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Absolute Measurements of the Thermal Conductivity of Mixtures of Alkene-Glycols with Water

M. J. Assael,[1] E. Charitidou,[1] S. Avgoustiniatos,[1] and W. A. Wakeham[1,2]

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New absolute measurements of the thermal conductivity of ethylene and propylene glycol and their mixtures with water are presented. The measurements were performed in a tantalum-type transient hot-wire instrument at atmospheric pressure, in the temperature range 295–360 K. The overall uncertainty of the reported values is estimated to be less than ±0.5%, an estimate confirmed by measurements of the thermal conductivity of water. The mixtures with water studied have compositions of 25, 50, and 75%, by weight. A recently proposed semiempirical scheme for the prediction of the thermal conductivity of pure liquids is extended to allow the prediction of the thermal conductivity of these mixtures from the pure components, as a function of both composition and temperature.

KEY WORDS: ethylene glycol; mixtures; propylene glycol; thermal conductivity; transient hot-wire technique; water.

1. INTRODUCTION

In recent years, there has been a growing interest in the application of solar energy for domestic environmental control, particularly in the countries of Southern Europe. The design of equipment for this purpose requires a knowledge of the thermal conductivity of the working fluids employed which adds to a growing demand for this type of information from the chemical industry. One of the most common applications of solar energy is for solar heating, which in the last decades has found extensive use as an

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[1] Department of Chemical Engineering, Aristotle University, GR54006 Thessaloniki, Greece.

[2] Permanent address: Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2BY, United Kingdom.

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alternative, inexpensive way of heating. The most common fluids used in solar heating equipment as the heat transfer medium are mixtures of ethylene or propylene glycol with water. These mixtures display a high thermal conductivity as well as a depression of the freezing point of water. For the latter reason the same mixtures are also used as antifreeze in car engines, with the addition of small quantities of inhibitors (generally phenols or aromatic amines) to prevent oxidation to acids. However, the thermal conductivity data for ethylene and propylene glycol and their mixtures with water found in literature display a wide discrepancy.

In this paper, new absolute measurements of the thermal conductivity of ethylene and propylene glycol mixtures with water are presented. The measurements have subsequently been used to develop a consistent correlation scheme, for the prediction of the thermal conductivity of these mixtures.

2. EXPERIMENTAL

In a series of recent papers [1–3], a computer-controlled transient hot-wire instrument has been described, and measurements of the thermal conductivity of water [2] and the alcohols, methanol to hexanol [2, 3], have been presented. The measurements were estimated to have an associated uncertainty of ±0.5%. For the heat source two anodized tantalum wires of 25 μm diameter were used in order to prevent polarization of the electrically conducting liquids, and for the present measurements the instrument has been employed unaltered. The measurements were carried out at atmospheric pressure and within the temperature range 295–360 K.

The methods of operation and data analysis remained as before [1], in particular the method of treating the effect of radiative heat transport adopted is the same as that proposed by Li et al. [4] and de Castro et al. [5]. As a check of the continuing good operation of the instrument, water was measured before and after each liquid. The values obtained for water were in full agreement with those reported earlier [2]. The samples of ethylene and propylene glycols were supplied by B.D.H. Chemicals, and after long treatment with molecular sieves, their purity was found to be better than 99.8%. To reduce further intake of moisture the cell was filled under vacuum. The mixtures were prepared gravitationally and the uncertainty in the composition was less than 0.005%. For each system three compositions were studied containing 25, 50, and 75% by weight of the glycol.

3. RESULTS

Tables I and II list the experimental thermal conductivity values of ethylene glycol, propylene glycol, and their mixtures with water. All of the measurements were performed at atmospheric pressure. The measured thermal conductivity values, λ, at constant pressure were fitted as a function of the absolute temperature, T, to the linear function

$$\lambda = \alpha_0 + \alpha_1 T \tag{1}$$

The values of the coefficients α_0 and α_1, for the pure components and the mixtures, are shown in Table III together with their variances and the standard deviation of the fits. It can be seen that the standard deviation of the fits amounts to ±0.2%. Figures 1 and 2, show plots of the deviations of the experimental data from Eq. (1) for pure ethylene and propylene glycol, respectively. The maximum deviation of the present measurements from the equation is ±0.35% for both liquids. In the same figures, the deviations of other investigators' data from the correlation of Eq. (1) are shown. It can be seen that the earlier values depart from the present correlation by as much as ±10%. Mallan [6] and Grassman et al. [7] also used a transient hot-wire technique, however, they did not have access to the full theory of the method so that their measurements were performed on a relative basis. Nevertheless, the measurements of Mallan show a deviation of only 1% from the present work, while those of Grassman et al. lie about 1.5% above the present values. All other measurements [8–19] were obtained in steady-state instruments, and in some cases, at least, the data reveal the disadvantages associated with such techniques.

