

Absolute Measurement of the Thermal Conductivity of Alcohol + *n*-Hexane Mixtures

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New absolute measurements, by the transient hot-wire technique, of the thermal conductivity of binary mixtures of *n*-hexane with methanol, ethanol, and hexanol are presented. The temperature range examined was 295–345 K and the pressure atmospheric. The concentrations studied were 75% by weight of methanol and 25, 50, and 75% by weight of ethanol and hexanol. The overall uncertainty in the reported thermal conductivity data is estimated to be $\pm 0.5\%$, an estimate confirmed by the measurement of the thermal conductivity of water. A recently extended semiempirical scheme for the prediction of the thermal conductivity of mixtures from the pure components is used to correlate and predict the thermal conductivity of these mixtures, as a function of both composition and temperature.

KEY WORDS: ethanol; methanol; mixtures; *n*-hexane; *n*-hexanol; thermal conductivity; transient hot-wire technique.

1. INTRODUCTION

In recent years, the sharp reduction of lead in gasolines led to the development of a growing number of processes in which alcohols and alkanes coexist to produce oxygenated additives for gasoline. These oxygenated products usually include methanol, ethanol, and mixtures of higher alcohols [1]. Methanol, the cost of which fluctuates at the level of premium-grade gasoline, presents the drawback of increasing the vapor pressure of the gasolines due to the existence of azeotropes with the hydrocarbons. Ethanol, although not yet competitive, may be preferable for political and economic reasons of energy self-sufficiency or for the use of surplus agriculture materials containing sugars, starch, and cellulose.

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More recently, the use of a mixture of higher alcohols than methanol has been one of the latest research objectives and could be resorted to in the event of another sharp rise in the cost of oil. Depending on the process, the hydrocarbons coexisting with the alcohols play the role of azeotropic agent, selective extraction solvent, or heat transfer fluid [1]. Data on the vapor-liquid equilibrium and the thermal conductivity of such mixtures are still very scarce.

For the specific study of the vapor-liquid equilibria of these mixtures, the Subcommittee on Thermodynamic Data of the International Union of Pure and Applied Chemistry in its Third Workshop Meeting in Budapest in 1987 decided to concentrate on five "key mixtures." These key mixtures were methanol, ethanol, and hexanol with *n*-hexane, ethanol with *n*-hexadecane, and butanol with *n*-decane and were typically selected as they display different types of hydrogen bonding and different sizes of molecules.

Accurate experimental measurements of the thermal conductivity of these mixtures are not available. Moreover, the measurements of this thermal conductivity will add to the very few accurate data existing on these mixtures, accuracy required for the development and testing of the few semiempirical schemes available today for the prediction of this property.

In this paper, accurate absolute measurements of the thermal conductivity of binary mixtures of *n*-hexane with methanol, ethanol, and hexanol are presented. The temperature range studied was 295–345 K and the pressure atmospheric.

2. EXPERIMENTAL

The technique employed in these measurements was the transient hot-wire technique with two anodized tantalum wires as the heat source. The instrument employed in these measurements has been described in detail elsewhere [2, 3]. The instrument was used unchanged for the present series of measurements which extend over a temperature range 295–345 K at atmospheric pressure. The usual experimental procedures were adopted, and measurements of the thermal conductivity of water were carried out to confirm the continued good operation of the equipment by comparison with our earlier results [3]. The samples of the liquids used were all supplied by B.D.H. Chemicals Ltd., with a nominal purity of 99.0% for *n*-hexane, 99.8% for methanol, 99.7% for ethanol, and 98.0% for hexanol. To increase their purity, the liquids were treated for a long period of time with molecular sieves. The mixtures were prepared gravimetrically and the uncertainty in their composition was less than 0.005%. The compositions studied, expressed as the weight percentage of the alcohol in the alcohol +

n-hexane mixtures, were 75% of methanol (mole fraction 0.890), 25, 50, and 75% of ethanol (mole fractions 0.384, 0.651, and 0.849, respectively), and 25, 50, and 75% of hexanol (mole fractions 0.219, 0.458, and 0.717, respectively). The study of methanol + *n*-hexane was restricted to only one concentration due to the immiscibility of this mixture at lower concentrations in the temperature range examined.

