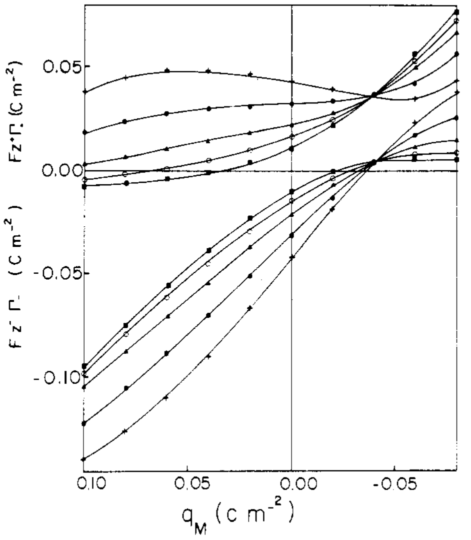

Figure 2. Ionic surface excess values vs. electrode charge, calculated as for Figure 1. [$HClO_4$] = (■) 0.05 M, (○) 0.1 M, (▲) 0.2 M, (●) 0.5 M, (+) 1.0 M.

i.e., a slight nonelectrostatic attraction of the ionic species to the surface.

Figure 2 represents the variation of the $F\Gamma_{H^+}$ and $F\Gamma_{ClO_4^-}$ values as calculated according to eq 2 and 3, respectively, with surface charge and electrolyte concentration. At the lowest concentrations ([$HClO_4$] < 0.05 M) the results approach the behavior predicted by the electrostatic model and observed for NaF solutions. At higher concentrations the nonelectrostatic attraction between the perchlorate ion and the electrode surface manifests itself by the higher than predicted Γ_{H^+} and $\Gamma_{ClO_4^-}$ values.

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Thermal Conductivity of Water and Oleum

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The paper reports measurements of the thermal conductivity of nominal 30, 39, and 65% oleum in the temperature range 20–50 °C at 0.1 MPa, performed by means of an absolute transient line-source technique. It is estimated that the overall uncertainty in the thermal conductivity data is less than ±1.5% on the basis of water measurements over the temperature range 0–95 °C.

Introduction

As part of a program in the evaluation of new heat exchanger performance, data on the thermal conductivity of oleum were required (*1*). Thermal conductivity measurements for sulfuric acid are few (*2*, *3*) and there appears to be none for oleum.

A precise determination of thermal conductivity for such a fluid is extremely difficult because of its strong reactivity, particularly its hydroscopic and ionic effects. Measurements are reported of the thermal conductivity of 30.5, 38.8, and 65.6% free SO_3 oleum in the temperature range 20-50 °C at 0.1 MPa performed by means of an absolute transient line-source technique. It is estimated that overall uncertainty on the thermal conductivity data is less than ±1.5% on the basis of cocurrent measurements on water over the temperature range 0-95 °C. Thirty-two measurements on the oleum samples and twenty-two measurements on distilled, demineralized water are reported.

Experimental Section

The measurements were performed with the transient hot-wire apparatus which has been described elsewhere (*4*, *5*). The instrument was used without major modification for the measurements reported here although there were some differences in the cell construction, cell thermostat, and experimental procedures, which were required for oleum; they will be described later.

In the transient line source method, a fine metal wire (typically 5–100 μm) immersed vertically in the fluid, and contained in a cylindrical enclosure initially at thermal equilibrium, is heated electrically from zero time. The device to a first approximation simulates an infinite line source of constant heat generation. The temperature rise at the wire surface in a time t_1 to t_2 is

$$\Delta T_W = \frac{Q_l}{4\pi\lambda}\ln\left(\frac{t_2}{t_1}\right) \quad \text{for } \frac{\alpha t}{a^2} > 30 \qquad (1)$$

where Q_l is the heat generated per unit length of wire of radius a. Equation 1 does not depend on the thermal diffusivity, α,

