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Thermal Conductivity of Liquid Toluene at Two Isotherms - 308.15 K and 320.15 K, and Pressures up to 300 MPa

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Abstract

The paper contains the results of measurements of the thermal conductivity of toluene in the liquid phase at two isotherms 308.15 K and 320.15 K and at pressures up to 300 MPa. The measurements were carried out with a transient hot-wire instrument and have an accuracy of ± 0.3%. The pressure dependency of the thermal conductivity of toluene has been investigated and a correlation has been developed. Also the representation of the thermal conductivity of pure liquids based on the hard-sphere theory of transport in liquids has been explored for toluene and the density dependency of the thermal conductivity has been given. It is shown that all of the experimental data may be represented to within ± 2% by a 'predictive' procedure based on the hard-sphere theory of liquids.

Keywords: Thermal conductivity, toluene, rigid hard-sphere, transient hot-wire instrument.

Introduction

Despite the fact that there has been a number of significant advances in the measurement and prediction of the thermal conductivity of liquids and liquid mixtures [1-3], the search for standard reference fluids for thermophysical properties (including thermal conductivity, and viscosity) still continues. Most of these advances have been limited to hydrocarbons and their mixtures [4, 6, 7]. Toluene is one hydrocarbon that has been recommended as a standard reference liquid for thermal conductivity by the Commission on Physicochemical Measurements and Standards of the Physical Chemistry Division of the International Union of Pure and Applied Chemistry (IUPAC) [5]. Most of the accurate experimental thermal conductivity data have been obtained with the transient hot-wire apparatus (THW) [1, 7-12]. The purpose of the present study is to use the THW method to obtain accurate experimental data for the thermal conductivity of toluene which can serve to firstly test accurate operation of the transient hot-wire apparatus used and secondly to test the applicability of the hard-sphere theory to thermal conductivity as a transport property [6, 18-23].

Experiments

The measurements were carried out in a transient hot-wire instrument for the measurement of the thermal conductivity of electrically insulating liquids described in detail elsewhere [8, 11, 12]. For the present work the cells of the instrument were equipped with platinum wires of 7 µm nominal diameter (purity ≥ 99.9%) supplied by Sigmund Cohn Corporation in a fashion described earlier [1]. An automatic Wheatstone bridge described elsewhere is employed to obtain the time evolution of temperature of the platinum wires during the application of a constant heat flux q Wm^{-1} to the transient hot-wire instrument. [11].

The essence of the method involves the determination of the time evolution of the temperature rise, ΔT_{id}, of a thin (7 µm) platinum wire immersed in the fluid over a period of one second following initiation of a constant heat flux, q, in the wire at time t = 0. The thermal conductivity, λ, of the fluid is derived from the basic working equation (1) of the transient hot-wire apparatus [8-11].

$$\Delta T_{id} = \frac{q}{4\pi\lambda} \ln \frac{4kt}{a^2 C} \qquad (1)$$

in which $k=\lambda/\rho C_p$ is the thermal diffusivity of the fluid, Cp is the heat capacity of the liquid, ρ is density of the liquid, a is the radius of the heated wire, t is the time elapsed from the beginning of the experiment, and C=1.781 a numerical constant. A precision of ± 0.5 mK is secured in the temperature rise measurements and the configuration of the instrument is such that convective and radiative heat transfer are completely eliminated so that it is possible to secure an accuracy of ±0.3% in the thermal conductivity data.

Toluene supplied by Fluka Chemicals Ltd with a purity in excess of 99.8% was degassed several times under vacuum. The thermal conductivity cells were filled by firstly evacuating them and subsequently introducing the liquid sample under pressure by the method described earlier [1]. The working equations for the analysis of the experimental data have been given elsewhere [3] and they are employed unchanged in this work.

The density and isobaric heat capacity values of pure toluene were required in order to make a number of small corrections during the analysis of the experimental data. For pure toluene, the density was obtained by employing the Tait-type equation proposed by Kashiwagi et al. [13]

$$\rho = \rho_o \left\{1 - Cln\left(\frac{D+P}{D+P_o}\right)\right\}^{-1} \qquad (2)$$

where P_o=0.1 MPa, C=9.143x10^{-2}. D and ρ_o are represented as functions of temperature by:

$$D = 440.47 - 1.6047T + 1.539x10^{-3}T^2 \qquad (3)$$

and

$$\rho_o = 1103.06 - 0.68074T - 4.229x10^{-4}T^2 \qquad (4)$$

where D is in MPa, ρ_o is in kgm^{-3} and T in K. and the uncertainty in the density is estimated to be ± 0.1%. The heat capacity of the liquid required to apply small corrections in the analysis of the experimental data which, in the present case, contributes no more than ±1% to the measured temperature rise was obtained from the compilation of Vargaftik [14]. . As a result, even quite large errors in the heat capacity have a negligible effect upon the reported thermal conductivity.