The quality of the existing thermal conductivity data for the mixtures of ethylene and propylene glycol with water is even poorer. Figure 3 contains a plot of the deviations of the thermal conductivity data of other investigators at 290 and 330 K for mixtures of ethylene glycol with water from the present results. Figure 4 shows the corresponding deviations for the propylene glycol–water system. The data of other authors have been interpolated in order to prepare these plots, but the additional error introduced is estimated to be no more than ±0.5%. From these figures it can be seen that deviations of the earlier data rise to as much as 15%, for the measurements of Bates and Hazzard [18], whereas the values reported by Riedel [8] and Vanderkooi et al. [19] are within 6–7% of the present measurements. The superior accuracy of the present results argues that they are to be preferred.

Table I. The Thermal Conductivity of Ethylene Glycol and Its Mixtures with Water as a Function of Temperature at Atmospheric Pressure (Compositions in Weight Percentage of Ethylene Glycol)

100%		75%		50%		25%	
T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)
296.62	249.0	296.21	306.4	297.40	389.1	297.38	480.0
302.55	250.2	301.69	310.6	301.92	392.6	298.29	482.7
308.95	251.5	308.48	313.7	307.97	398.0	301.89	487.7
315.03	253.1	313.83	317.4	313.47	402.6	307.79	496.8
321.15	253.8	324.03	322.7	319.47	407.1	313.25	503.2
327.60	256.1	328.03	324.8	325.83	412.7	318.63	508.1
333.79	258.7	334.72	329.0	329.47	417.0	319.46	511.3
340.26	259.1	341.22	331.7	336.26	422.0	324.59	516.0
346.80	262.0	348.84	335.9	342.01	425.1	329.90	525.4
355.33	262.9	355.10	338.6	347.57	429.2	335.52	529.2

Table II. The Thermal Conductivity of Propylene Glycol and Its Mixtures with Water as a Function of Temperature at Atmospheric Pressure (Compositions in Weight Percentage of Propylene Glycol)

100%		75%		50%		25%	
T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)
297.79	201.5	296.60	257.7	295.94	354.2	297.27	465.5
303.95	202.8	303.01	260.5	302.14	360.9	304.02	472.0
311.26	204.0	308.64	263.1	308.47	366.5	309.35	481.5
317.96	205.9	317.71	267.1	315.81	372.4	316.79	489.3
324.72	207.0	324.46	269.3	316.73	372.9	320.07	493.9
331.89	208.5	331.76	274.5	324.35	380.0	324.55	500.8
337.59	210.6	338.39	276.2	330.13	383.7	331.18	507.8
345.50	211.6	344.70	278.8	337.42	388.6	337.70	515.7
353.16	212.4			345.07	395.2		

Table III. Coefficients of the Least-Squares Straight-Line Fit of the Thermal Conductivity as a Function of Temperature (Compositions in Weight Percentage)

	α_0 ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	α_1 ($\mathrm{\mu W \cdot m^{-1} \cdot K^{-1}}$)	σ (%)
Ethylene glycol/water (weight percentage of ethylene glycol)			
100%	174.41 ± 3.2	250 ± 9	±0.2
75%	146.27 ± 2.8	544 ± 8	±0.1
50%	146.77 ± 4.7	816 ± 10	±0.2
25%	98.16 ± 9.8	1290 ± 30	±0.2
0%	209.20 ± 15.4	1342 ± 48	±0.2
Propylene glycol/water (weight percentage of propylene glycol)			
100%	139.62 ± 2.3	208 ± 7	±0.2
75%	125.63 ± 3.9	445 ± 12	±0.2
50%	114.48 ± 5.8	815 ± 18	±0.2
25%	88.68 ± 8.4	1266 ± 26	±0.2
0%	209.20 ± 15.4	1342 ± 48	±0.2

