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The Thermal Conductivity of Liquid Mixtures at Elevated Pressures[1]

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This paper reports new, absolute measurements of the thermal conductivity of liquid mixtures of *n*-heptane and isooctane in the pressure range 0.1 to 430 MPa for temperatures of 307.85 and 337.15 K. The results represent a preliminary investigation of the advantages of attempting to describe the isothermal composition dependence of the thermal conductivity of liquid mixtures along isochores, rather than isobars as has been traditional. However, no significant differences were found between the composition dependences in the two circumstances, possibly due to the lack of experimental data on the density of these mixtures. The availability of a theoretical description of the isochoric composition dependence suggests that this is the most appropriate description which reinforces the need for further high-pressure measurements of the thermal conductivity and density.

KEY WORDS: alkanes; mixtures; thermal conductivity.

1. INTRODUCTION

There have been only a small number of measurements of the thermal conductivity of liquid mixtures [1]. Of these measurements only a very small fraction has been performed in instruments which are known to yield accurate results because, for the most part, they preceded the development of the modern transient hot-wire method. Furthermore, almost all

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measurements have been performed at a constant pressure (usually 1 atm), which is also the situation to which most procedures of the estimation of the thermal conductivity of liquid mixtures refer [2].

The most successful theory of the transport properties of pure liquids is that based on a combination of a rigid-sphere model of the fluid with the Enskog theory [3]. It is a fundamental result of this theory that the transport properties of a liquid depend primarily upon its density and, to a lesser extent, its temperature, and not directly upon the pressure. Indeed, the application of the essential results of this theory has allowed a powerful correlation and prediction scheme to be developed for the thermal conductivity and viscosity of a wide range of hydrocarbon liquids [4, 5]. On the basis of these observations for pure fluids, it is reasonable to expect that the same theory, generalized to mixtures, might be equally successful. However, there have been only a few applications of these ideas to the viscosity of liquid mixtures [6] and, so far as it is possible to discern, none at all to thermal conductivity. This situation is, of course, related to a lack of appropriate experimental data because the determination of the density dependence of the thermal conductivity of a liquid mixture requires measurements under very high pressures (up to 500 MPa) and an equation of state for the mixture.

In an earlier paper [7] the application of a modern transient hot-wire instrument to the measurement of the thermal conductivity of a pure liquid at pressures up to 700 MPa and temperatures in the range 300–360 K has been described. The present paper describes the application of the same technique to measurements of the thermal conductivity of mixtures of *n*-heptane and isooctane under a similar range of conditions and provides preliminary experimental results. This particular system has been selected for the initial study, partly for experimental convenience and partly because the two pure components have significantly different thermal conductivities at the same pressure. The intention of this preliminary investigation is, first, to establish whether the composition dependence of the thermal conductivity at constant pressure is sufficiently simple that an extensive investigation is unwarranted and, second, to ascertain whether the composition dependence at constant molar density may be a more appropriate circumstance in which to examine the behavior.

2. EXPERIMENTAL

The high-pressure transient hot-wire instrument employed for the present measurements is essentially that described by Menashe and Wakeham [7]. However, as detailed elsewhere [8] the wire mounting mechanism now incorporates a spring to eliminate electrostrictive oscillations of the wire resistance during the transient temperature rise measurements. In addition, use is made of the improved computer-controlled automatic measurement bridge described by Wakeham and Zalaf [9] in order to secure a higher resolution in the temperature rise measurements. In all other respects the instrument remained unchanged, but for the present application to mixtures, it has been necessary to consider both the working equations of the method and the procedures for filling the thermal conductivity cell.