Results

Pressure Dependence of the Thermal Conductivity

Owing to the modifications to the transient hot-wire apparatus employed for the present measurements, it was appropriate to verify the correct operation of the instrument in accordance with the theory. Table I lists the present results for the thermal conductivity of pure toluene along two isotherms – 308.15 K and 320.15 K. In each case, the experimental results have been corrected to nominal temperatures by application of small linear temperature corrections that never exceeded ±0.2%. It is estimated that the thermal conductivity listed has an accuracy of ±0.5% and a slightly better precision of ±0.3%.

For the purpose of comparison, the experimental data were represented by correlating equations of the form

$$\lambda(x,T,P) = \lambda'(x,T)\left\{1+\sum_{i=0} b_i P_i^{*i}\right\} \qquad (5)$$

where

$$P^* = (P-P')/P' \qquad (6)$$

and P'=150 MPa is a scaling parameter and is approximately the average pressure along an isotherm. The values of the coefficients b_i were determined by a nonlinear optimization technique described elsewhere [15, 16] that minimized the average relative deviation defined for the thermal conductivity (property X) by eq. (7):

$$\Delta_{AAD,X} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\left|X_i - X_{i,fit}\right|}{X_i}\right), \qquad (7)$$

where X_i is an experimental datum, $X_{i,fit}$ is calculated from the correlation applied at the same state point, and N is the total number of points. The maximum absolute relative deviation ($\Delta_{\mathrm{MAD,X}}$) and the relative bias ($\Delta_{\mathrm{Bias\ X}}$) were calculated using eq. (8) and (9) respectively:

$$\Delta_{MAD,X} = Max\left(\frac{\left|X_i - X_{i,fit}\right|}{X_i}\right), \qquad (8)$$

$$\Delta_{Bias,X} = \frac{1}{N}\sum_{i=1}^{N}\frac{(X_i - X_{i,fit})}{X_i}, \qquad (9)$$

The values of the coefficients b_i, the scaling parameter and the statistical parameters of the thermal conductivity for toluene are included in Table II. Figure 1 contains a comparison of the present experimental results and those Nieto de Castro et al. [17] for toluene with those of the correlating equation. The deviation plot has a maximum deviation of ±0.3% which is consistent

Table I. Thermal Conductivity of Toluene

Temperature, T (K)	Pressure, P (MPa)	Density, ρ_r (kg/m^3)	Thermal conductivity $\lambda(T_{nom}, \rho_r)$ (mW.m^{-1}.K^{-1})	 $\lambda(T_{nom}, P)$ (mW.m^{-1}.K^{-1})
		T_{nom} = 308.15 K		
307.13	0.1	854.17	130.5	130.1
307.19	14.8	865.6	134.6	134.3
307.24	43.1	884.7	142.3	142.0
307.27	43.3	884.8	142.4	142.2
307.04	76.7	903.7	150.3	150.1
307.07	100.4	915.3	156.1	156.0
307.55	102.0	915.7	156.8	156.7
307.35	150.4	936.2	166.4	166.3
307.63	207.4	956.2	175.2	175.2
308.69	211.4	956.9	176.2	176.3
307.72	239.1	966.1	180.0	180.0
307.50	239.3	966.3	179.7	179.6
307.51	274.0	976.3	183.5	183.5
307.84	275.2	977.0	185.5	185.4
307.59	305.5	984.8	190.3	190.3
		T_{nom} = 320.15 K		
320.24	0.1	841.7	126.3	126.2
320.46	25.1	861.9	133.7	133.8
320.46	65.4	887.9	145.5	145.6
320.43	65.1	887.7	145.6	145.7
320.71	108.0	909.7	155.3	155.5
320.78	108.1	909.7	155.2	155.4
320.85	135.1	921.6	160.9	161.1
320.85	135.1	921.6	161.0	161.2
321.02	171.7	936.0	168.2	168.5
321.10	220.2	952.8	176.9	177.2
320.86	254.4	963.5	182.2	182.4
320.06	286.1	973.1	186.5	186.5
320.96	286.1	972.6	186.5	186.7
320.06	305.5	978.4	189.2	189.2
320.07	305.5	978.4	189.5	