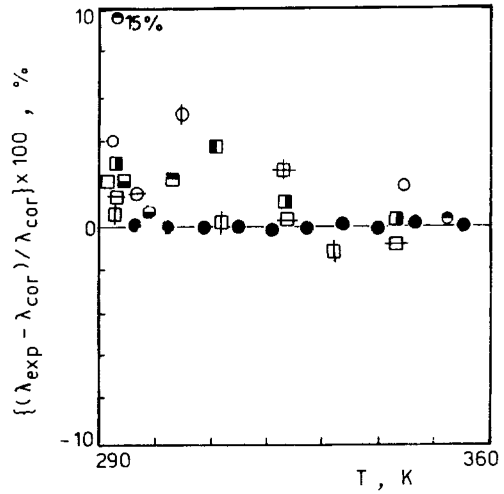

Fig. 1. Deviations of the experimental thermal conductivity values of ethylene glycol, from Eq. (1). (●) Present work; (⬓) Ref. 7; (◨) Ref. 8; (□) Ref. 9; (⊞) Ref. 10; (⏀) Ref. 11; (⊖) Ref. 12; (◒) Ref. 13; (⊟) Ref. 14; (⊞) Ref. 15; (⬒) Ref. 16; (◨) Ref. 17; (◓) Ref. 18; (○) Ref. 19.

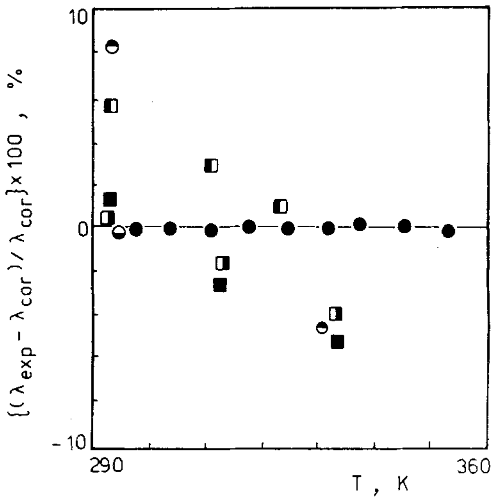

Fig. 2. Deviations of the experimental thermal conductivity values of propylene glycol, from Eq. (1). (●) Present work; (■) Ref. 6; (◨) Ref. 8; (◒) Ref. 13; (◧) Ref. 17; (◓) Ref. 18.

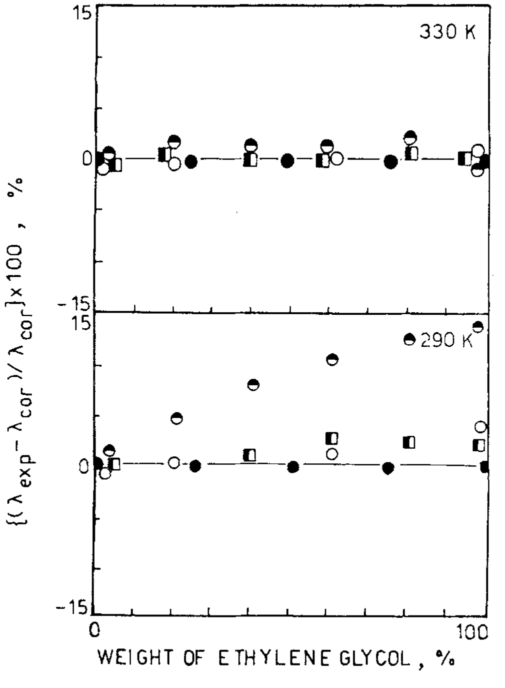

Fig. 3. Deviations of experimental thermal conductivity values of ethylene glycol/water mixtures, from the present work, at 290 and 330 K. (●) Present work; (◧) Ref. 8; (◓) Ref. 18; (○) Ref. 19.