When used for measurements on pure liquids it has been our practice to evacuate the flexible enclosure of the thermal conductivity cell and then allow the degassed liquid to enter under gravity [7]. In general, such a procedure cannot be used for liquid mixtures because the different volatilities of the various components will lead to composition changes in the liquid phase during filling that are not easily evaluated. While this difficulty can be overcome by a radical change of the filling procedure, it was not deemed appropriate in the present, preliminary investigation to resort to this. Consequently, a pair of liquids was selected to form the mixtures under investigation for which the volatilities were nearly the same and for which the pure component thermal conductivity over the range of conditions of interest had been measured. The fluids *n*-heptane and isooctane satisfied these conditions and possessed the additional advantage that, at the same pressure, the thermal conductivities of the two pure components were some 30% different, a feature particularly valuable for the purposes of the present study. Owing to the near-match of the volatilities of the two pure components, the cells could be filled with the mixtures using the same procedure as before with an entirely negligible additional uncertainty in the mixture composition. The mixtures were manufactures gravimetrically from the pure components *n*-heptane and isooctane, supplied by BDH Chemicals Ltd., with a stated purity of 99.5 and 99.8%, respectively. The pure samples were degassed before use. The uncertainty in the composition of the mixtures is estimated to be $\pm 0.1\%$.

The basic working equations of the transient hot-wire technique are given elsewhere [10] for pure fluids. However, when applied to mixtures the thermal diffusive separation of components accompanying the imposition of a temperature gradient must be considered. This problem has been considered in some detail by Khalifa et al. [13] for the case of mixtures of gases conforming to the perfect-gas equation of state. Their analysis shows that the thermal conductivity determined by the transient hot-wire technique is that appropriate to conditions of zero diffusive flux and the equilibrium composition of the mixture. It is not possible to repeat this analysis for a liquid mixture because it requires an equation of state for the mixture such that an analytic treatment of the problem is feasible and such an equation is not available. However, because the essential result of the work of Kestin et al. is determined by the boundary condition that there can be no mass flux in the hot wire [13], it is reasonable to assert that the same result pertains to liquid mixtures. Thus, we associate the thermal conductivity of the mixture determined in the transient hot-wire measurement with the composition of the equilibrium mixture *and* the reference temperature [10, 13].

In the analysis of the experimental data it is necessary to apply a small correction (<0.1%) to the measured temperature rise. For this purpose, values of the density of the liquid mixture and the heat capacity are required. These have been estimated according to the procedures recommended by Reid et al. [2], which yield a sufficient accuracy for the present purpose. The measurements have been carried out in the pressure range 0.1 to 450 MPa for nominal temperatures of 307.85 and 337.15 K.

It is an essential feature of the transient hot-wire technique that the corrected, measured temperature rise of the wire should be a linear function of the logarithm of the heating time, *t*. Figure 1 shows that this is indeed the case for the present measurements on the mixtures of *n*-heptane and isooctane. The figure contains a plot of the deviations of the measured temperature rise from a linear fit to it as a function of ln *t* for a typical experimental run. It is clear that the expected linearity is amply confirmed within a maximum deviation of less than 0.03%.

On the basis of this and similar plots and upon the uncertainty in other characteristics of the equipment, the accuracy of the reported thermal conductivity is estimated to be one of ±0.3%.

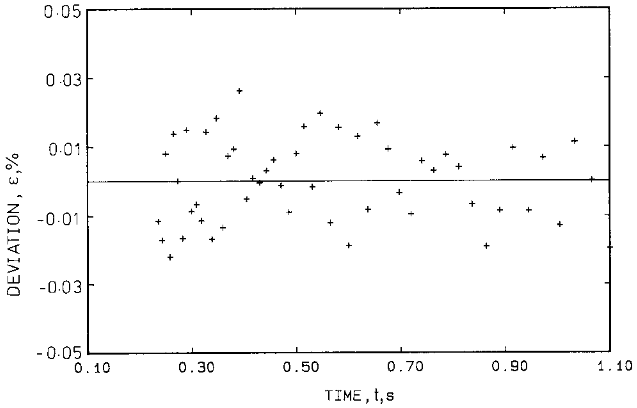

Fig. 1. Deviations of the measured values of ΔT_{id} from a straight-line fit to them for a measurement in an *n*-heptane–isooctane mixture. $\varepsilon = [(\Delta T - \Delta T_{fit})/\Delta T_{fit}] \times 100$. $x_{c_7} = 0.4886$, $P = 202.7$ MPa, $T = 307.85$ K.