3. RESULTS

The overall uncertainty in the reported thermal conductivity measurements is estimated to be better than $\pm 0.5\%$, an estimate which is confirmed by measuring water after every mixture [3]. Tables I, II, and III show the experimental thermal conductivity values of each mixture at atmospheric pressure as a function of temperature. The thermal conductivity values for each mixture have been represented by a linear function of the absolute temperature T , as

$$\lambda = \lambda_0[1 + \alpha(T - 298.15)] \quad (1)$$

where λ_0 is the thermal conductivity at 298.15 K extrapolated (or interpolated) from the experimental values, and α the linear thermal conductivity gradient for the temperature region studied. The values of λ_0 and α for each mixture are shown in Table IV. The corresponding values of our earlier measurements of the thermal conductivity of methanol, ethanol,

Table I. The Thermal Conductivity of Methanol + *n*-Hexane Mixture as a Function of Temperature at Atmospheric Pressure (Concentrations in Weight Percentage of Methanol)

75% Methanol	
T (K)	λ (mW · m ⁻¹ · K ⁻¹)
299.34	166.6
301.90	165.3
305.59	165.3
308.73	164.7
311.72	164.2
316.52	163.6
318.63	163.4
320.57	163.1
324.19	162.2

Table II. The Thermal Conductivity of Ethanol + *n*-Hexane Mixtures as a Function of Temperature at Atmospheric Pressure (Concentrations in Weight Percentage of Ethanol)

25% Ethanol		50% Ethanol		75% Ethanol	
<i>T</i> (K)	λ (mW · m ⁻¹ · K ⁻¹)	<i>T</i> (K)	λ (mW · m ⁻¹ · K ⁻¹)	<i>T</i> (K)	λ (mW · m ⁻¹ · K ⁻¹)
298.13	121.1	297.91	131.5	298.11	145.4
303.04	119.9	301.86	130.8	301.60	144.3
306.70	118.8	305.12	130.7	303.65	144.6
310.68	117.6	308.42	129.7	307.04	143.9
315.02	116.5	311.32	129.5	310.68	143.0
323.19	115.3	312.13	129.1	313.88	142.3
324.31	114.7	315.47	129.2	318.26	142.0
328.67	114.5	321.04	127.9	322.07	141.3
		323.97	127.9	323.70	141.2
		326.68	127.3	326.16	140.9
				329.19	139.9

hexanol [4], and *n*-hexane [5] are also shown for comparison purposes. In the same table the absolute standard deviations of the fits are also displayed. It can be seen that the maximum standard deviation of the present measurements is $\pm 0.22\%$. Figure 1 shows the deviations of the present measurements from Eq. (1). It can be seen that the maximum deviation is 0.3%. Comparison of the present experimental measurements with those of other investigators cannot be performed as, to our knowledge, the thermal conductivity of these mixtures has not been measured again.

Table III. The Thermal Conductivity of Hexanol + *n*-Hexane Mixtures as a Function of Temperature at Atmospheric Pressure (Concentrations in Weight Percentage of Hexanol)

25% Hexanol		50% Hexanol		75% Hexanol	
<i>T</i> (K)	λ (mW · m ⁻¹ · K ⁻¹)	<i>T</i> (K)	λ (mW · m ⁻¹ · K ⁻¹)	<i>T</i> (K)	λ (mW · m ⁻¹ · K ⁻¹)
297.64	124.9	297.82	132.3	295.90	138.6
301.00	124.3	301.40	131.8	301.42	137.6
304.65	123.5	305.00	131.6	306.89	136.8
310.11	122.7	309.68	130.6	312.12	136.1
314.00	121.8	317.66	129.7	316.57	135.5
318.36	121.2	324.27	128.8	322.00	134.7
323.47	120.6	329.67	128.7	325.81	134.0
328.27	119.9	339.44	127.3	335.26	132.8
		342.59	126.9		

Table IV. Coefficients of the Least-Squares Straight-Line Fit of the Thermal Conductivity of Alcohol + *n*-Hexane Mixtures as a Function of Temperature, Eq. (1) (Concentrations in Weight Percentage of Alcohol)

