Thermal Conductivity Measurement of Polyglycol Alkyl Ethers at Temperatures from (303.15 to 393.15) K

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Experimental values of the thermal conductivity of five pure polyglycol alkyl ethers are presented in a temperature range from (303.15 to 393.15) K at a pressure of 1 MPa. Measurements were made with a Setaram C-80 II calorimetric device equipped with a suitable vessel setup and an auxiliary thermostat to measure at high-temperature conditions using the steady-state coaxial cylinders method. The measured values of the thermal conductivity were compared with data reported in the literature. The reliability and accuracy of the experimental method were confirmed with the measurements on pure benzene with well-known thermal conductivity values. Our data agreed with the limited data available in the literature and were correlated using an empirical expression. The uncertainty of the results was estimated to be within ± 2.0 %, and the reproducibility of the data was better than ± 0.5 %.

1. Introduction

Transport properties of polyglycol alkyl ethers are needed in many industrial and scientific applications such as calculation of design parameters, efficient operation of high-temperature energy generating systems, and prediction of heat and mass transfer coefficients. Thermal conductivity is an important thermophysical property, values of which are required in almost all heat transfer calculations especially when dealing with the convective heat transfer process of fluids and lubricants.[1,2] Accurate measurements of this property are very difficult, principally because of natural convection caused by imposed temperature difference, which makes the experimental values too high and, in some cases, exceeding about 20 % of the usual engineering tolerance.

Only limited experimental thermal conductivity data of polyglycol alkyl ethers liquid over a wide range of temperatures are available in the literature. Therefore, there is a sustained demand for new reliable thermal conductivity data of these polyglycols.

The main objective of the paper is to provide new accurate experimental thermal conductivity data for five polyglycol alkyl ethers in a wide temperature range (303.15 to 393.15) K. These compounds are ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, and dipropylene glycol dimethyl ether. The present results considerably expand the available thermophysical property database for these polyglycol alkyl ethers. These data are indispensable and required in the diverse fields of refrigeration technology.

Several researchers have reported the measurement of the thermal conductivity of liquids using different equipment based on steady-state or transient methods. Among all the steady-state and transient methods employed, most reliable results are obtained from the hot wire,[3−6] flat plate,[7] concentric cylinder,[8] and the concentric spheres.[9]

In this experimental work, we performed our measurements using a Setaram C-80 II calorimeter equipped with calorimetric vessels suitable for obtaining the thermal conductivity λ according to the steady-state coaxial cylinders method.[10,11] An auxiliary thermostat is needed to work at temperatures above 353.15 K. Moreover, a pressure of 1 MPa was applied to increase saturation temperature above boiling temperature of the respective liquids to avoid evaporation of the compounds.

There are very few experimental data on the thermal conductivity of polyglycol alkyl ethers.[1,12,13] Also, there are not many reports of the fluid measured by using a C-80 Setaram calorimeter.[10,11,14]

2. Experimental Apparatus and Procedure

Materials. Ethylene glycol dimethyl ether (> 99 % mass fraction), diethylene glycol dimethyl ether (> 99.5 % mass fraction), triethylene glycol dimethyl ether (> 98 % mass fraction), tetraethylene glycol dimethyl ether (> 98 % mass fraction), and dipropylene glycol dimethyl ether (> 99 % mass fraction) were purchased from Fluka and used without any further purification because some are unstable. Methanol (Panreac, > 99.8 % mass fraction), toluene (Sigma-Aldrich, > 99.8 % mass fraction), and benzene (Panreac, > 99.8 % mass fraction) were distilled and kept over molecular sieves. These three compounds, together with Millipore water (resistivity less than 18.2 MΩ·cm, Milli-Q quality), were used in the calibration and the validation of the measurement method.

Thermal Conductivity Cell. The thermal conductivity of the pure polyglycol alkyl ethers was measured by the coaxial cylinders method using a thermal conductivity cell (model 31/1442) attached to a C-80 II Setaram calorimeter. We have chosen this method to check the reliability and repeatability of the measurements. The apparatus and procedure were described previously.[13,15]

An illustration of the cell,[16] together with principle of the thermal conductivity setup, is given in Figure 1. The thermal conductivity cells are filled inside of the calorimeter. Each vessel