3. RESULTS

Table I lists the thermal conductivity data for mixtures of *n*-heptane and isooctane with mole fractions of *n*-heptane of 0.4886 and 0.7442, respectively. For the two mixtures, the measurements have been performed along two isotherms at 307.85 and 337.15 K. The measured thermal conductivity has been corrected to the nominal temperature at the experimental pressure and in the reference density by means of the procedure described elsewhere [7]. Since the magnitude of this correction did not exceed ±0.1%, the additional uncertainty introduced in the tabulated thermal conductivity is negligible.

Due to the unavailability of experimental data on the density of mixtures of *n*-heptane and isooctane at high pressures, no values for the thermal conductivity corrected to nominal temperatures at the reference density are given at this stage.

Table I. The Thermal Conductivity, λ, of Mixtures of *n*-Heptane and Isooctane[a]

Mole fraction $x_{C_7} = 0.4886$				Mole fraction $x_{C_7} = 0.7442$			
$T_{nom} = 307.85$ K		$T_{nom} = 337.15$ K		$T_{nom} = 307.85$ K		$T_{nom} = 337.15$ K	
P	λ	P	λ	P	λ	P	λ
1.5	103.8	1.8	97.8	2.1	111.7	2.1	106.0
6.0	105.7	1.9	98.0	8.9	115.0	2.1	106.1
6.0	105.8	13.5	103.9	24.2	121.4	14.9	112.1
6.0	105.7	29.2	110.8	24.2	121.6	15.0	112.1
14.3	109.3	29.2	110.8	44.0	129.0	52.6	126.2
14.3	109.3	53.4	120.7	104.2	148.1	101.4	142.0
26.3	113.9	102.5	136.3	104.3	147.9	103.9	142.9
52.7	123.5	102.5	136.4	152.4	160.1	151.0	155.4
52.7	123.6	153.5	149.7	205.3	172.1	200.1	166.3
78.2	131.3	206.1	161.7	256.8	182.2	205.4	167.5
78.5	131.4	256.5	171.9	307.1	191.0	254.3	177.7
108.3	139.9	306.2	181.3	353.6	198.7	254.5	177.6
144.5	148.8	353.3	188.8	409.7	207.2	305.2	186.8
144.5	148.8	403.2	196.4			305.6	186.8
202.8	161.6					353.1	195.0
202.8	161.7					412.3	204.1
253.6	171.2						
310.1	180.8						
356.7	187.7						
401.6	194.3						
443.9	200.1						

[a] P in MPa and λ in $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$.

Table II. Coefficients of the Correlation of the Thermal Conductivity as a Function of Pressure According to Eq. (1)

Mole fraction of *n*-heptane	T (K)	λ' $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	P' (MPa)	a_1	a_2	a_3	a_4
0.0	307.85	147.80	200.0	0.2532	−0.0750	0.0265	−0.0013
0.0	337.15	145.68	200.0	0.2685	−0.0744	0.0337	−0.0077
0.4885	307.85	161.00	200.0	0.2473	−0.0635	0.0348	−0.0127
0.4885	337.15	160.28	200.0	0.2652	−0.0514	0.0429	−0.0345
0.7442	307.85	170.86	200.0	0.2429	−0.0545	0.0343	−0.0182
0.7442	337.15	166.47	200.0	0.2571	−0.0610	0.0343	−0.0151
1.0	307.85	182.33	200.0	0.2358	−0.0551	0.0348	−0.0132
1.0	337.15	178.40	200.0	0.2565	−0.0695	0.0469	−0.0166

