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Thermal Conductivity of Oct-1-ene in the Temperature Range 307 to 360 K at Pressures up to 0.5 GPa

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New measurements of the thermal conductivity of liquid oct-1-ene in the temperature range 307 to 360 K at pressures up to 0.5 GPa have been performed. The experimental data have an estimated uncertainty of $\pm 0.3\%$. Within the limited range of pressures for which data for the density of the liquid are available, it has proved possible to represent all of the thermal conductivity results by means of a single equation with just one temperature-dependent parameter. This representation is based on the ideas of the hard-sphere theory of fluids and is consistent with that employed earlier for alkanes.

KEY WORDS: hard-sphere theory; high pressures; liquid; oct-1-ene; thermal conductivity.

1. INTRODUCTION

In an earlier series of papers [1–10] the results of accurate measurements of the thermal conductivity of normal, branched, and cyclic alkanes have been reported at pressures up to 0.7 GPa. Using ideas based upon the hard-sphere theory of dense fluids [11], it has been possible to represent the density dependence of the thermal conductivity of all of the liquid alkanes studied by means of a universal correlation with a single temperature-dependent parameter.

Indeed, in a preliminary fashion, the same scheme has been extended to the viscosity for a wider range of *n*-alkanes [9]. The representation offers the advantage of accurate extrapolation of thermal conductivity data

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to thermodynamic states other than those studied experimentally and even to other alkanes. It is therefore worthwhile to consider the extension of the scheme to other groups of liquids. However, such an extension requires density data for the liquids at elevated pressures, and they are frequently not available.

Prompted by a parallel investigation into the viscosity of alkenes at elevated pressures and by the recent availability of density data for oct-1-ene at pressures up to 0.26 GPa [12], we have begun a study of the thermal conductivity of the alkenes with this particular system.

2. EXPERIMENTAL

The measurements of thermal conductivity have been carried out in the high-pressure transient hot-wire instrument described elsewhere [1]. A new set of platinum wires was installed for the present work but otherwise the instrument and its operating procedures remained unchanged. The measurements were carried out along four isotherms within the temperature range 307–360 K at pressures upto 0.5 GPa. The oct-1-ene sample was supplied by BDH Chemicals Ltd. with a purity better than 99%. After distillation and degassing, analysis confirmed a purity in excess of 99.9%.

The density of oct-1-ene in the appropriate temperature range for pressures up to 0.26 GPa has been determined by Isdale and his collaborators [12]. These data, together with the heat capacity data compiled by Vargaftick [13], have been employed to make small corrections during the analysis of the measurements. It is worthwhile to record here that there was no evidence of radiation absorption in any measurement [14] so that the data reported in the next section are "radiation-free" values.

3. RESULTS

Tables I to IV list the experimental data for the thermal conductivity of oct-1-ene along the four isotherms at 307.65, 320.65, 344.15, and 360.15 K as a function of pressure and density. At the higher pressures the density is not quoted since the pressures lie beyond the range of the density measurements. The correction of the experimental data to uniform nominal temperatures has been accomplished in the manner described elsewhere [1]. In no case did the correction amount to more than $\pm 0.2\%$ so that the additional uncertainty introduced is negligible. The uncertainty in the reported thermal conductivity data is estimated to be one of $\pm 0.3\%$, whereas that in the associated density is $\pm 0.2\%$.

Table I. The Thermal Conductivity of Oct-1-ene at $T_{nom} = 307.65$ K

Pressure P (MPa)	Density ρ (kg · m^{-3})	Thermal conductivity (mW · m^{-1} · K^{-1})	
		$\lambda(T_{nom}, \rho)$	$\lambda(T_{nom}, P)$
7.173	709.6	124.6	124.6
14.74	716.1	128.2	128.1
14.74	716.1	128.4	128.4
21.44	721.5	131.2	131.1
42.23	736.3	139.1	138.9
45.52	737.8	140.3	140.5
59.54	746.8	145.1	144.9
70.97	752.5	148.8	148.9
80.11	757.5	152.2	152.1
97.48	765.5	156.7	156.7
104.7	768.6	158.6	158.6
147.7	785.4	168.1	168.1
201.1	802.5	180.8	181.0
249.4	816.3	190.2	190.3
288.3	826.6	197.3	197.4

