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Liquid Thermal Conductivities of Acetonitrile, Diethyl Sulfide, Hexamethyleneimine, Tetrahydrothiophene, and Tetramethylethylenediamine

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The liquid thermal conductivities of acetonitrile, diethyl sulfide, hexamethyleneimine, tetrahydrothiophene, and tetramethylethylenediamine have been measured by means of a transient double-hot-wire apparatus. The thermal conductivity measurements were taken at temperatures ranging from 0 to 60 °C and at ambient pressure.

Introduction

Accurate thermal conductivity values are required in the accurate and efficient design of heat-transfer equipment. Typically, the thermal conductivity of a fluid is predicted if no experimental data are available. Group contribution methods are a common prediction technique. In order for a group contribution method to be reliable, sufficient and accurate data are needed to regress the contribution for each group. Because few thermal conductivity data are available for nitrogen- and sulfur-containing compounds, measurements have been preformed on acetonitrile, diethyl sulfide, hexamethyleneimine, tetrahydrothiophene, and tetramethylethylenediamine.

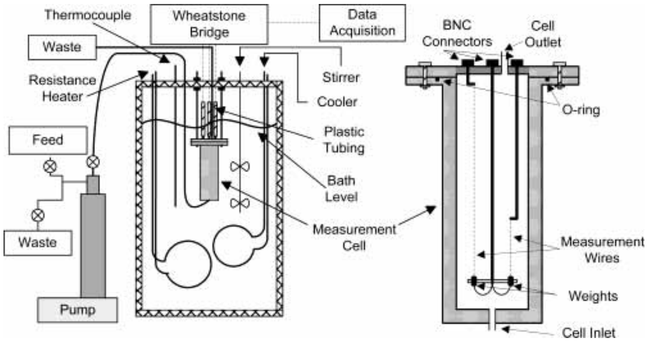

Figure 1. Schematic of the thermal conductivity apparatus.

Experimental Section

Materials. All of the chemicals used in this work were purchased from Sigma-Aldrich. The purities of acetonitrile, diethyl sulfide, hexamethyleneimine, tetrahydrothiophene, and tetramethylethylenediamine as reported by Sigma-Aldrich are 99.82%, 99.97%, 98.5%, 99.0%, 99.9%, and 99.0%, respectively. No additional purification was performed.

Apparatus. Thermal conductivity measurements were performed using the transient double-hot-wire apparatus shown in Figure 1. The measurement cell is constructed of stainless steel and has a volume of 150 mL. The measurement wires are 99.99% pure platinum and have a diameter of 2.032×10^{-3} mm. Once the cell has been assembled, it is completely submerged in a thermostating liquid bath. A Bayley precision temperature controller maintains the bath temperature constant to within ±0.01 K. A LabView data acquisition system is used to acquire the necessary data.

Procedure. The thermal conductivity of a fluid is measured by first charging the measurement cell with the desired fluid. The thermostating bath is then set to the desired temperature, and the cell temperature is allowed to reach equilibrium. Once the cell has reached equilibrium, a voltage (7−9 V) is briefly (~1 s) allowed across the measurement wires. The voltage across the high-resistance platinum wires creates a heat flux in the measurement fluid. The resistances of the measurement wires were recorded at 0.001-s intervals by means of a Wheatstone bridge and the LabView data acquisition system.

The resistance versus temperature dependence of the measurement wires was predetermined so that the resistance change data could be transformed into temperature change data. The thermal conductivity was then found by comparing the change in temperature versus time data to the appropriate solution of the transient energy equation.

A solution to the transient energy equation given by Carslaw and Jeager[1] is shown in eq 1, where q is the heat flux, λ is the thermal conductivity, t is the time, r_o is the radius of the wire, $C = 1.781...$ is the exponential of Euler's constant, and $a = \lambda/(\rho C_p)$ is the thermal diffusivity in which ρ is the density and C_p is the isobaric heat capacity. This equation assumes that a heat flux is being applied radially by an infinitely small line source to an infinite fluid that has temperature-independent properties. Because these assumptions are not exactly met by the experimental setup, ΔT_{id} must be corrected before the thermal conductivity can be regressed. A significant correction arises from the fact that the heat source is a platinum wire that has a finite size and is capable of conducting heat. To correct for this nonideality eq 1 needs to be modified as shown in eq 2, where δT represents the correction terms and ΔT_w is the measured temperature change of the fluid. Typically, the correction constitutes a change to the regressed thermal conductivity of less than 0.8%. A comprehensive discussion

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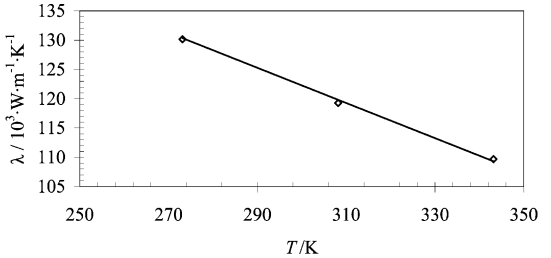

Figure 2. Comparison of the liquid thermal conductivity of *n*-heptane (◇, present work) to a reference correlation (line, Nieto de Castro et al.[3]).