The experimental data for the thermal conductivity for each mixture along an isotherm have been represented by a polynomial of the form

$$\lambda(x_{c_7}, T, P) = \lambda'(x_{c_7}, T)\left[1 + a_i\left(\frac{P - P'}{P'}\right)^i\right] \qquad (1)$$

Table II contains the coefficients of this equation which secure the optimum representation of the experimental data together with the corre-

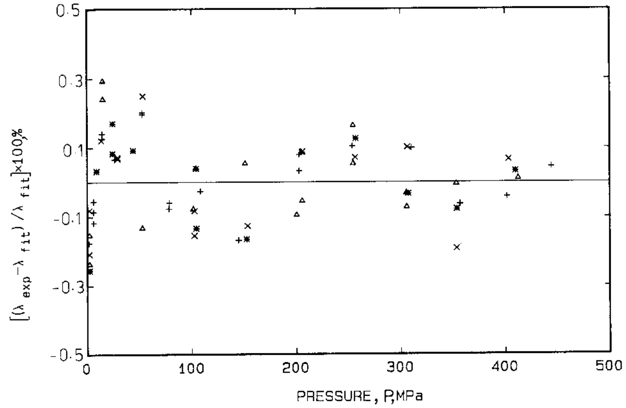

Fig. 2. Deviations of the thermal conductivity of *n*-heptane–isooctane mixtures from their correlation as a function of pressure with Eq. (1). (+) $x_{c_7} = 0.4886$; $T = 307.85$ K. (×) $x_{c_7} = 0.7442$; $T = 307.85$ K. (*) $x_{c_7} = 0.4886$; $T = 337.15$ K. (Δ) $x_{c_7} = 0.7442$; $T = 337.15$ K.

sponding values for the pure fluids taken from our earlier work [7, 14]. Figure 2 displays the deviations of the thermal conductivity from the representation for the mixtures. The deviations do not exceed ±0.3%, whereas the standard deviation of the order of 0.2% is consistent with the estimated precision of the data.

4. DISCUSSION

4.1. The Isobaric, Isothermal Composition Dependence

In order to satisfy the first purpose of the present work, it is necessary to examine the composition dependence of the thermal conductivity of the

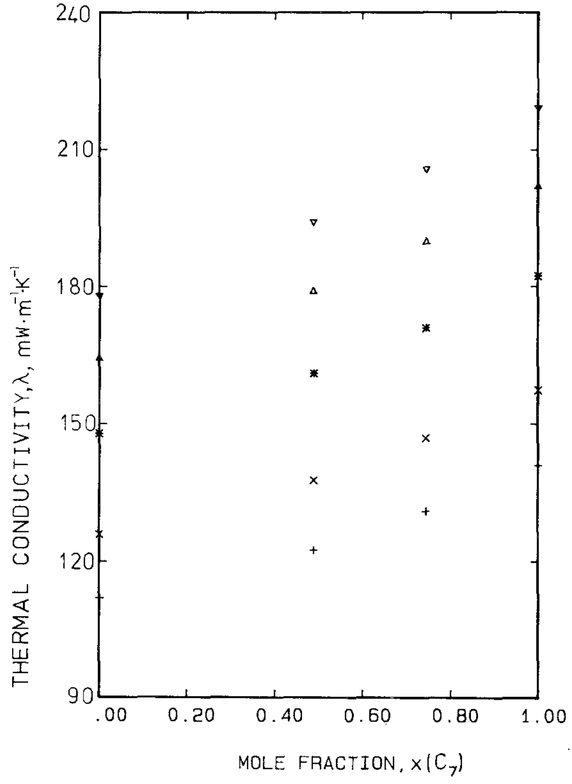

Fig. 3. The composition dependence of the thermal conductivity of *n*-heptane–isooctane mixtures along isobars for $T_{\mathrm{nom}} = 307.85$ K. (+) 50 MPa; (×) 100 MPa; (*) 200 MPa; (Δ) 300 MPa; (∇) 400 MPa.

mixtures for isotherms along isobars. For this purpose, the pressure-dependent correlation of Eq. (1) has been employed for the mixtures and the pure components. In addition, the data for the pure liquids have been corrected to the nominal isotherms employed in the current study. Figures 3 and 4 show the resultant isobaric, isothermal composition dependence for the two isotherms. The composition dependence is significantly different from linearity. The deviations amount to as much as 3% at the lowest pressures.