	λ_0 (mW · m ⁻¹ · K ⁻¹)	α (10 ⁻³ K ⁻¹)	σ (%)
0% Methanol	120.58	-2.639 ± 0.050	± 0.14
75% Methanol	166.37	-0.917 ± 0.060	± 0.15
100% Methanol	198.32	-0.378 ± 0.050	± 0.13
0% Ethanol	120.58	-2.639 ± 0.050	± 0.14
25% Ethanol	120.78	-1.848 ± 0.100	± 0.22
50% Ethanol	131.42	-1.099 ± 0.053	± 0.15
75% Ethanol	145.22	-1.116 ± 0.050	± 0.16
100% Ethanol	161.21	-0.525 ± 0.043	± 0.11
0% Hexanol	120.58	-2.639 ± 0.050	± 0.14
25% Hexanol	124.78	-1.322 ± 0.050	± 0.12
50% Hexanol	132.29	-0.899 ± 0.033	± 0.15
75% Hexanol	138.17	-1.057 ± 0.019	± 0.06
100% Hexanol	144.71	-1.327 ± 0.050	± 0.18

4. DISCUSSION

In a series of recent papers [4, 6], a semiempirical scheme for the prediction of the thermal conductivity of a wide range of liquids was developed. According to this scheme, based on concepts related to the

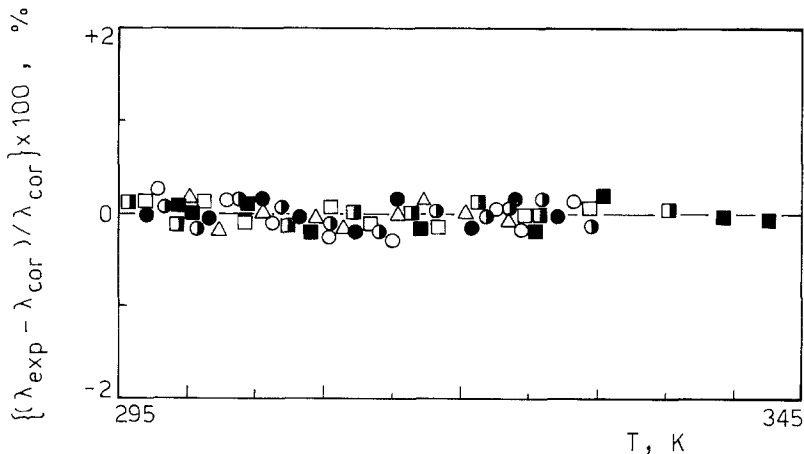


Fig. 1. Deviations of the experimental thermal conductivity values from Eq. (1). Methanol + *n*-hexane mixture: (Δ) 75%. Ethanol + *n*-hexane mixtures: (\circ) 25%; (\bullet) 50%; (\bullet) 75%. Hexanol + *n*-hexane mixtures: (\square) 25%; (\blacksquare) 50%; (\blacksquare) 75%.

application of the Enskog theory to the van der Waals model of a dense fluid [6–9], the experimental quantity

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

for a particular liquid is a function only of the ratio of the molar volume, V , to a characteristic molar volume V_0 [6]. Here, M represents the molar mass, R the universal gas constant, and T the absolute temperature. The dependence of λ^* on the ratio V/V_0 was found to be universal [6–8] and was represented by the equation

$$\ln \lambda^* = 4.8991 - 2.2595 \ln(V/V_0) \quad (3)$$

Adopting the hypothesis that the universality of the function λ^* extends beyond the normal alkanes, Eqs. (2) and (3) were employed to evaluate the characteristic molar volume, V_0 , of a wide range of pure liquids. The final equation for the characteristic molar volume, V_0 , expressed as molecular-group contributions, is [6]

$$V_0 = V_0^N + V_0^{1B} + V_0^{1OH} + V_0^{2OH} \quad (4)$$

where

$$\begin{aligned} 10^6 V_0^N(\theta, n_c) &= \sum_{i=0}^2 \sum_{j=0}^3 a_{ij} n_c^j \theta^i \\ 10^6 V_0^{1B}(\theta, n_c) &= \sum_{i=0}^1 \sum_{j=0}^1 b_{ij} n_c^j \theta^i \\ 10^6 V_0^{1OH}(\theta, n_c) &= \sum_{i=0}^1 \sum_{j=0}^2 c_{ij} n_c^j \theta^i \\ 10^6 V_0^{2OH}(n_c) &= \sum_{j=0}^1 d_j n_c^j \end{aligned}$$