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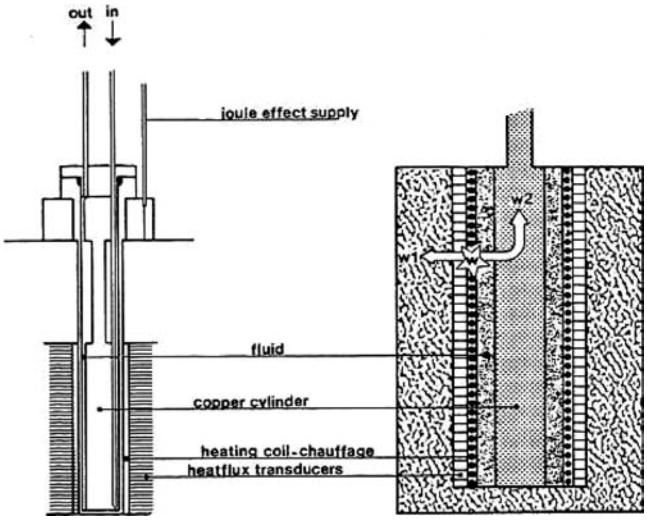

Figure 1. Schematic diagram of the measuring thermal conductivity cell for the C-80 II Setaram calorimeter.[16]

has an inner cylinder made of gold-plated copper and an outer cylinder made of stainless steel. Around the outer cylinder is wound a heating coil, and the whole device is set in a stainless steel container. When thermal equilibrium is reached, a current intensity is applied through the heating wire of the measurement cell only for a discrete period of time to obtain a constant power W dissipated by the Joule effect. The dissipated power goes through both the detector, W_1, and the liquid, W_2, which transmits the heat to the copper cylinder and then to the environment. At this point, an exothermic signal is recorded. A power input of 100 mW to the measurement cell was sent for about 2100 s to record the corresponding calorimetric signal due to the thermal conductivity coefficient of the liquid. The signal reading was repeated at least nine times for each equilibrium temperature.

The calorimetric signal S and the thermal conductivity λ are correlated by eq 1.

$$\lambda = \frac{-S + A}{B \cdot S + C} \qquad (1)$$

where S and λ are in μV and $W \cdot m^{-1} \cdot K^{-1}$, respectively. A, B, and C are the calibration constants and a function of the temperature.

Auxiliary Thermostat. An auxiliary thermostat (Setaram, model 31/1444) together with the Temperature Programmer Regulator (Setaram, model 31/4235) are absolutely needed if the measurements are carried out at temperatures above 353.15 K. The auxiliary thermostat consists of a cover whose temperature can be controlled, and it is placed on the top of the calorimetric block. The aim of this thermostat is to prevent heat loss through the calorimeter top to favorize better thermal stability and to get greater accuracy of results. The control temperature is always 5 K above the calorimetric block temperature.

Pressure System. The method used for obtaining working pressure is the same used previously for heat capacity at constant pressure measurements.[13] The pressure over the liquid sample was applied with nitrogen through a tube of 1.6 mm diameter. To avoid diffusion of nitrogen into the sample, 4 m of the tube completely filled with the sample was used between the vessel and the inlet gas.

Calibration Curve and Validation. Calibration curves were built for each working temperature (303.15, 333.15, 363.15, and 393.15) K using Millipore water, methanol, and benzene. The calorimetric signals obtained (S/μV) and recommended values of thermal conductivity[17,18] were used to calculate calibration constants in eq 1 for each temperature.

To check and confirm the accuracy of the method, the procedure results for pure benzene were compared with recommended values.[19] Excellent agreement is found within 0.9 % in all temperature ranges. This excellent agreement for the test measurements confirms the reliability and accuracy of the present measurement for polyglycol alkyl ethers and the operation of the instrument.

Table 1. Experimental (λ_{exp}) and Reference (λ_{ref}) Thermal Conductivity Values for Benzene at Several Temperatures and Relative Deviations at 1 MPa

T/K	λ_{exp}/($W \cdot m^{-1} \cdot K^{-1}$)	λ_{ref}/($W \cdot m^{-1} \cdot K^{-1}$)	deviation %
302.75	0.1409	0.1396	0.9
332.54	0.1304	0.1298	0.4
362.39	0.1194	0.1200	−0.5
392.16	0.1101	0.1102	−0.1

Table 2. Experimental Thermal Conductivity Values for Five Polyglycol Alkyl Ethers at Several Temperatures at 1 MPa