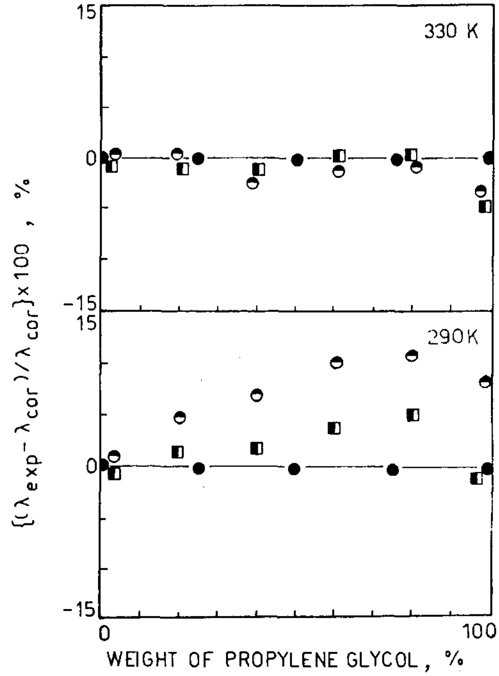

Fig. 4. Deviations of experimental thermal conductivity values of propylene glycol/Water mixtures, from the present work, at 290 and 330 K. (●) Present work; (◧) Ref. 8; (◒) Ref. 18.

4. REPRESENTATION OF THE MIXTURE THERMAL CONDUCTIVITY

In a series of recent papers [20–22] concerned with the application of the Enskog theory to the Van der Waals model of a dense fluid [23, 24], it has been shown that the experimental quantity (with all quantities measured in SI units)

$$\lambda^* = 1.9362 \times 10^7 (M/RT)^{1/2} \lambda V^{2/3} \tag{2}$$

for a particular liquid is a function only of the ratio of the molar volume, V to a characteristic molar volume V_0 [22], so that

$$\lambda^* = F(V/V_0) \tag{3}$$

Here, M is the molecular weight, R the gas constant, T the absolute temperature, and V_0 a characteristic molar volume displaying a weak dependence on temperature only. Equation (3) implies that it should be possible to superimpose plots of experimental curves of λ^* against $\ln V$ for a single fluid at a series of temperatures merely by imposing relative shifts along the $\ln V$ axis. Assigning a reference value to V_0 for one fluid at the lowest temperature for which accurate measurements of the thermal conductivity exist, the amount of shift required will produce the values of V_0 at every temperature. Li et al. [21] used the accurate measurements of 11 hydrocarbon liquids over the temperature range 110–370 K and for pressures up to 600 MPa to determine the function $F(V/V_0)$ of Eq. (3). The single curve of λ^* as a function of reduced molar volume can be represented by the equation,

$$\lambda^* = 4.8991 - 2.2595 \ln(V/V_0) \tag{4}$$

Adopting the hypothesis that the universality of the function λ^* extends beyond the normal alkanes, and in particular to the alkene glycols, Eqs. (2) and (4) may be employed to evaluate the characteristic molar volumes, V_0, for the two pure liquids studied here. The values of V_0 thus calculated can be represented as a function of the absolute temperature by the linear function,

$$V_0 = b_0 + b_1 T \tag{5}$$

The values of the coefficients b_0 and b_1 for ethylene glycol, propylene glycol, and water are shown in Table IV. Equations (2), (4), and (5) can be then used to correlate the pure components' thermal conductivities. In Fig. 5, the deviations of the present experimental thermal conductivities of the pure components from the correlation scheme of Eqs. (2), (4), and (5) are shown. The maximum deviation is less than ±0.35%.

According to the kinetic theory of hard-sphere fluid mixtures, the properties of the mixture are derived from the properties of the pure components and a characteristic volume of the interaction of unlike species [23]. However, a simpler approach is possible if a characteristic volume is

Table IV. Coefficients of the Least-Squares Straight-Line Fit of the Characteristic Molar Volume as a Function of Temperature, Eq. (5)

	b_0 ($10^{-6}\,\mathrm{m^3 \cdot mol^{-1}}$)	b_1 ($10^{-9}\,\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$)
Water	6.228	6.238
Ethylene glycol	25.44	18.44
Propylene glycol	32.07	33.72