Table II. The Thermal Conductivity of Oct-1-ene at $T_{nom} = 320.65$ K

Pressure P (MPa)	Density ρ (kg · m^{-3})	Thermal conductivity (mW · m^{-1} · K^{-1})	
		$\lambda(T_{nom}, \rho)$	$\lambda(T_{nom}, P)$
8.352	699.6	121.2	121.6
14.65	705.4	124.7	124.9
24.79	713.9	129.3	129.6
48.21	730.8	138.7	138.8
70.06	743.8	145.9	145.9
91.86	754.9	153.0	153.0
147.6	777.8	167.0	167.1
187.2	791.4	175.8	175.8
199.5	795.1	178.8	178.9
279.3	817.8	194.5	194.5
298.3	—	—	197.9
343.0	—	—	205.4
399.7	—	—	213.8
447.7	—	—	220.8
492.1	—	—	227.5

Table III. The Thermal Conductivity of Oct-1-ene at $T_{nom} = 344.15$ K

Pressure P (MPa)	Density ρ (kg · m^{-3})	Thermal conductivity (mW · m^{-1} · K^{-1})	
		$\lambda(T_{nom}, \rho)$	$\lambda(T_{nom}, P)$
29.73	700.9	128.3	128.3
53.42	718.3	135.0	134.8
97.68	742.8	149.9	149.9
151.1	765.5	164.3	164.1
203.5	783.0	176.5	176.5
248.3	796.3	185.9	185.8
302.8	810.9	196.1	196.3
345.1	—	—	203.7
393.6	—	—	212.0
449.2	—	—	220.3
496.8	—	—	227.3

For the purposes of *interpolation* we have represented the pressure dependence of the thermal conductivity of oct-1-ene along each isotherm by an equation of the form

$$\lambda = \lambda' \left\{ 1 + \sum_{i=1}^{4} a_i [(P - P')/P']^i \right\} \tag{1}$$

The coefficients which secure the optimum representation of the data are listed in Table V. Figure 1 shows the deviations of the present

Table IV. The Thermal Conductivity of Oct-1-ene at $T_{nom} = 360.15$ K

Pressure P (MPa)	Density ρ (kg · m^{-3})	Thermal conductivity (mW · m^{-1} · K^{-1})	
		$\lambda(T_{nom}, \rho)$	$\lambda(T_{nom}, P)$
22.43	683.1	118.5	118.6
55.02	709.1	132.3	132.3
100.2	734.9	147.4	147.5
154.7	758.2	162.4	162.5
205.1	775.5	174.4	174.5
241.0	786.7	182.5	182.6
298.8	—	—	193.6
351.1	—	—	203.2
399.6	—	—	211.7

Table V. Coefficients of the Correlation of the Thermal Conductivity of Oct-1-ene According to Eqs. (1), (4), and (5)

Temperature T(K)	λ' (mW · m^{-1} · K^{-1})	P' (mPa)	$10a_1$	10^2a_2	10^2a_3	10^2a_4	10^6V_0 (m^3 · mol^{-1})
307.65	180.337	200	2.358	−3.089	−1.229	−7.372	99.435
320.65	179.120	200	2.279	−5.689	3.952	−1.464	99.286
344.15	175.689	200	2.556	−5.957	1.773	−0.251	98.988
360.15	173.468	200	2.577	−6.108	4.034	−1.644	98.840

experimental data from this correlation and includes the results of the only earlier set of measurements at pressures upto 50 MPa [15]. The present data do not depart from the correlation by more than ±0.7% over the entire range of pressures. The agreement with the results of Naziev and Abasov [15] is within the mutual uncertainty of the two sets of data in the limited range of overlapping pressures, although the present results are of a higher accuracy.

