Thermal Conductivity of Organic Silicates

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IN THE SEARCH for new materials having a wide, stable liquid range to act as heat transfer media at high temperatures, the organic esters of inorganic acids have been of great interest (*13*). Some of the most successful are the TAS liquids, which consist of alkyl or aryl esters of silicic acid, $Si(OR)_4$, and their mixtures. The formulas characterized in Table I have found extensive commercial use for controlled heating up to 400° C. and are formulated for low setting point and good thermal stability.

Besides the calculation of heat transfer rates, there is a theoretical incentive for studying the thermal conductivity of large, complex molecules, since Bondi (*2*) has shown that the values are generally higher than those predicted by the simple theories of liquid thermal conductivity. The transient hot wire method was chosen for the measurements, since it requires only simple apparatus, gives results in a relatively short time, is suitable for both liquids and solids, and is capable of accuracy equal to that of steady-state methods (*15*).

EXPERIMENTAL

Materials. Samples were supplied by Hygrotherm Engineering, Ltd., from large production batches, which normally have reproducible physical properties (*9*). Only TPS was a single, pure material, melting sharply at 51° C. to give a water-white liquid. TAS 155 was made from C_7 to C_9 hydrocarbons containing 60% of C_8, so that it was predominantly octyl silicate. The other liquids probably contained both inter- and intramolecular mixtures in equilibrium. The liquids were kept under dry nitrogen at all times to avoid hydrolysis, except where TAS 160 was deliberately exposed to air for a month to form a thick, polymerized gel.

Apparatus. The transient wire method used was a modification of that described for molten salts (*15*). The sample was held in a borosilicate glass cell (Figure 1) in the center of a mercury-expansion thermostat of temperature constancy better than 0.01° C. A wire of thermopure platinum, 0.1-mm. diameter × 100 mm., immersed in the sample, was heated by direct current and was connected in a three-lead Wheatstone bridge. The rate of rise of wire temperature was thus found by reading the bridge galvanometer deflection at intervals of 3.33 seconds or by means of a fast-response potentiometric recorder. After a few seconds heating the wire became effectively a line source and thermal conductivity could be found by the relation

$$K = \frac{q}{4\pi} \times \frac{d \ln t}{d\theta} \tag{1}$$

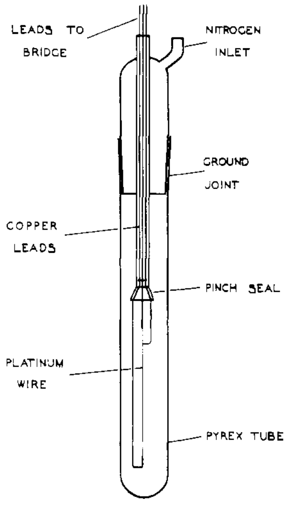

Figure 1. Thermal conductivity cell

The heating rate per unit length, q, was found from current and average resistance of the wire. Current was measured to 0.05% from the potential across a standard ohm in series with the wire. Wire length was measured to 0.1% and corrected for thermal expansion. Resistance was measured to 0.1% with a small current before the main heating, and was corrected for the temperature rise of 1° to 2° by the method of Gillam and others (*8*). This also gave the absolute temperature within 0.5°, since the wire was calibrated at the ice, steam, naphthalene, and sulfur points.

With an observed maximum variation of $d\ln t/d\theta$ of $\pm 2\%$, the maximum estimated error was $\pm 2.8\%$. This was confirmed by measurements on previously reported liquids covering a wide range of conductivity and temperature. The results given in Table II indicate an absolute accuracy of better than $\pm 3\%$.

The effects of heat loss to the leads and nonradial heat flow at the wire ends were balanced out by means of the potential tapping near one end. Thus there were equal effects in opposing bridge arms, so that only the "center" of the wire was effectively measured. Convection was initially negligible, because of the vertical wire position and small temperature rise, but began after 30 to 60 seconds, when the θ *vs.* $\ln t$ plot diverged from linearity and readings were discontinued. No divergence from linearity was noted for solid samples. Radiation was calculated to be less than 0.1% of the total heat transfer, because of the small wire diameter and low emissivity.

Table I. Properties of TAS Liquids (*9*)

Name	Composition	M.W. Av.	ρ, G./Cc.	C_P, Cal./G. ° C.	μ, Cp.	Temp., ° C.
TAS 130	Isopropyl + isobutyl silicate (1:1)	287	0.883	0.47	2.4	20
TAS 155	Octyl silicate	545	0.892	0.52	12	20
TAS 160	Phenyl + cresyl silicate (3:1)	428	1.15	0.38	28	20
TAS 183S	Phenyl silicate + diphenyltriphenoxysilane (1:1)	...	..	...	...	...
TAS 190	Phenyl + resorcinyl silicate (3:1)	416	1.20	0.37	62	20
TPS	Phenyl silicate	400	1.15	0.38	9	50

Table II. Trial of Transient Measurement Method

Liquid	Temp., ° C.	$10^4 K^a$, Cal./Cm. Sec. ° C. Obsd.	Lit.	Ref.
Water	0.5	13.7	13.45	(*6*)
	22	14.55	14.5	(*6*)
Sulfuric acid, 98%	23	7.26	7.47	(*3*)
Glycerol	24	6.65	6.89	(*6*)
Sulfur	187.5	3.55	3.58	(*10*)
Paraffin oil	21	2.92	3.02	(*6*)
	57.5	2.93	3.01	(*6*)
	101	2.85	3.0	(*6*)
	106	2.92	3.0	(*6*)
	165.5	2.82	2.9	(*6*)

^{a} Each value is the mean of 3-5 measurements.