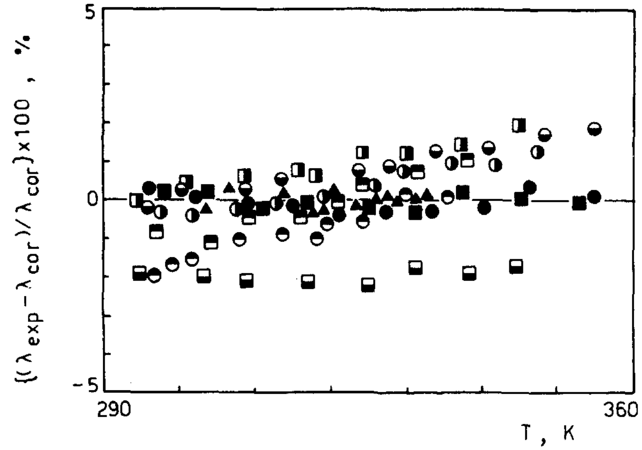

Fig. 5. Deviations of the experimental thermal conductivity values from the correlating scheme, Eqs. (2) and (4)–(6). (●) Ethylene glycol; (■) propylene glycol; (▲) water. Ethylene glycol/water: (◒) 75%; (◑) 50%; (◓) 25%. Propylene glycol/water: (⬓) 75% (◨) 50%; (⬒) 25%.

identified which represents the behavior of the entire mixture. Thus, we identify the mixture with a hypothetical pure fluid with a mole-fraction average molecular weight, a mass-fraction average density, and a characteristic molar volume V_0^{mix}. The characteristic molar volume V_0^{mix} is given by the mixing rule,

$$V_0^{\mathrm{mix}} = XV_0^{\mathrm{I}} + (1-X)\,V_0^{\mathrm{II}} - X(1-X)\,C \qquad (6)$$

where V_0^{I} and V_0^{II} are the characteristic molar volumes of the pure components, X the mole fraction of species I, and C a constant characteristic of the pure components but independent of temperature and composition. The value of C has to be determined from the experimental measurements of the mixture thermal conductivity and the pure components V_0, using Eqs. (2) and (4)–(6). The value of C was consequently found to be equal to $6.5 \times 10^{-6}\,\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$ for the ethylene glycol and water mixtures, and $10.7 \times 10^{-6}\,\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$ for the propylene glycol and water mixtures.

Figure 5 contains the deviations of the experimental thermal conductivities for the mixtures from those correlated by the scheme of Eqs. (2) and (4)–(6). The maximum deviation of any data point taken over all the mixtures is one of ±2.5%. This method of representation is simple to use and has the advantage that the value of C for a particular system can be determined from just one measurement of the thermal conductivity of a single mixture at one temperature. However, the scheme has no predictive power because the thermal conductivities of the pure components are necessary to derive the corresponding values of V_0^{I} and V_0^{II}.

5. PREDICTION

In a recent paper [22], a molecular group contribution-based scheme was developed for the *prediction* of the characteristic molar volume, V_0, for a wide range of liquids. The final equation for the total characteristic molar volume of the pure liquids, expressed as group contributions, is

$$V_0 = V_0^{\mathrm{N}} + V_0^{1\mathrm{B}} + V_0^{1\mathrm{OH}} + V_0^{2\mathrm{OH}} \tag{7}$$

where,

$$10^6 V_0^{\mathrm{N}}(\theta, n_{\mathrm{c}}) = \sum_{i=0}^{2} \sum_{j=0}^{3} a_{ij} n_{\mathrm{c}}^j \theta^i$$

$$10^6 V_0^{1\mathrm{B}}(\theta, n_{\mathrm{c}}) = \sum_{i=0}^{1} \sum_{j=0}^{1} b_{ij} n_{\mathrm{c}}^j \theta^i$$

$$10^6 V_0^{1\mathrm{OH}}(\theta, n_{\mathrm{c}}) = \sum_{i=0}^{1} \sum_{j=0}^{2} c_{ij} n_{\mathrm{c}}^j \theta^i$$

$$10^6 V_0^{2\mathrm{OH}}(n_{\mathrm{c}}) = \sum_{j=0}^{1} d_j n_{\mathrm{c}}^j$$

