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Absolute Measurements of the Thermal Conductivity of Mixtures of Alcohols with Water

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New absolute measurements of the thermal conductivity of mixtures of methanol, ethanol, and propanol with water are presented. The measurements were performed in a tantalum-type transient hot-wire instrument at atmospheric pressure, in the temperature range 300–345 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, of methanol and ethanol and 50%, by weight, of propanol. 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: ethanol; methanol; mixtures; propanol; thermal conductivity; transient hot-wire method; water.

1. INTRODUCTION

In the preceding paper [1], a new semiempirical scheme for the correlation and prediction of the thermal conductivity of a wide range of liquids is presented. The scheme is based on an extension of concepts derived from the rigid-sphere model of dense-fluid transport properties [2–6] and was developed as group contributions to the molecular volume. Predicted values of the thermal conductivity are shown to differ less than ±4% from accurate experimental values over the temperature range 110–370 K and at pressures up to 600 MPa.

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Few accurate measurements of the thermal conductivity of liquid mixtures exist. The present series of measurements was performed in order to examine the application of this scheme to mixtures.

2. EXPERIMENTAL

In a series of recent papers [7–9], a computer-controlled transient hot-wire instrument has been described, and measurements of the thermal conductivity of water [8] and the alcohols, methanol to hexanol [8, 9], have been presented. The measurements were shown to display an uncertainty of ±0.5%. For the heat source, two anodized tantalum wires of 25-μm diameter were used, in order to prevent polarization of 25-μm diameter were used, in order to prevent polarization of the electrically conducting liquids. For the present measurements, the instrument has been employed unaltered. The measurements were carried out at atmospheric pressure and the temperature range examined was 300–345 K. The method of treating the effect of radiative heat transport adopted is the same as that proposed by Li et al. [10] and Nieto de Castro et al. [11]. 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 [8].

The samples of the alcohols were supplied by B.D.H. Chemicals Ltd. with a nominal purity of 99.8% for methanol, 99.7% for ethanol, and 99.8% for propanol. These samples were treated for a long period of time with molecular sieves to reduce the water content. Consequent gas chromatography analysis showed a purity of better then 99.9% for all alcohols. The sample of water used was also supplied by the same company (HPLC grade). The mixtures were prepared gravitationally and the uncertainty in the composition was less than 0.005%. Three compositions for methanol and ethanol mixtures with water were studied, 25, 50, and 75%, by weight. In the case of propanol and water mixture, a 50%, by weight, composition was examined.

3. RESULTS

In Tables I, II, and III the experimental thermal conductivity values of methanol, ethanol, propanol, and their mixtures with water are presented. The pure-component values have been reported in earlier papers [8, 9] and are included here only for comparison purposes. All measurements were performed at atmospheric pressure and the temperature range examined was 300 to 345 K. The measured thermal conductivity values,

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

100%		75%		50%		25%	
T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})
301.30	198.3	304.03	261.2	304.26	342.8	305.19	453.6
304.28	197.8	307.10	262.3	308.02	344.9	308.83	459.4
306.32	197.4	310.70	262.6	311.18	346.4	311.02	461.1
310.37	197.5	313.71	263.9	315.33	348.5	315.21	467.8
313.07	197.1	317.25	264.2	317.85	350.5	319.64	472.5
316.01	197.4	320.32	265.2	320.59	352.3	323.45	477.2
318.97	196.9	323.67	265.5	326.72	357.0	326.29	480.3
323.07	196.0	326.56	267.5	328.92	358.4	328.59	483.2
325.41	196.4						

λ, were fitted as a function of the absolute temperature, T, to the linear function

$$\lambda = \alpha_0 + \alpha_1 T \qquad (1)$$

The values of the coefficients α_0 and α_1, for the pure components and the mixtures, are shown is Table IV together with their variances and the

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

100%		75%		50%		25%	
T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})
305.74	160.7	300.98	227.0	302.12	311.5	301.52	434.9
311.13	160.0	307.46	228.5	305.80	314.5	306.17	440.5
312.69	160.1	310.48	228.5	310.13	315.9	310.20	444.7
316.15	159.6	315.79	229.2	315.57	318.5	315.57	451.7
319.87	159.1	318.68	228.3	320.07	320.6	319.67	455.2
323.96	159.0	322.3	228.9	325.51	322.9	322.54	459.4
325.82	158.8	326.27	230.1	333.16	326.1	327.64	465.1
328.95	159.0	327.67	229.8	336.17	326.8	332.61	472.7
331.43	158.3	332.54	230.6	339.03	328.8		
335.06	158.0						