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Table I. The Thermal Conductivity of Oleum

run no.	temp, °C	power, mW/cm	$\lambda(\sigma)$, mW/(cm K)	current direction
		A. 30.5% free SO_3		
25-1	23.16	3.4	2.430 (±0.006)	fwd
25-2	50.62	3.7	2.557 (±0.009)	fwd
25-3	50.63	3.7	2.561 (±0.007)	rev
25-4	41.64	2.3	2.491 (±0.008)	rev
25-6	41.58	2.3	2.514 (±0.006)	fwd
25-7	41.67	2.3	2.485 (±0.008)	rev
25-8	26.98	4.9	2.454 (±0.005)	rev
25-9	26.61	2.2	2.453 (±0.009)	fwd
25-10	26.70	2.2	2.453 (±0.006)	rev
		B. 38.8% free SO_3		
37-1	50.65	5.3	2.444 (±0.003)	fwd
37-2	50.62	5.3	2.420 (±0.003)	fwd
37-3	50.65	5.3	2.464 (±0.009)	rev
37-4	40.13	5.1	2.430 (±0.003)	fwd
37-5	40.17	5.1	2.445 (±0.005)	rev
37-6	30.40	5.0	2.422 (±0.002)	rev
37-7	30.20	5.0	2.420 (±0.004)	fwd
		C. 65.6% free SO_3		
68-1	26.21	4.9	2.047 (±0.004)	fwd
68-2	26.41	4.9	2.038 (±0.003)	rev
68-3	49.93	5.3	2.092 (±0.006)	rev
68-4	49.96	5.3	2.099 (±0.005)	fwd
68-5	41.69	5.2	2.075 (±0.004)	fwd
68-6	41.66	5.2	2.074 (±0.005)	rev
68-7	30.40	5.0	2.053 (±0.007)	rev
68-8	30.34	5.0	2.034 (±0.003)	fwd
68-9	30.35	5.0	2.036 (±0.005)	fwd
68-10	30.41	5.0	2.036 (±0.004)	fwd
68-11	30.37	5.0	2.039 (±0.006)	rev
68-12	26.06	4.9	2.005 (±0.005)	fwd
68-13	26.08	4.9	2.011 (±0.004)	rev
68-14	26.08	4.9	2.016 (±0.005)	rev
68-15	26.12	4.9	2.014 (±0.004)	fwd

of the fluid and yields, similar to steady-state methods, thermal conductivity directly. Corrections are needed for finite wire heat capacity, nonconstant heat generation, radiation, and parasitic heat losses. The theory and its experimental application are described in ref 5.

The cell used consisted of a 62.5-μm diameter platinum wire having potential leads (62.5 μm diameter) located 13.08 cm apart. The wire was located centrally in a precision bore Pyrex glass tube 1 cm in diameter sealed with high-density polythene end caps. The thermostat consisted of an aluminum block drilled to accommodate the cell and a reference platinum resistance thermometer. A controlled oil bath [Lauda HTS] provided an external temperature controlled circulation, external to the dry nitrogen purged glovebox, necessary for oleum.

In all, 32 measurements on oleum and 22 measurements on water are reported at power levels between 2 and 10 mW/cm. Voltage potential drops over the length of the wire are thought to be below those required to initiate ionization; this factor was further checked by reversal of the current direction in the hot wire circuit for both fluids. Each experimental run was executed between 5 and 10 s; the digital voltmeter of the data acquisition system, under control of the LSI-11, takes up to 200 readings, at times variable, under control of between 25 and 350 ms apart; the first reading can be adjusted to be from 1 to 350 ms from initiation of the experiment. These data are then processed according to experimental criteria to obtain the conductivity (*5*). Each experimental run was separated by approximately $^1/_2$-h intervals in order to reestablish thermal equilibrium. It required approximately 1-2 h to establish each temperature level.

Samples of oleum were analyzed before and after tests (*1*). We believe the measurements are accurate to better than 1.5%; test measurements on water before, during, and after the oleum program were reproducible to better than 1%.