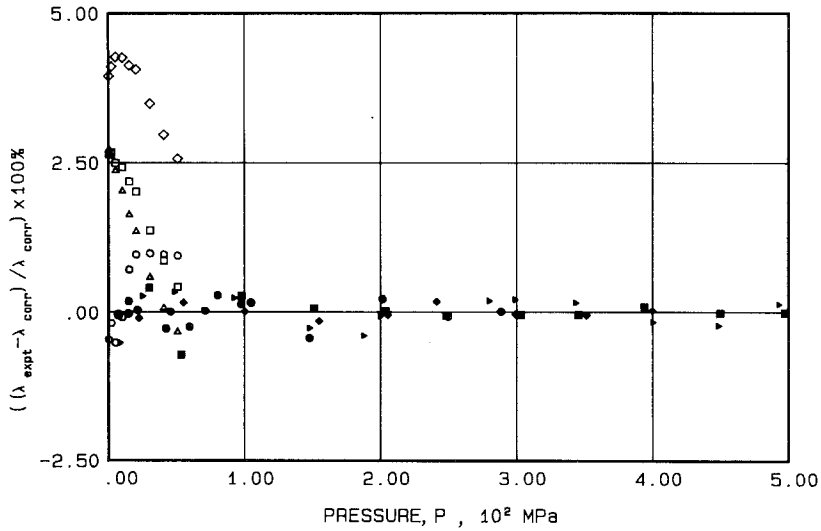

Fig. 1. Deviations of the thermal conductivity data for oct-1-ene from the correlation of Eq. (1). Present work: (●) 307.65 K; (▶) 320.65 K; (■) 344.15 K; (◆) 360.15 K. Naziev and Abasov [15]: (△) 307.65 K; (□) 320.65 K; (○) 344.15 K; (◇) 360.15 K.

4. DISCUSSION

The hard-sphere model of the dense fluid state [9, 11] shows that the quantity, λ^*, defined in terms of experimental quantities by the equations

$$\lambda^* = 1.936 \times 10^7 \lambda V^{2/3} (RT/M)^{-1/2} \tag{2}$$

$$= F_\lambda (V/V_0) \tag{3}$$

should be a function only of the ratio V/V_0. Here, V is the molar volume of the fluid, V_0 a characteristic hard-core volume, T the absolute temperature, M the molar mass of the fluid, and R the universal gas constant.

In previous analyses [7, 9] Eqs. (2) and (3) have been used as the basis for a correlation scheme for the thermal conductivity of liquid alkanes. For this purpose the essential feature of the results of the model, that $\lambda^* = F_\lambda(V/V_0)$ is retained, but V_0 is allowed to be temperature dependent to reflect the finite steepness of the repulsive wall of a real intermolecular pair potential. Furthermore, the function F_λ is determined not from a hard-sphere model, but from the experimental data themselves for a number of alkanes.

Here, we apply a similar analysis to the experimental thermal conductivity of oct-1-ene, initially without reference to the results of the earlier work for alkanes. The analysis is begun by adopting an (essentially) arbitrary value for V_0 at the lowest isotherm. This allows the construction of the function λ^* vs. $\ln(V/V_0)$ for that isotherm. Subsequently, if Eqs. (2) and (3) are obeyed by the fluid it should be possible to superimpose plots of λ^* vs. $\ln V$ for the other isotherms on that for the reference isotherm merely by choosing a suitable value for V_0. In this way values of V_0 for all the isotherms have been determined and they are listed in Table V. It has been found that the best representation of the single, composite curve λ^* vs. (V/V_0) is given by the simple equation

$$\ln \lambda^* = 4.9339 - 2.3458 \ln(V/V_0) \tag{4}$$

Figure 2 contains the deviations of the present experimental data from this correlation which contains just one adjustable parameter. It can be seen that, with the exception of one point, the deviations do not exceed $\pm 0.8\%$. The standard deviation of the fit is one of $\pm 0.4\%$. Although this exceeds the uncertainty in the thermal conductivity alone, it is consistent with the combined uncertainty in the thermal conductivity and the density. The correlation can therefore be employed for extrapolation of the present data to regions of state not covered in the present study.