RESULTS

Experimental data are given in Table III and Figures 2, 3, and 4, where each value is the mean of three to five measurements having an average range of ±1.1%. At room temperature, the thermal conductivity varies only between 2.75 and 3.35 × 10^{-4} cal./cm. sec. ° C. for the six liquids, so that a value of 3.1 × 10^{-4} ±10% may be used for this class of liquid. The same average value of 3.1 × 10^{-4} ±3% was reported for the analogous organic phosphate liquids (*5*).

The conductivity falls linearly with increase of temperature within the estimated accuracy of the data, as usually found for organic liquids well below the critical point. The temperature coefficients shown in Table III vary between -1.0×10^{-7} and -3.3×10^{-7} cal./cm. sec. °C.^{2}, so that conductivity may vary 3 to 20% over the working temperature range of these liquids.

There is a slight tendency for conductivity to increase with increasing molecular weight in this series, but side chains tend to lower conductivity and confuse this trend.

Table III. Results of Conductivity Measurements

Substance	Temp., ° C.	$10^4 K$, Cal./Cm. Sec. ° C.	$10^7 dK/dT$, Cal./Cm. Sec. ° C.^{2}
TAS 130	-79	3.09	-3.3
	0	2.92	
	25	2.74	
	61	2.63	
TAS 155	-79	3.59	-3.0
	0	3.37	
	23	3.28	
	61	3.16	
TAS 160	0	3.07	-1.3
	22.5	3.04	
	61	2.99	
Hydrolyzed	23.5	3.52	
TAS 183S	0	3.19	-2.5
	23	3.12	
	61	3.04	
TAS 190	0	3.28	-1.2
	22	3.27	
	78	3.19	
	133	3.15	
	180	3.10	
TPS, solid	0	5.40	
solid	20.5	4.68	
	30	3.30	-1.0
	40.5	3.21	
	52.5	3.22	
	85	3.20	

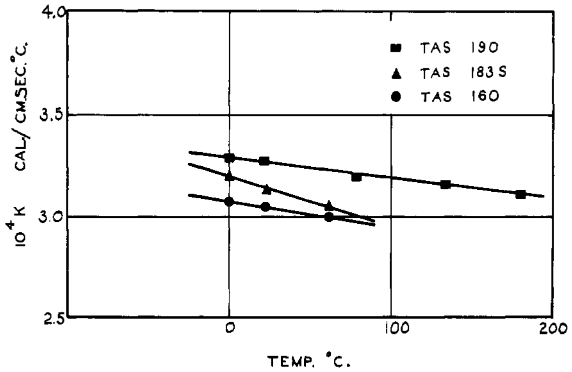

Figure 2. Thermal conductivity of aryl silicates

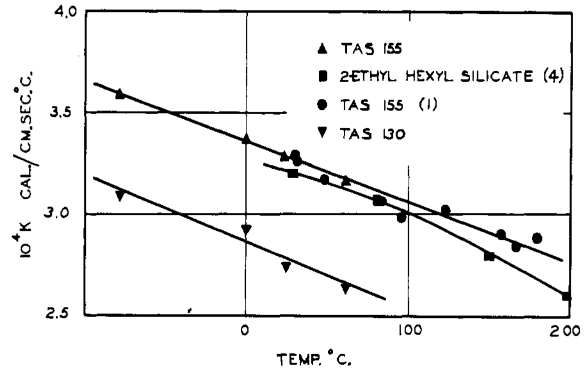

Figure 3. Thermal conductivity of alkyl silicates

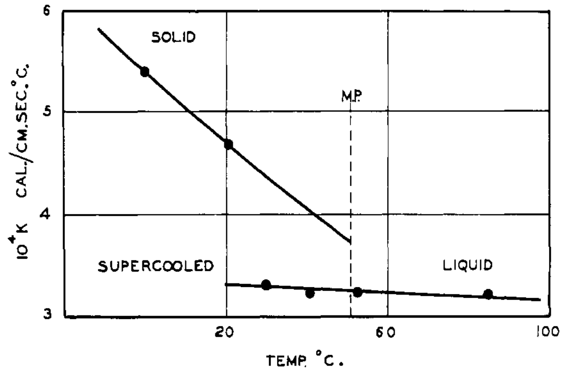

Figure 4. Thermal conductivity of phenyl silicate

Thus the addition of two —OH groups to TPS gives TAS 190 with a slight decrease in conductivity. The addition of —OH and —CH_3 to TPS gives TAS 160 with a 7% reduction in conductivity. Similar trends were found by Dick and McCready (*7*) for ethers and esters of high molecular weight.