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 is a straight chain of n_c carbon atoms. The second term represents an additive contribution, if six of the carbon

Table V. The Coefficients a_{ij} , b_{ij} , c_{ij} , and d_j of Eq. (4) in $\text{m}^3 \cdot \text{mol}^{-1}$

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	—	—	—

atoms are in a benzene ring arrangement. The third term represents an additive contribution for the case where one hydrogen atom is replaced by an OH group, while the fourth term refers to the case where a second OH group substitutes for a second hydrogen atom. The scheme described by Eqs. (2), (3), and (4) was shown [6] to be able to predict values of the thermal conductivity within $\pm 4\%$ in the temperature range 110–370 K and for pressures up to 600 MPa.

In order to correlate the mixtures' thermal conductivities, the procedure adopted was the one used to correlate our earlier measurements of mixtures of alcohols and glycols with water [10, 11]. According to this procedure, it was 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:

$$V_0^{\text{mix}} = XV_0^I + (1 - X)V_0^{II} - X(1 - X)C \quad (5)$$

where V_0^I and V_0^{II} are the characteristic molar volumes of the pure components, and X 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 $15.3 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ in the case of the methanol + n -hexane mixtures, $9.6 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ for the ethanol + n -hexane mixtures, and $-8.3 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ for the hexanol + n -hexane mixtures. In Fig. 2 the deviations of the experimental thermal conductivities of the mixtures from those correlated by the scheme of Eqs. (2)–(5) are shown. It can be seen that the maximum deviation of all

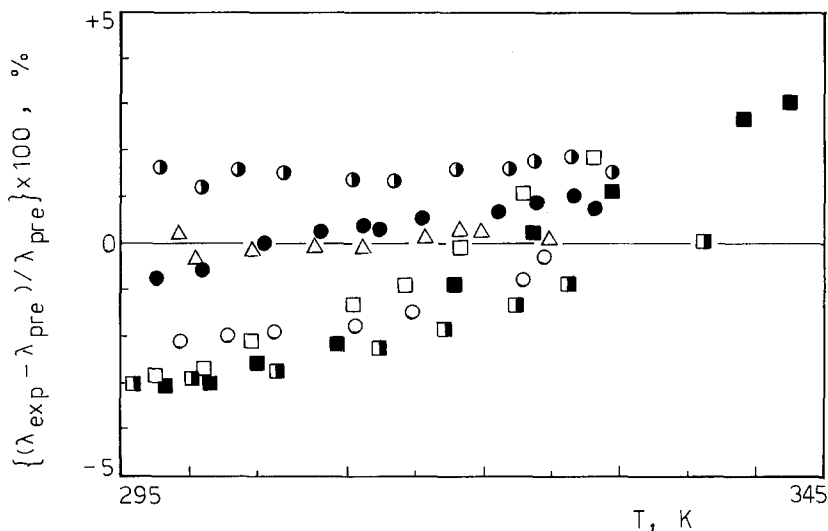


Fig. 2. Deviations of the experimental thermal conductivity values from the predictive scheme, Eqs. (2)–(5). Methanol + *n*-hexane mixture: (Δ) 75%. Ethanol + *n*-hexane mixtures: (\circ) 25%; (\bullet) 50%; (\ominus) 75%. Hexanol + *n*-hexane mixtures: (\square) 25%; (\blacksquare), 50%; (\blacksquare) 75%.

mixtures is $\pm 3\%$. Thus, as in the case of the alcohols + water mixtures [10] and the glycols + water mixtures [11], this scheme was found very useful in correlating or predicting the values of the thermal conductivity of the mixtures. The advantages of this scheme is that it is simple to use, and 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. (5), although for mixtures of compounds in an homologous chemical series, it seems that it should be possible to correlate the value of this constant.

5. CONCLUSIONS

New absolute measurements of the thermal conductivities of binary mixtures of methanol, ethanol, and hexanol with *n*-hexane are reported in the temperature range 295–345 K at atmospheric pressure, with an estimated uncertainty of $\pm 0.5\%$.

A recently developed correlative scheme for the thermal conductivity of mixtures, based on molecular-group contribution ideas, was found to represent the thermal conductivity of the mixtures with an uncertainty of $\pm 3\%$.

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