and

$$\theta = T/273.15$$

where θ is a nondimensional temperature defined for computational convenience and n_{c} is the total number of carbon atoms in the molecule. The values of the coefficients a_{ij}, b_{ij}, c_{ij}, and d_j are given in Table V. In this equation for the total characteristic molar volume, the first term represents the contribution to V_0 if the chain was a straight chain of n_{c} carbon atoms. The second term represents an additive contribution, if six of the carbon atoms were in a benzene ring arrangement. The third term represents an additive contribution for the case where one hydrogen atom is substituted by an OH^- group, while the fourth term refers to the case where a second OH^- group substitutes a second hydrogen atom. The scheme described by Eq. (7) and Eqs. (2) and (4) was shown to be able to predict values of the thermal conductivity of a wide range of liquids within $\pm 4\%$ in the temperature range 110–370 K and for pressures up to 600 MPa.

Table V. The Coefficients a_{ij}, b_{ij}, c_{ij}, and d_j of Eq. (7)

		$m^3 \cdot mol^{-1}$			
i	j	a_{ij}	b_{ij}	c_{ij}	d_j
0	0	+6.3918	−14.700	−0.1630	+4.40
0	1	+9.7389	−2.8280	−4.5280	+0.70
0	2	+0.84785	—	+0.7807	—
0	3	−0.013132	—	—	—
1	0	0	+8.1945	+1.7209	—
1	1	−4.57722	−0.52991	+4.4797	—
1	2	0	—	−0.69653	—
1	3	0	—	—	—
2	0	0	—	—	—
2	1	+1.40555	—	—	—
2	2	0	—	—	—
2	3	0	—	—	—

With the aid of this group contribution scheme, Eq. (7) can be used to obtain the characteristic molar volumes of the pure components directly without the need for measurements of the pure components properties. Subsequently, Eqs. (2), (4), and (6) can be employed to calculate the thermal conductivity of the mixtures by means of the same mixing rule as in Section 4. Figure 6 contains a plot of the deviations of the experimental thermal conductivities for the pure components and all of the mixtures

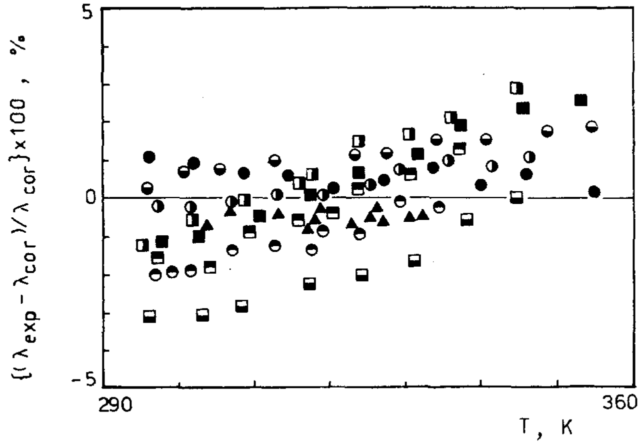

Fig. 6. Deviations of the experimental thermal conductivity values from the predictive scheme, Eqs. (2), (4), (6), and (7). (●) Ethylene glycol; (■) propylene glycol; (▲) water. Ethylene glycol/water: (◒) 75%; (◑) 50%; (◓) 25%. Propylene glycol/water: (⬓) 75%; (◨) 50%; (⬒) 25%.

from their predicted values. It can be seen that the maximum deviation is one of ±3.2%. Although greater than the experimental uncertainty the scheme offers a means of evaluating the thermal conductivity of liquid mixtures over a wide range of pressure, temperature, and composition, from just a measurement of the thermal conductivity of a single mixture of arbitrary composition.

6. CONCLUSIONS

New measurements of the thermal conductivity of ethylene glycol, propylene glycol, and their mixtures with water have been reported. The measurements were performed at atmospheric pressure in a tantalum-type transient hot-wire instrument, in the temperature range 290–360 K, with an uncertainty of ±0.5%.

A correlating scheme for the thermal conductivity of mixtures based on the experimental pure components' values has been developed. The scheme was found to correlate the thermal conductivity of the mixtures with an uncertainty of ±2.5%. An alternative representation with more predictive power, based on a recently developed molecular group contributions scheme, was found to represent the thermal conductivity of the mixtures with an uncertainty of ±3.2%.

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