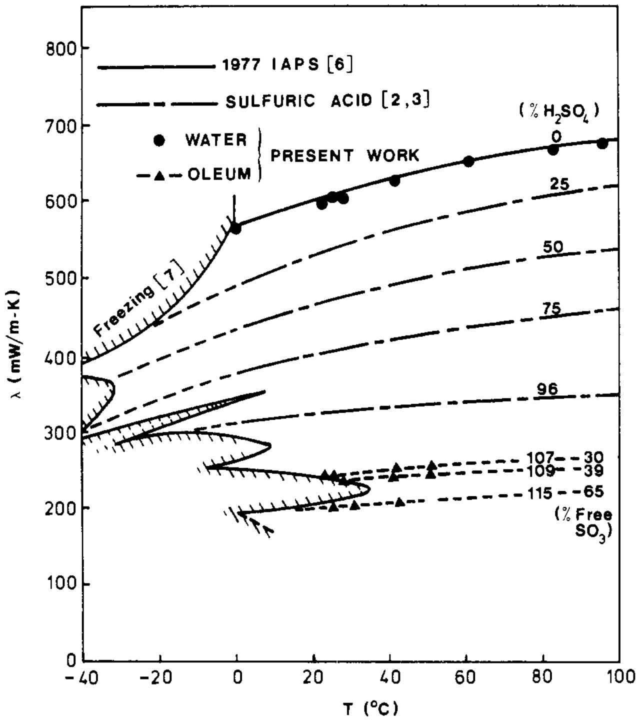

Figure 1. Thermal conductivity of water and oleum.

Table II. Thermal Conductivity of Oleum

$\lambda = a_0 + a_1 T$, mW/(cm K); T in °C

% free SO_3	a_0, mW/(cm K) (σ)	$10^{-2}a_1$, mW/(cm K^2) (σ)
30.5	2.33_6 (±0.02)	0.41_7 (0.05)
38.8	2.39_2 (±0.03)	0.10_3 (±0.07)
65.6	1.94_1 (±0.01)	0.31_3 (±0.04)

Table III

Thermal Conductivity of Water (0-100 °C; Cell 14)

run no.	temp, °C	power, mW/cm	λ, mW/(cm K)	remarks
14-1	82.50	5.85	6.661 ± 0.015	sample 1
14-2	82.47	8.99	6.690 ± 0.008	
14-3	67.01	5.59	6.514 ± 0.033	sample 2
14-4	82.47	10.31	6.684 ± 0.017	
14-5	27.34	5.25	6.077 ± 0.009	sample 3
14-6	25.65	4.89	6.047 ± 0.039	
14-7	24.97	4.87	6.090 ± 0.034	
14-8	24.63	8.56	6.015 ± 0.029	sample 4
14-9	24.31	8.56	6.010 ± 0.031	
14-10	24.29	8.60	6.022 ± 0.015	sample 5
14-11	24.24	4.86	6.062 ± 0.018	
14-12	23.28	8.56	6.013 ± 0.026	
14-13	23.38	3.98	6.033 ± 0.015	
14-14	0.10	3.67	5.602 ± 0.012	
14-15	0.11	5.10	5.623 ± 0.027	
14-16	0.04	3.02	5.611 ± 0.018	
14-17	0.04	3.02	5.597 ± 0.023	
14-18	41.23	5.16	6.294 ± 0.036	
14-19	60.37	5.48	6.500 ± 0.025	
14-20	60.39	9.65	6.550 ± 0.029	
14-21	95.34	6.00	6.793 ± 0.019	
14-22	95.33	6.99	6.809 ± 0.014	sample 6

Correlation Equation: λ(mW/cm K) $= a_0 + a_1 t + a_2 t^2$, t in °C

coefficients	std dev
a_0(mW/cm K) = 5.61_1	±0.012
a_1(mW/cm K^2) = 0.0193_0	±0.00067
a_1(mW/cm K^3) = $-0.75_5 \times 10^{-4}$	$\pm 0.72 \times 10^{-5}$

Results and Discussion

The results for oleum are shown in Table I and plotted in Figure 1. Data at 30.5 and 38.8% free SO_3 were obtained within 1 to 2 °C of freezing (*7*).

The data for each strength were fitted to equations of linear form as shown in Table II.

The results obtained for water are reported in Table III and also shown in Figure 1. Agreement to IAPS (1977) (*6*) is better than 1.5%, the results reported here being slightly lower. Plotted also in Figure 1 are the smoothed data for dilute aqueous solutions of H_2SO_4 (*2*, *3*).