4.2. The Isochoric, Isothermal Composition Dependence

In accordance with the indications of the rigid-sphere theory of fluids, it is worthwhile examining the composition dependence of the thermal

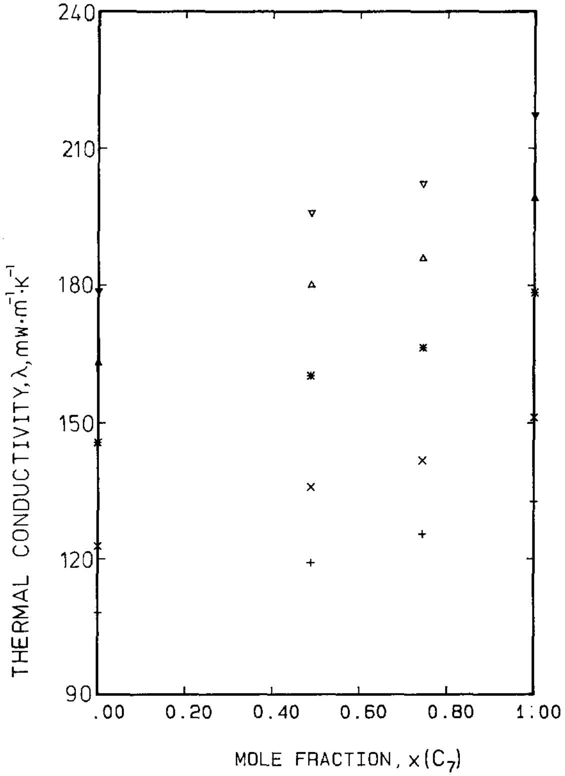

Fig. 4. The composition dependence of the thermal conductivity of *n*-heptane–isooctane isobars along isobars for $T_{\mathrm{nom}} = 337.15$ K. (+) 50 MPa; (×) 100 MPa; (*) 200 MPa; (Δ) 300 MPa; (∇) 400 MPa.

conductivity of mixtures along isochores rather than isobars. There are, however, no measurements of the density of mixtures of *n*-heptane and isooctane at elevated pressures so that it is necessary to make estimates of the latter in order to perform the preliminary examination intended here.

The density has been estimated from the literature values for the pure components [15, 16] assuming zero volume change on mixing. It is judged that the overall accuracy is of the order of $\pm 1\%$. The corresponding uncertainty in the thermal conductivity is of the same order of magnitude. In addition, the data for the pure fluids have been corrected to the nominal isotherms employed in this work.

Figures 5 and 6 show the isochoric, isothermal composition dependence of the thermal conductivity of the mixtures. This does not appear to be more linear than the isobaric dependence.

