10	−0.117 20	0.400 96	13	21
2-Methylpropane-2-thiol	16.898 60	1.171 31	1.510 73	7	11
Pentane-1-thiol	5.816 65	0.515 96	0.598 07	32	52
2-Methylbutane-2-thiol	−0.032 40	0.144 99	0.008 95	3	4
Hexane-1-thiol	−0.994 16	0.093 07	−0.022 89	2	4
Heptane-1-thiol	2.700 74	0.312 85	0.326 39	34	56
Octane-1-thiol	−0.559 88	0.197 84	−0.192 48	3	4
2-Methyloctane-2-thiol	−0.190 59	0.272 23	−0.283 14	32	52

[a] % deviation = $100|\epsilon_{\text{exptl}} - \epsilon_{\text{calcd}}|/\epsilon_{\text{exptl}}$.

Table IV. Results for Viscosity Data Fitted to Equation 3

Compound	$-\alpha$	$\beta \times 10^{-5}$	$-\gamma \times 10^{-8}$	$\delta \times 10^{-10}$	% deviation $\times 10^2$ [a]	
					Mean	Max
Propane-1-thiol	60.669 90	0.520 03	0.152 82	0.152 01	41	87
Butane-1-thiol	39.597 00	0.330 26	0.095 82	0.095 25	34	63
Butane-2-thiol	58.868 30	0.505 22	0.148 84	0.148 74	28	54
2-Methylpropane-2-thiol	−63.012 60	−0.578 27	−0.171 25	−0.165 01	9	17
Pentane-1-thiol	−35.228 10	−0.291 05	−0.084 03	0.083 83	32	61
2-Methylbutane-2-thiol	43.353 60	0.366 75	0.107 88	0.109 26	35	60
Hexane-1-thiol	39.538 70	0.331 37	0.096 56	0.097 24	28	57
Heptane-1-thiol	41.688 40	0.351 19	0.102 61	0.103 91	22	43
Octane-1-thiol	51.381 60	0.444 01	0.132 11	0.135 56	26	52
2-Methyloctane-2-thiol	36.671 60	0.306 64	0.089 60	0.092 20	40	78

[a] % deviation = $100|\eta_{\text{exptl}} - \eta_{\text{calcd}}|/\eta_{\text{exptl}}$.

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Glossary

n_D	refractive index (sodium D-line)
T	temperature, K
t	temperature, °C
g	Kirkwood correlation factor
M	formula weight in g mol^{-1}
K	Boltzmann constant
N	Avogadros number
ΔF_η	activation energy of viscous flow in kcal mol^{-1}
R	molar gas constant in cal mol^{-1} deg^{-1}
cP	centipoise
a,b,c	constants in eq 1
A,B,C	constants in eq 2
h	Planck's constant
V	molar volume

Greek Letters

ϵ	low-frequency dielectric constant
ϵ_∞	high-frequency dielectric constant, approximated as $1.027 \times n_D^2$
η	viscosity in cP
ρ	density in g cm^{-3}
μ	dipole moment in Debye units
$\alpha,\beta,\gamma,\delta$	constants in eq 3

Table V. Kirkwood Correlation Factors and Activation Energy

Compound	μ,[a] D	Temp, °C	g	ΔF_η (kcal mol^{-1})
Propane-1-thiol	1.54	0	0.93	2.64
		15	0.95	2.70
		30	0.97	2.75
		45	0.98	2.80
Butane-1-thiol	1.55	0	0.91	2.82
		20	0.93	2.90
		40	0.95	2.97
		60	0.96	3.02
Butane-2-thiol	1.60	0	0.98	2.80
		15	0.99	2.86
		30	1.01	2.91
		45	1.20	2.96
2-Methylpropane-2-thiol	1.59	10	1.03	3.01
		20	1.05	3.02
		30	1.06	3.03
		40	1.07	3.05
Pentane-1-thiol	1.51	0	0.96	3.01
		20	1.01	3.08
		40	1.02	3.17
		60	1.03	3.23
2-Methylbutane-2-thiol	1.58	0	1.02	3.08
		20	1.03	3.12
		40	1.04	3.17
		60	1.05	3.21
Hexane-1-thiol	1.53	0	0.94	3.21
		20	0.95	3.26
		40	0.96	3.34
		60	0.98	3.39
Heptane-1-thiol	1.56	0	0.88	3.41
		20	0.92	3.45
		40	0.91	3.52
		60	0.92	3.57
Octane-1-thiol	1.53	0	0.91	3.62
		20	0.94	3.63
		40	0.97	3.68
		60	0.99	3.73
2-Methyloctane-2-thiol	1.65	0	0.91	3.73
		20	0.93	3.74
		40	0.96	3.79
		60	0.95	3.82

[a] The values of μ taken from ref 1 and 9.[a]

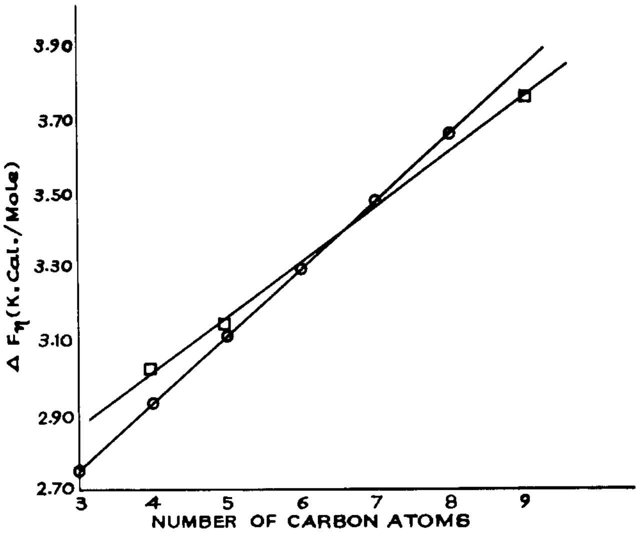

Figure 1. Dependence of the activation energy of viscous flow (ΔF_η) of the normal alkanethiols ○ and tertiary alkanethiols □ upon chain length at 30 °C.

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