Conclusion

Absolute measurements of the thermal conductivity of oleum and water are reported in the temperature range 0–95 °C. The results are believed accurate to ±1.5%.

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Thermal Conductivity of Phenol (C_6H_5OH)

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The paper reports measurements of the thermal conductivity of solid and liquid reagent grade phenol over the temperature range 30–200 °C at pressures to 0.5 MPa, performed by means of an absolute transient line source instrument. At the melting point there is a depression of the expected conductivity of 0.02 mW/(cm K); the ratio of λ_s:λ_a is 1.13:1. It is estimated that the overall uncertainty in the data is less than ±1.5% on the basis of measurements made of two samples with two different cells.

Introduction

Most empirical expressions relate the thermal conductivity of normal simple liquids as linear functions of temperature over their normal melting point to boiling point range. The majority of measurements to date support such a description, except for water. Past measurements on toluene did show a substantial prefreezing depression (*1*) which was attributed to molecular cluster formation. New measurements on solid and liquid phenol reported here also provide evidence of a slight prefreezing in addition to significant increase upon solidification.

Experimental Section

A modification of the absolute transient line source instrument (*2*, *3*) was employed by using samples of BDH and Fisher detached crystal reagent grade phenol. The two cells employed for the work were of 25 and 50 μm diameter platinum. The 25-μm cell (cell 2) was 10.65 cm long, used without potential leads; the 50-μm cell utilized a working length of 9.11 cm between potential leads. The measurements shown in Figure 1 and Table I are obtained with a precision of approximately 6000 ppm by measuring the voltage–time behavior of the platinum cell wire source immersed in the substance and pulsed with a constant current sufficient to produce temperature rises of 1 to 2 °C in 5 s. Experimental procedures are such that end conduction, convection, and radiation heat loss effects can be minimized (*2*).

Table I. Thermal Conductivity of Phenol (C_6H_5OH)[a]

temp, °C	λ, mW/(cm K)	comment
28.3	1.79_2	cell 2, solid (Fisher) anisotropic effects
41.9	1.56	cell 2, liquid (Fisher) anisotropic effects
43.2	1.57_8	cell 1, liquid (BDH)
49.2	1.57_0	cell 1, liquid (BDH)
58.1	1.55	cell 2, liquid (Fisher)
62.0	1.56_4	cell 1, liquid (BDH)
80.0	1.54_7	cell 1, liquid (BDH)
101.0	1.51_5	cell 1, liquid (BDH)
120.0	1.49_1	cell 1, liquid (BDH)
149.7	1.45_8	cell 1, liquid (BDH)
149.7	1.45_3	cell 1, liquid (BDH)
173.1	1.41_6	cell 1, liquid (BDH)
172.6	1.41_4	cell 1, 0.68 MPa nitrogen overpressure
197.8	1.39_2	cell 1, liquid (BDH) 0.4 MPa nitrogen overpressure

[a] $\lambda_l = 1.66 - 0.00143t$ mW/(cm K). $\lambda_a/\lambda_l = 1 - 0.0125 \exp(-1.4298/T^{*1/2})$. t, °C; T, K.

In all, 11 measurements with cell 1 and 3 measurements with cell 2 are reported. The results of cell 1 are considered more reliable, since they were obtained by using potential leads and hence are not subject to axial and radial conduction losses (*4*). Each experimental run was executed between 3 and 10 s; a digital voltmeter of the data acquisition system takes up to 200 readings, at time variable between 25 and 350 ms; the first reading can be adjusted to be from 1 to 350 ms from initiation of the experiment. Values above the normal boiling point were obtained by using a slight nitrogen overpressure. In order to determine the effects of this overpressure, we made duplicate measurements at 173 °C (Table I). The theory and its experimental application are described elsewhere (*2*).

Discussion

Previous measurements of phenol (*5*–*8*) are also shown in Figure 1; agreement is best (±2%) with ref 5, 6, and 7; the work of Jamieson (*8*) is 3.3% lower at 60 °C and in agreement at 160 °C.

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