T/K	λ_{exp}/($W \cdot m^{-1} \cdot K^{-1}$)
Ethylene Glycol Dimethyl Ether $C_4H_{10}O_2$ (CAS number 110-71-4)	
302.75	0.1518
332.54	0.1403
362.39	0.1268
392.16	0.1154
Diethylene Glycol Dimethyl Ether $C_6H_{14}O_3$ (CAS number 111-96-6)	
302.75	0.1522
332.54	0.1423
362.39	0.1300
392.16	0.1194
Triethylene Glycol Dimethyl Ether $C_8H_{18}O_4$ (CAS number 112-49-2)	
302.75	0.1543
332.54	0.1452
362.39	0.1354
392.16	0.1250
Tetraethylene Glycol Dimethyl Ether $C_{10}H_{22}O_5$ (CAS number 143-24-8)	
302.75	0.1584
332.54	0.1501
362.39	0.1411
392.16	0.1295
Dipropylene Glycol Dimethyl Ether $C_8H_{18}O_3$ (CAS number 111109-77-4)	
302.75	0.1295
332.54	0.1219
362.39	0.1135
392.16	0.1043

3. Results and Discussion

As mentioned in the previous section, initially measurements were performed on liquid benzene between (303.15 and 393.15) K to evaluate the reliability of our data in comparison with the literature. In Table 1, the results obtained from the pure benzene are shown with the literature data proposed.[18,19] The probable error is estimated as 0.9 %.

The thermal conductivity for five polyglycol alkyl ethers is shown in Table 2. The accuracy of the temperature and pressure is estimated to be 0.02 K and 0.06 MPa, respectively. Uncertainty for thermal conductivity was better than 2 % in all cases. All these are expanded uncertainties with a coverage factor of 2 (95 % probability). An example of the uncertainty budget for pressure, temperature, and thermal conductivity is shown in Table 3, which have been calculated using the recommended

Table 3. Uncertainty Budget for Pressure, Temperature, and Thermal Conductivity for Diethylene Glycol Dimethyl Ether at 392.16 K and 1 MPa

		units	estimate	probability distribution	$u(x)$
$u(\lambda_{ref})$	reference material: water	$W\cdot m^{-1}\cdot K^{-1}$	0.0028	normal	0.0028
	reference material: toluene	$W\cdot m^{-1}\cdot K^{-1}$	0.0007	normal	0.0007
	reference material: methanol	$W\cdot m^{-1}\cdot K^{-1}$	0.0006	normal	0.0006
$u(S)$	repeatability	mV	0.0016	normal	0.0016
	resolution		$1\cdot10^{-5}$	normal	$2.9\cdot10^{-6}$
$u(T)$	stability		0.01	normal	0.01
	resolution	K	0.01	rectangular	$2.9\cdot10^{-3}$
	calibration		0.01	normal	0.005
$u(p)$	calibration		0.001	normal	0.0005
	Resolution	MPa	0.001	rectangular	$2.9\cdot10^{-4}$
	stability		0.001	normal	0.0005
	specifications		0.0325	normal	0.0325
$U(a)$				$k = 2$	$1.0\cdot10^{-3}$
$U(b)$				$k = 2$	$2.6\cdot10^{-2}$
$U(c)$				$k = 2$	$3.8\cdot10^{-2}$
$\boldsymbol{U(T)}$		**K**		$\boldsymbol{k = 2}$	**0.02**
$\boldsymbol{U(p)}$		**MPa**		$\boldsymbol{k = 2}$	**0.06**
$\boldsymbol{U(\lambda)}$		$\boldsymbol{W\cdot m^{-1}\cdot K^{-1}}$		$\boldsymbol{k = 2}$	**0.0022**

Table 4. Fitting Coefficients of Equation 2

compound	$A_0\cdot10^1$ ($W\cdot m^{-1}\cdot K^{-1}$)	$A_1\cdot10^4$ ($W\cdot m^{-1}\cdot K^{-2}$)
ethylene glycol dimethyl ether	2.781	−4.157
diethylene glycol dimethyl ether	2.654	−3.674
triethylene glycol dimethyl ether	2.539	−3.278
tetraethylene glycol dimethyl ether	2.562	−3.207
dipropylene glycol dimethyl ether	2.152	−2.818

guide EA-4/02.[20] In this example, diethylene glycol dimethyl ether at 392.16 K and 0.1 MPa was selected because it was the worst case from the point of view of uncertainty (1.7 %).