Table II. Coefficients for the representation of the Thermal Conductivity of Toluene as a function of pressure according to Eq. (5)

T (K)	λ' (mW.m^{-1}.K^{-1}	P' (MPa)	$10^2 b_1$	$10^2 b_2$	$10^2 b_3$	$10^2 b_4$
308.15	166.323	150	1.6237	-6.4183	1.484	2.4849
320.15	164.280	150	1.7934	-3.4680	1.0615	-0.7428
Statistical Parameters:			$10^2\Delta_{AAD}$	$10^2\Delta_{MAD}$	$10^2\Delta_{Bias}$	
This work			0.0	0.3	0.0	
Nieto de Castro, et al. [17]			0.3	2.4	0.3	

with the estimated precision of the experimental results. However, the experimental data of Nieto de Castro et al [17] gave a maximum deviation of 2.4% from those of the present correlation equation. Figure 2 shows the thermal conductivity of toluene as afunction of pressure at two isotherms – 308.15 K and 320.15 K.

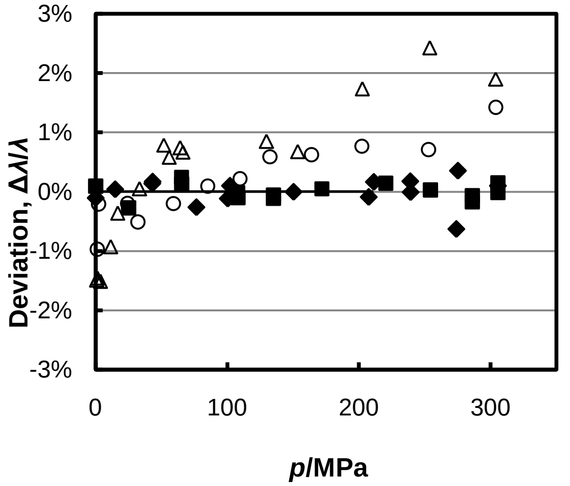

Figure 1. Deviations of experimental thermal conductivity data of toluene from the correlation of Eq. (5). This work: ♦ 308.15 K, ■ 320.15 K; Nieto de Castro, *et al*. [17]: Δ 308.15 K, ○ 320.15 K.

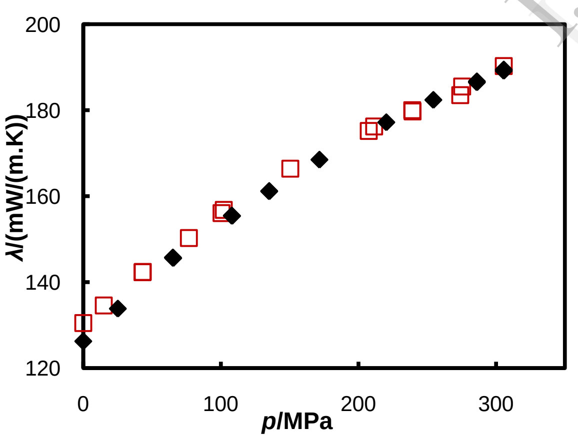

Figure 2. Thermal conductivity of toluene as a function of pressure. □ 308.15 K, ♦ 320.15 K

Density Dependence of Thermal Conductivity

Chandler [18] in his work demonstrated the transport coefficients of rough hard sphere molecules can be directly related to the smooth hard-sphere (subscript shs) transport coefficients. Thus a corresponding relation between experimental transport coefficients (subscript exp) of rough non-spherical was assumed by Assael, et al. [19-23] and for thermal conductivity we have:

$$\lambda_{exp} = R_{\lambda}\lambda_{shs} \tag{10}$$

where R_λ is the roughness factor and accounts for the effects of non-spherical molecular shape. Assael, Dymond and their collaborators in a series of papers [19-23] have investigated the manner in which the model of a hard-sphere fluid can be used as a basis of procedure to represent the experimental data for the transport properties of polyatomic liquids and their mixtures.