Results for TAS 155 shown in Figure 3 are in good agreement with those of Baxter, Vodden, and Davies (*1*), who used a steady-state concentric cylinder cell, differences being well within the combined experimental error. The results of Cecil, Koerner, and Munch (*4*) for a very similar compound, 2-ethylhexyl silicate, are also shown in Figure 3, and are 2 to 3% lower than the TAS 155 results. This just significant difference may indicate that a branched chain gives lower conductivity than the equivalent straight chain.

The conductivity of the polymer gel obtained by partial hydrolysis of TAS 160 in moist air is 15% higher than that of the liquid at room temperature, so that slight hydrolysis during use should have negligible effect on thermal conductivity.

The addition of diphenyltriphenoxysilane to TPS gives TAS 183S, which has a conductivity some 5% lower than TPS. Since a small negative deviation due to mixing would be expected, it is evident that the conductivity of diphenyltriphenoxysilane is almost the same as that of TPS.

There appears to be no marked change of conductivity on supercooling liquid TPS by 20°, in agreement with observations on water and sulfur. On freezing, however, there is a sharp rise of conducivity as the more ordered solid state is formed, and at the melting point the value of K_L/K_S is 0.86. It is notable that the average value of K_L/K_S for six ionic salts was also found to be 0.86 ± 0.13 (*16*).

DISCUSSION

A number of equations, both empirical and theoretical, for the calculation of liquid thermal conductivity may be tested for the TAS liquids using reported physical property data (*9*). The earliest and most successful correlation is that of Weber (*17*)

$$K = 0.00428\, C_p \rho\, V^{-1/3} \text{ cal./cm. sec. } ^\circ\text{C.} \qquad (2)$$

The empirical constant, 0.00428, gives 15% average error for 46 common liquids. For the TAS liquids, predictions are 10 to 30% low.

An empirical correlation due to Smith (*14*)

$$K = 0.000011 + (C_P - 0.45)^3/155 + V^{-1/3}/800 + \mu^{0.11}/10^4 \text{ cal./cm. sec. } ^\circ\text{C.} \qquad (3)$$

predicts thermal conductivity with only 8% average error for TAS liquids.

Simple theories of liquid thermal conductivity are often based on vibrational energy transfer between molecules in a cubic arrangement. The Kincaid and Eyring equation (*11*)

$$K = 2.79\,\gamma^{-1/2}\, kU_S(N/V)^{2/3} \qquad (4)$$

is adequate for simple molecules, but has been shown (*2*) to give low results for large, complex molecules which apparently do not vibrate as a whole, but in segments. Thus it is instructive to substitute measured thermal conductivities in Equation 4 to obtain values of the segment size effective for thermal conduction.

This is possible for some TAS liquids if the sonic velocity U_S is calculated by the bond-increment method. Thus

$$U_S = (R\rho/M)^3 \qquad (5)$$

where R is the sum of values for all the bonds in the molecule, taken from tabulations of Lagemann (*12*) and Weissler (*18*). Then the ratio of specific heats, γ, may be found from the thermodynamic formula

$$\gamma = 1 + \frac{\alpha^2 U_S^2 MT}{C_P} \qquad (6)$$

The segment sizes, V_x, obtained for TPS, TAS 130, and tetra(2-ethylhexyl) silicate at 50°, shown in Table IV, are much closer to the molar volume of the basic groups than to the molar volume of the whole molecules. This indicates fairly independent vibration of the basic groups. The molecules consist of four large organic groups attached tetrahedrally to silicon through oxygen, and it is well known that free rotation around the Si-O bond is possible. The relatively high viscosity and ease of supercooling of TAS liquids also suggest interlocking of the molecules, bringing the organic groups into close proximity. Thus the transfer of heat almost entirely by interaction of the organic groups, as suggested by segment sizes, is physically conceivable. In the case of tetra(2-ethylhexyl) silicate, the 2-ethylhexyl groups themselves have some flexibility, similar to that shown by Bondi (*2*) for hexane and decane, making the segment size effectively about half the molar volume of a 2-ethylhexyl group.

Table IV. Segment Volume for Thermal Conduction at 50°

Liquid	V_x, Cc.	V, Cc.	Basic Group	V, Cc.
Tetraphenyl silicate (TPS)	120	356	Phenyl	90
Diisopropyl	72	335	Isopropyl	75
Diisobutyl silicate (TAS 130)			Isobutyl	96
Tetra(2-ethylhexyl) silicate	68	627	2-Ethylhexyl	163

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NOMENCLATURE

C_P = specific heat at constant pressure
k = Boltzman constant
q = heating rate per unit wire length
K = thermal conductivity
N = Avogadro number
M = molecular weight
R = molar sound velocity bond increment
t = time
T = absolute temperature
U_S = speed of sound in liquid
V = molar volume
V_x = segment size for thermal conduction
α = coefficient of thermal expansion
γ = ratio of specific heats
μ = viscosity of liquid
ρ = density of liquid
θ = temperature rise

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