Thermal conductivity values were fitted with temperature using a linear eq 2 for each compound, where units are $W\cdot m^{-1}\cdot K^{-1}$ and K, respectively. In Table 4, coefficients of eq 2 are shown for polyglycol alkyl ether.

$$\lambda = A_0 + A_1\cdot T \qquad (2)$$

Finally, experimental results were compared with literature values. Thermal conductivity for ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether can be found,[12] at (298.15 and 323.15) K and 0.1 MPa. Thermal conductivity for ethylene glycol dimethyl ether was reported[21] at temperatures from (243 to 353) K at pressures up to 30 MPa. Figure 2 shows the comparison of the present work and the literature[12,21] values for ethylene glycol dimethyl ether. Relative deviations between this work and literature values were 4.2 % and 2.2 %, respectively. Also, this work and literature[12] values for diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether are plotted in Figure 3. Relative deviations were less than 5 % in all cases, although the experimental results of this study show a trend toward a lower thermal conductivity with temperature than literature values.

4. Conclusions

The thermal conductivities of five polyglycol alkyl ethers have been measured with a coaxial-cylinder (steady-state) technique using a C-80 II Setaram microcalorimeter at a temperature range from (303.15 to 393.15) K. The total uncertainty of the thermal conductivity was estimated to be less than 2 %. Measured values of thermal conductivity were compared with reported data in

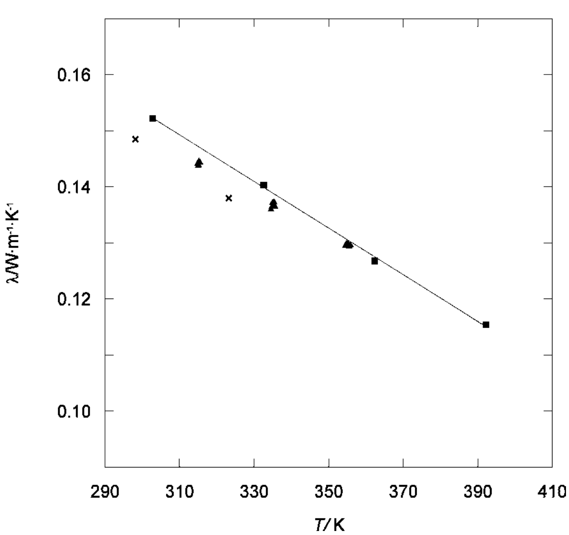

Figure 2. Variation of the thermal conductivity with the temperature for ethylene glycol dimethyl ether. ■, This work, experimental values; ___, calculated values by eq 2; ▲, ref 20; ×, ref 12.

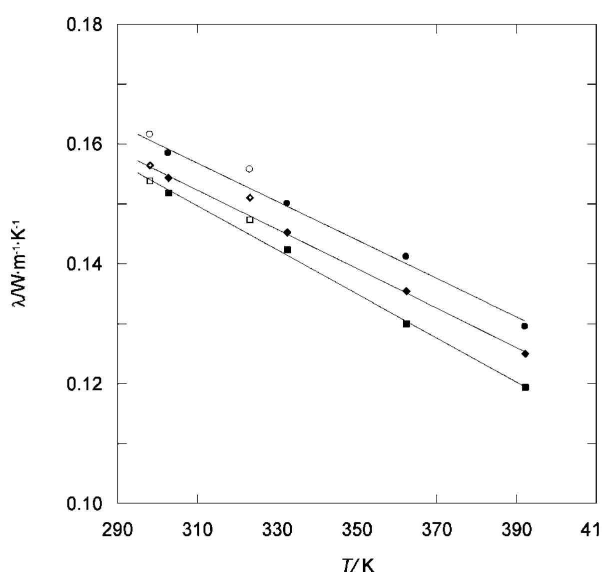

Figure 3. Variation of the thermal conductivity with the temperature for diethylene glycol dimethyl ether: ■, this work, experimental values; ___, calculated values by eq 2; □, ref 12. Triethylene glycol dimethyl ether: ♦, this work, experimental values; ___, calculated values by eq 2; ◇, ref 12. Tetraethylene glycol dimethyl ether: ●, this work, experimental values; ___, calculated values by eq 2; ○, ref 12.

the literature showing deviations lower than 5 %. The reliability of the experimental method was confirmed with the measurement of thermal conductivity of benzene showing excellent agreement (better than 0.9 %). Experimental results of thermal conductivity were fitted with temperature using analytical equations.

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