The systems they considered in their investigations included normal alkanes and their mixtures as well as pure aromatic hydrocarbons, organic and inorganic molecules. The success of the proposed scheme of Assael et al. [19-23] is noteworthy and it is worthwhile to examine the extent to which the present experimental data for toluene, as a standard reference liquid for thermal conductivity can be represented by the established scheme. For the purpose of establishing the extent to which the present system conforms to the scheme of Assael et al. [19-23], we employ a reduced thermal conductivity, λ^*, which is given in terms of experimental quantities as,

$$\lambda^{*}_{\exp} = 1.936\times10^{7}\left[\frac{M}{RT}\right]^{1/2}\frac{\lambda_{\exp}V^{2/3}}{R_{\lambda}} \tag{11}$$

here $\lambda_{\exp}$ is the measured thermal conductivity of the fluid with a molar mass M, a molar volume, V at a temperature T. As a result of the modifications of the rough hard-sphere theory of dense fluids, the thermal conductivity may be represented as:

$$\lambda^{*} = R_{\lambda}\lambda^{*}\left(V/V_{o}\right) \tag{12}$$

[16-20], wherein R_λ is a roughness factor for the thermal conductivity which is temperature and density independent, while $\lambda^*(V/V_o)$ is a function only of the ratio of the molar volume, V, to the characteristic molar volume V_o, which, for a particular fluid, depends only on temperature. Values of R_λ and $V_o(T)$ for the system determined using a reference function $\lambda^*(V/V_o)$ and a well-established curve fitting procedure described elsewhere [8,15].

Prediction Scheme

In order to examine the ability of the general scheme of Dymond, Assael and their collaborators

[19-23] to predict the present experimental data, we have employed their proposed universal representation of λ^* as a reference function. It is given by

$$\log\left(\lambda^*_{\exp}/R_\lambda\right)=\sum_{i=0}^{4}a_{\lambda_i}\left(1/V_r\right)^i \qquad (13)$$

where,

$$V_r=V/V_o^u \qquad (14)$$

and the superscript u indicates the use of the universal function of Eq. (13) in the definition of V_o. The coefficients $a_{\lambda i}$ are given in the work of Assael et al. [19-23]. For pure toluene studied here the values of R_λ and V_o have been determined by means of the superimposition of the experimental values of λ* for the pure liquid at each temperature upon the universal function given by Eq. (13).

Figure 3 shows a plot of the deviations of the experimental data from those predicted by the predictive scheme developed by Assael et al [23]. The results have a maximum deviation of ±2% which is consistent with the claims of Assael et al. [19-23] that their procedure has an accuracy of ±6% for the estimation of the thermal conductivity of pure liquids and their mixtures. Thus, their procedure can be employed to predict the thermal conductivity of toluene over a relatively wide range of thermodynamic states with the same level of confidence. Furthermore the density dependency of the reduced thermal conductivity of the toluene can be represented by a single function $\lambda^*(V/V_o)$.

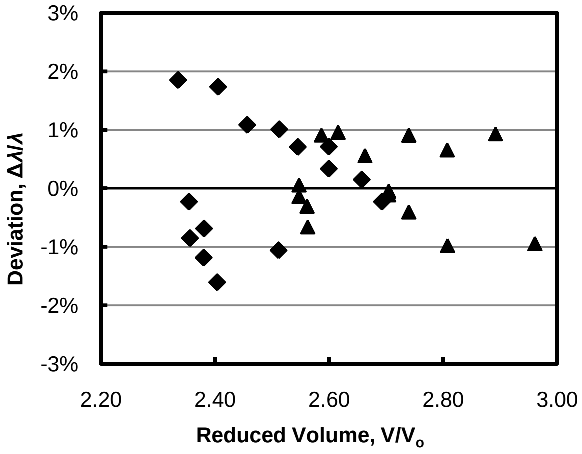

Figure 3. Deviations of experimental thermal conductivity data of toluene from their representation by means of the predictive scheme of Assael et al. [23], Eq. (13). ♦ 308.15 K, ▲ 320.15 K.

Conclusions

New accurate experimental data for the thermal conductivity of toluene have been obtained over a wide range of pressures up to 300 MPa and at two isotherms (308.15 K and 320.15 K) using the transient hot-wire method. The pressure dependence of the thermal conductivity of toluene has successfully been represented by a correlation with an estimated accuracy of less than ±1%. The predictive procedure developed based on the rigid-sphere theory, is able to generate values with an uncertainty of ±2% which are less than ±6% claimed for the procedure by Assael et al. [19-23].

At a higher level of precision, however, the present experimental data confirm the universality of the density dependence of the reduced thermal conductivity of liquids. It is important to note that one of the major attributes of the hard-sphere theory, which isolates the temperature dependence of the thermal conductivity within a hard-core volume, is still valid.

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