Table 1. Liquid Thermal Conductivities λ of Acetonitrile, Diethyl Sulfide, Hexamethyleneimine, Tetrahydrothiophene, and Tetramethylethylenediamine

compound	T (K)	λ (10^3 W·m^{-1}·K^{-1})
acetonitrile	273.15	207
	293.15	195
	313.15	183
diethyl sulfide	273.15	145
	293.15	140
	313.15	137
	333.15	130
hexamethyleneimine	273.15	141
	293.15	137
	313.15	131
	333.15	126
tetramethylethylenediamine	273.15	120
	288.15	117
	303.15	115
	318.15	112
	333.15	110
tetrahydrothiophene	273.15	154
	293.15	150
	313.15	144
	333.15	135

of all corrections that can be applied is given by Kestin et al.[2]

$$\Delta T_{\mathrm{id}} = \frac{q}{4\pi\lambda}\left[\ln(t) + \ln\left(\frac{4a}{r_{\mathrm{o}}^{2}C}\right)\right] \qquad (1)$$

$$\Delta T_{\mathrm{id}} = \Delta T_{\mathrm{w}} + \sum_{i}\delta T_{i} \qquad (2)$$

Using eqs 1 and 2, the thermal conductivity is regressed from the slope of ΔT_{w} versus ln(time) data. It is also possible to determine the thermal diffusivity from the intercept of this same set of data, but only the thermal conductivity is reported in this work.

Results and Discussion

The transient double-hot-wire apparatus was calibrated with *n*-heptane. Calibration points were taken using *n*-heptane at (0, 35, and 70) °C. The calibration points are compared to the correlation reported by Nieto de Castro et al.[3] in Figure 2. The calibration shows excellent agreement with the reference data over the entire temperature range of interest.

The thermal conductivities of acetonitrile, diethyl sulfide, hexamethyleneimine, tetrahydrothiophene, and tetramethylethylenediamine are listed in Table 1. Each data point reported in Table 1 represents an average of 6−10 data points taken at the specified conditions. Duplicate points were run to determine the precision of the transient double-hot-wire apparatus. The duplicates gave an error of less the ±0.8% at the 95% confidence level for all of the data reported. The uncertainty of the experimental data measured by the transient hot-wire method is ±2.0%. This uncertainty is based on previous measurements and calibration data.

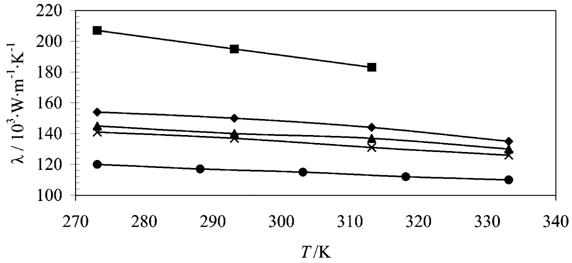

Figure 3. Experimental liquid thermal conductivities of ■, acetonitrile; ▲, diethyl sulfide; ×, hexamethyleneimine; ●, tetramethylethylenediamine; and ◆, tetrahydrothiophene.

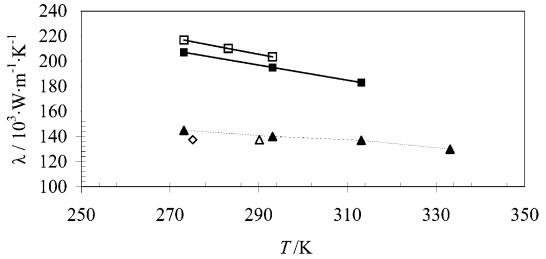

Figure 4. Comparison of the liquid thermal conductivity data acquired here to data reported in the literature for acetonitrile (■, present work; □, Qun-Fang et al.[5]) and diethyl sulfide (▲, present work; ◇, Weber;[6] △, Tye and Powell[7]).

The data are also given in Figure 3. As expected, all of the thermal conductivity values decrease linearly as the temperature increases. The lighter molecules have a higher thermal conductivity than the heavier molecules. It has been suggested that the thermal conductivity of diamines has a nonlinear temperature dependence.[4] However, this nonlinearity is a result of association, and because the diamine studied in this work, tetramethylethylenediamine, does not associate, it is expected to give a linear temperature dependence. This was confirmed by the measurements.

Acetonitrile and diethyl sulfide are the only two compounds in this data set that have available liquid thermal conductivity data in the literature. Experimental thermal conductivity data for acetonitrile have been reported in the literature by Qun-Fang et al.[5] and for diethyl sulfide by Weber[6] and Tye and Powell.[7] The comparison of the reported values and the values determined in this work is shown in Figure 4. The data reported in this work are within ∼4% of the data previously reported in the literature.

Conclusions

The liquid thermal conductivities for acetonitrile, diethyl sulfide, hexamethyleneimine, tetrahydrothiophene, and tetramethylethylenediamine at temperatures between (0 and 60) °C and ambient pressure hava been reported. All of the data follow the expected trends with temperature and compare well with other experimental data previously reported. The data will provide valuable information for regressing contributions for group contribution prediction methods for nitrogen- and sulfur-containing compounds.

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