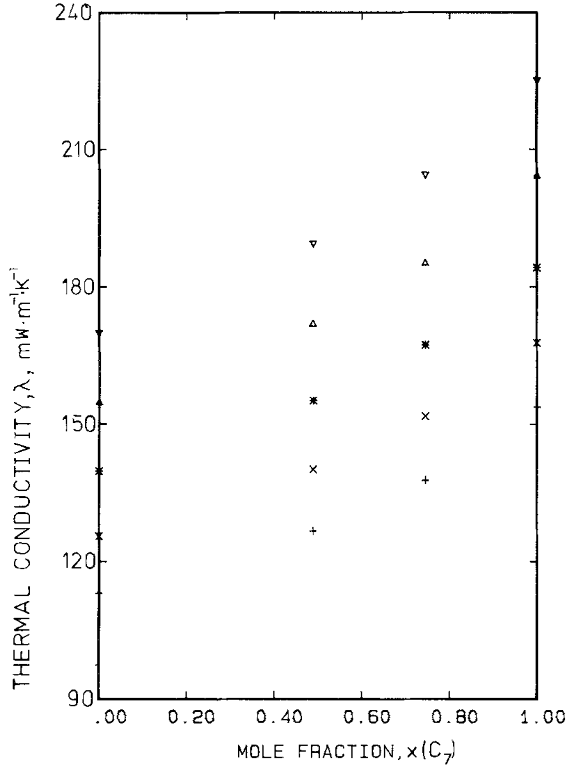

Fig. 5. The composition dependence of the thermal conductivity of *n*-heptane–isooctane mixtures along isochores for $T_{\text{nom}} = 307.85$ K. $(+)$ $\rho = 725\ \text{kg}\cdot\text{cm}^{-3}$; $(\times)$ $\rho = 750\ \text{kg}\cdot\text{cm}^{-3}$; $(*)$ $\rho = 775\ \text{kg}\cdot\text{cm}^{-3}$; (Δ) $\rho = 800\ \text{kg}\cdot\text{cm}^{-3}$; (∇) $\rho = 825\ \text{kg}\cdot\text{cm}^{-3}$.

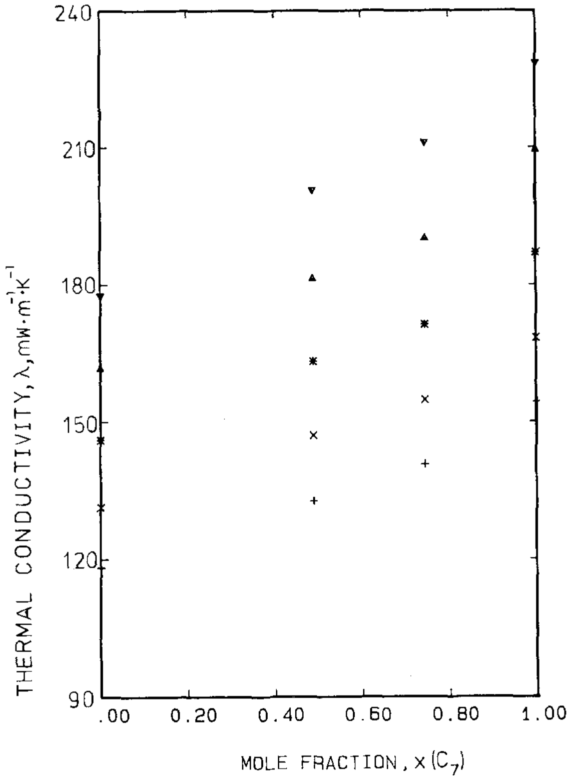

Fig. 6. The composition dependence of the thermal conductivity of *n*-heptane–isooctane mixtures along isochores for $T_{\mathrm{nom}} = 337.15$ K. (+) $\rho = 725$ kg · cm^{-3}; (×) $\rho = 750$ kg · cm^{-3}; (*) $\rho = 775$ kg · cm^{-3}; (Δ) $\rho = 800$ kg · cm^{-3}; (∇) $\rho = 825$ kg · cm^{-3}.

5. CONCLUSIONS

New experimental results of the thermal conductivity of mixtures of *n*-heptane and isooctane have been obtained using the transient hot-wire technique.

A preliminary investigation of the composition dependence of the thermal conductivity of liquid mixtures at elevated pressures has been conducted. The results do not indicate which of the isobaric, isothermal composition dependence or the isochoric, isothermal composition dependence is simpler. At this preliminary stage of the work, it is thought that the use of more accurate values for the density of the mixtures will permit a more reliable comparison.

The rigid-sphere theory provides an appropriate basis for a description of the isochoric dependence of the thermal conductivity which will be attempted in later work.

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