Because the thermal conductivity of oct-1-ene is represented by a form of equation which proved successful for a variety of alkanes, it is

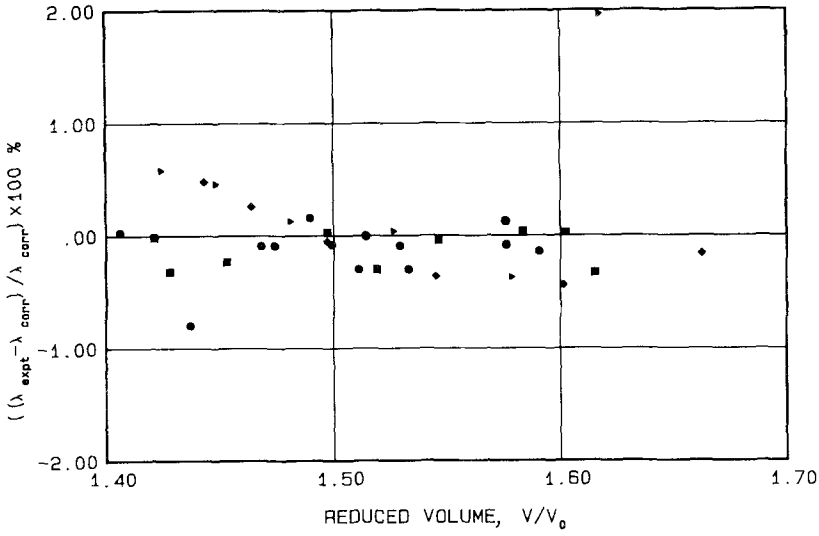

Fig. 2. Deviations of the thermal conductivity of oct-1-ene from the correlation of Eq. (4) as a function of reduced volume. (●) 307.65 K; (■) 320.65 K; (▶) 344.15 K; (◆) 360.15 K.

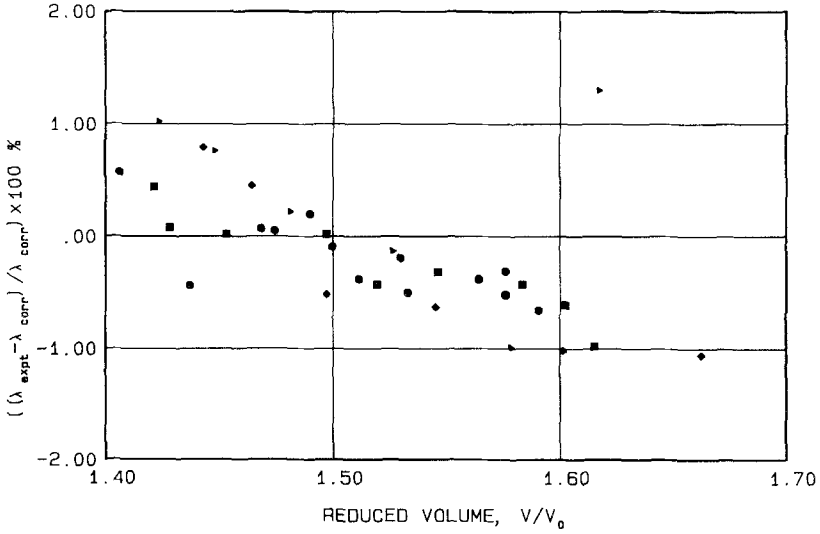

Fig. 3. Deviations of the thermal conductivity of oct-1-ene from the correlation of Eq. (5) universal among the alkanes. (●) 307.65 K; (■) 320.65 K; (▶) 344.15 K; (◆) 360.15 K.

worthwhile to examine this correspondence more closely. For this purpose we have attempted to fit the thermal conductivity of oct-1-ene to the equation best describing the data for the alkanes [7],

$$\ln \lambda^* = 4.8991 - 2.2595 \ln(V/V_0) \tag{5}$$

Indeed, it is by means of such a fit for the lowest isotherm alone that the value of V_0(307.65 K) has been determined for the preceding analysis. Figure 3 shows the deviations of the thermal conductivity data for oct-1-ene from this universal correlation, using the V_0 values listed in Table V.

Although there is some evidence of systematic deviations of the data from the universal correlation, they never exceed $\pm 1\%$. This observation suggests that prediction of the thermal conductivity of other liquid alkenes may be possible over a wide range of states provided that it is possible to determine the core volume V_0 from just a few measurements.

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