Table III. The Thermal Conductivity of Mixtures of Propanol and Water as a Function of Temperature at Atmospheric Pressure (Compositions in Weight Percentage of Propanol)

100%		50%		0%	
T (K)	λ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	T (K)	λ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	T (K)	λ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)
300.44	149.1	307.10	312.3	303.85	614.4
304.59	148.9	310.16	314.3	306.98	623.3
309.87	148.0	313.09	316.3	313.56	631.3
312.18	148.2	316.35	318.6	317.75	635.0
316.12	147.4	319.96	320.3	318.79	635.7
322.01	147.3	323.36	322.0	319.81	640.6
326.43	146.0	331.46	326.0	323.50	642.7
331.22	146.0	334.82	328.5	325.74	646.7
335.26	145.4			326.79	648.9
340.74	145.6			327.51	648.0
				330.79	652.7
				332.71	655.3

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

	α_0 ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	α_1 ($\mathrm{\mu W \cdot m^{-1} \cdot K^{-1}}$)	σ (%)
Methanol/water			
100%	220.7 ± 3.7	−75 ± 11	±0.1
75%	185.5 ± 6.2	249 ± 20	±0.1
50%	147.6 ± 7.2	639 ± 23	±0.1
25%	73.7 ± 7.9	1247 ± 24	±0.1
0%	209.2 ± 15.4	1342 ± 48	±0.2
Ethanol/water			
100%	186.4 ± 2.2	−84 ± 6	±0.1
75%	198.7 ± 5.0	95 ± 15	±0.2
50%	178.5 ± 3.8	443 ± 12	±0.1
25%	75.8 ± 7.5	1190 ± 24	±0.1
0%	209.2 ± 15.4	1342 ± 48	±0.2
Propanol/water			
100%	179.2 ± 2.4	−100 ± 7	±0.2
50%	139.2 ± 4.9	565 ± 15	±0.1
0%	209.2 ± 15.4	1342 ± 48	±0.2

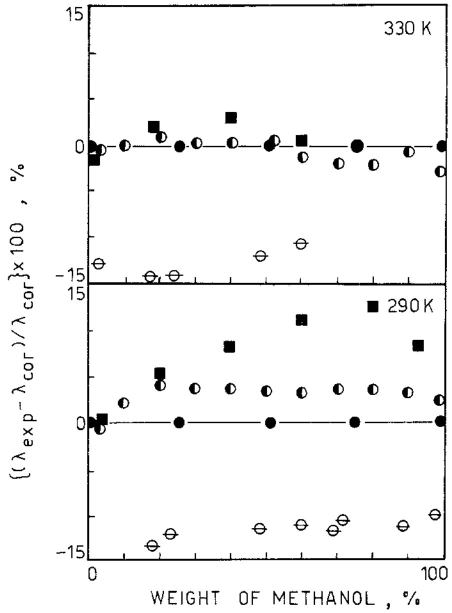

Fig. 1. Deviations of experimental thermal conductivity values of methanol/water mixtures, from the present work, at 290 and 330 K. (●) Present work; (■) Ref. 12; (—⊖—) Ref. 13; (◐) Ref. 14.

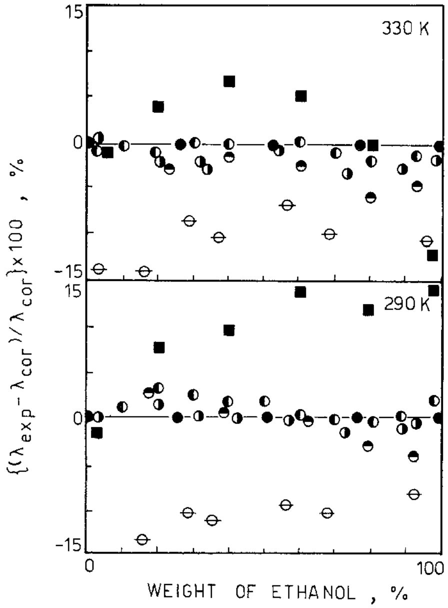

Fig. 2. Deviations of experimental thermal conductivity values of ethanol/water mixtures, from the present work, at 290 and 330 K. (●) Present work; (■) Ref. 12; (—⊖—) Ref. 13; (◐) Ref. 14; (◑) Ref. 15; (◓) Ref. 16.

standard deviations of the fits. It can be seen that the standard deviation of the fits is less than ±0.2%. Figure 1 shows a plot of the deviations of the thermal conductivity of other investigators at 290 and 330 K for mixtures of methanol with water, from the present work. Figure 2 shows the deviations for ethanol–water mixtures. The apparatuses used by these investigators were all steady state-type instruments. To prepare these plots, a small amount of interpolation was used for the other investigators, producing an error of about ±0.5%. It can be seen in these figures that deviations extend to ±15%, in the measurements of Bates and Hazzard [12] and Filippov [13]. The values of Riedel [14], Tsedeberg [15], and Popov and Malov [16] are within ±5% of the present measurements. In the case of the 50%, by weight, propanol–water mixture, the values of Riedel [14] are within ±3% of the present measurements.

4. REPRESENTATION OF THE MIXTURE THERMAL CONDUCTIVITY

In a series of recent papers [2–4] on concepts related to the application of the Enskog theory to the van der Waals model of a dense fluid [5, 6], it has been shown that the experimental quantity,

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

for a particular liquid is a function only of the ratio of the molar volume, V, to a characteristic molar volume V_0 [4], 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. [3] 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,

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

Adopting the hypothesis that the universality of the function λ^* extends beyond the normal alkanes, and in particular to the alcohols, Eqs. (2) and (4) may be employed to evaluate the characteristic molar volumes, V_0, for the 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 methanol, ethanol, propanol and water have been reported earlier [4] and are shown in Table V.

In order to correlate the mixtures thermal conductivity, the procedure adopted was the one used to correlate our earlier measurements of mixtures of ethylene and propylene glycols with water [17]. According to this procedure, it was been postulated that the mixture will be an equivalent liquid with a mole fraction average molecular weight, a mass fraction average density, and a characteristic molar volume, V_0^{mix}, given by the following mixing rule;

$$V_0^{\text{mix}} = X V_0^{\text{I}} + (1 - X)\, V_0^{\text{II}} - X(1 - X)\, C \tag{6}$$

where V_0^{I} and V_0^{II} are the characteristic molar volumes of the pure components, and X is the molar fraction. C was found to be a constant characteristic of the pure components, independent of temperature and composition, and determined by the experimental measurements. The value of C was consequently found to be equal to $0.75 \times 10^{-6}\ \text{m}^3 \cdot \text{mol}^{-1}$ for the methanol water mixtures, $2.75 \times 10^{-6}\ \text{m}^3 \cdot \text{mol}^{-1}$ for the ethanol water mixtures and $5.5 \times 10^{-6}\ \text{m}^3 \cdot \text{mol}^{-1}$ for the propanol water mixture. In Fig. 3 the deviations of the experimental thermal conductivities of the mixtures from those correlated by the scheme of Eq. (2) and Eqs. (4)–(6) are shown. It can be seen that the maximum deviation of all mixtures is one of ±2.2%. The advantages of this scheme is that it is simple to use and

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

	b_0 $(10^{-6}\ \text{m}^3 \cdot \text{mol}^{-1})$	b_1 $(10^{-9}\ \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
Water	6.228	6.238
Methanol	12.495	1.187
Ethanol	20.762	1.556
Propanol	31.222	1.568

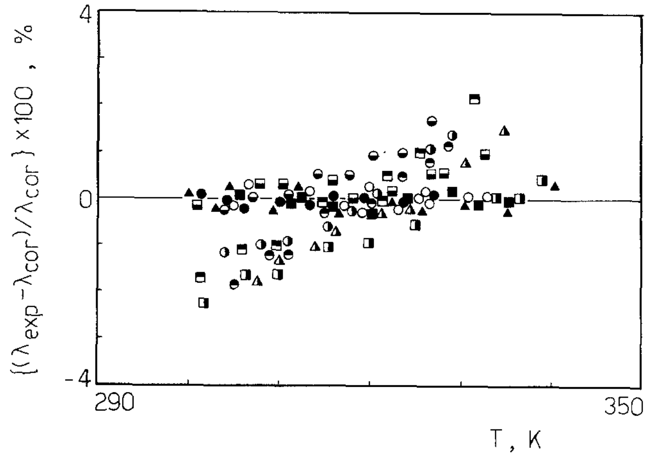

Fig. 3. Deviations of the experimental thermal conductivity values from the correlating scheme, Eq. (2) and Eqs. (4)–(6). (●) Methanol; (■) ethanol; (▲) propanol; (○) water. Methanol/water: (◒) 75%; (◑) 50%; (◓) 25%. Ethanol/water: (⬓) 75%; (◨) 50%; (⬒) 25%. Propanol/water: (△) 50%.

the value of C for a particular mixture can be determined from just one measurement of the thermal conductivity of a single mixture at one temperature. Furthermore, it seems that it might be possible to correlate the values of the constant C. This scheme, however, 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 [4], 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

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

where

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

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

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

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

and

$$\theta = T/273.15$$

where θ is a nondimensional temperature defined for computational convinience 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 VI. In this equation for the total characteristic molar volume, the first term represents the contribution to V_0 if the chain were 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 is reffered 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 within ±4% in the temperature range 110–370 K and for pressures up to 600 MPa.

Applying 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.

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

		$\mathrm{m^3 \cdot mol^{-1}}$			
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	—	—	—

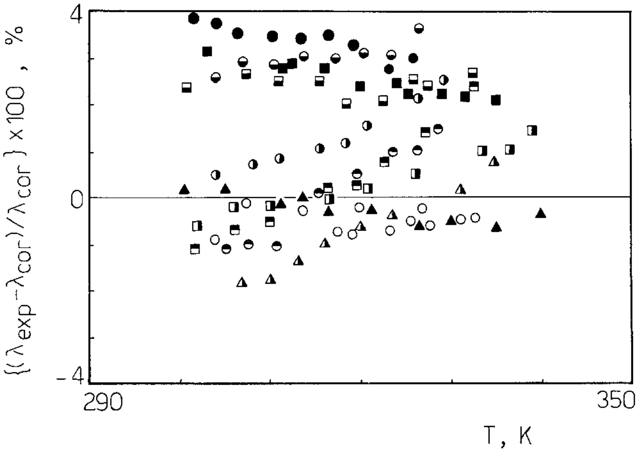

Fig. 4. Deviations of the experimental thermal conductivity values from the predictive scheme, Eqs. (2), (4), (6), and (7). (●) Methanol; (■) ethanol; (▲) propanol; (○) water. Methanol/water: (◒) 75%; (◑) 50%; (◓) 25%. Ethanol/water: (⬓) 75%; (◨) 50%; (⬒) 25%. Propanol/water: (△) 50%.

Subsequently, Eqs. (2), (4), and (6) can be employed to calculate the thermal conductivity of the mixtures applying the same mixing rule as in the previous section. The same values of the constant *C* were found to fit the experimental data best. Figure 4 shows the deviations of the experimental thermal conductivities of the pure components and the mixtures from their predicted values. It can be seen that the maximum deviation is $\pm 4\%$. The advantage of this scheme in relation to the previous one discussed is that measurements of the thermal conductivity of the pure components are not required. Just a single measurement of a mixture at one temperature is required to calculate the value of the constant *C* in Eq. (6), although for mixtures of compounds in a homologous chemical series, it seems that it should be possible to correlate the value of this constant.

6. CONCLUSIONS

New measurements of the thermal conductivity of the mixtures of methanol, ethanol, and propanol with water are reported. The measurements were performed at atmospheric pressure in a tantalum-type transient hot-wire instrument, in the temperature range 300–345 K, with an uncertainty of $\pm 0.5\%$.

A correlating scheme for the thermal conductivity of mixtures based on the experimental pure components values was examined. The scheme was found to correlate the thermal conductivity of the mixtures with an uncertainty of ±2.2%. An alternative representation with more predictive power, based on a recently developed molecular-group contribution scheme, was found to represent the thermal conductivity of the mixtures with an uncertainty of ±4%.

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