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The Thermal Conductivity and Viscosity of Benzene

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New absolute measurements of the thermal conductivity of liquid benzene are reported. The measurements have been carried out in the temperature range 295–340 K, at atmospheric pressure, in a transient hot-wire instrument. The accuracy of the measurements is estimated to be ±0.5%. The measurements presented in this paper have been used, in conjunction with other high-pressure measurements of thermal conductivity and viscosity, to develop a consistent theoretically based correlation for the prediction of these properties. The proposed scheme permits the density dependence of the thermal conductivity and viscosity of benzene, for temperatures between 295 and 375 K and pressures up to 400 MPa, to be represented successfully by two equations containing just two parameters characteristic of the fluid at each temperature.

KEY WORDS: benzene; thermal conductivity; transient hot-wire technique; viscosity.

1. INTRODUCTION

In a recent paper, de Castro *et al.* [1] presented accurate correlations for the thermal conductivity of liquid water, toluene, and *n*-heptane as internationally accepted standards. Their work, based upon a critical evaluation of experimental methods and measurements, was carried out under the auspices of the Sub-Committee on Transport Properties of Commission I.2 of the International Union of Pure and Applied Chemistry and formed the first step toward the establishment of a large body of consistent standard reference data. In their initial study liquid benzene was also included, but no correlation for its thermal conductivity was proposed due to a high discordancy of the literature data. Thus, the need for accurate measurements of the thermal conductivity of benzene was apparent. In this paper, new

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absolute accurate measurements of the thermal conductivity of liquid benzene are presented. The measurements have been carried out in the temperature range 295–340 K, at atmospheric pressure, in a transient hot-wire instrument. The accuracy of the experimental results is estimated to be ±0.5%.

The measurements presented in this paper, in conjunction with the high-pressure thermal conductivity measurements of Li et al. [5] and the viscosity measurements of Dymond et al. [23], have been used to develop a consistent correlation for the prediction of these two properties. The proposed correlation scheme is constructed on a theoretically based treatment of the van der Waals model for a liquid. This scheme permits the prediction of the density dependence of the thermal conductivity and viscosity of benzene, for temperatures between 295 and 375 K and pressures up to 400 MPa, to be represented successfully by two equations containing just two parameters characteristic of the fluid at each temperature.

2. EXPERIMENTAL

In a previous paper [2] a transient hot-wire instrument for the measurement of the thermal conductivity of liquids was described. The accuracy of the instrument was estimated to be ±0.5%. For the present measurements, the instrument has been employed unchanged. The measurements were carried out at atmospheric pressure and the temperature range examined was 295–340 K. The sample of benzene was supplied by B. D. H. Chemicals Ltd. and the purity was found to be better than 99.8%.

The method of treating the effect of radiative heat transport adopted is the same as that proposed by Li et al. [3] and de Castro et al. [4]. As a check of the continuing good operation of the instrument, toluene was measured before and after the measurements of benzene. The values obtained for toluene were in full agreement with those reported earlier [2].

3. RESULTS

Table I shows the experimental data for the thermal conductivity of benzene at atmospheric pressure as a function of temperature. The thermal conductivity values have been represented by a linear function of the absolute temperature T, as

$$\lambda = 241.43 - 0.3334\,T \tag{1}$$

Table I. The Thermal Conductivity of Benzene as a Function of Temperature at Atmospheric Pressure

Temperature (K)	Thermal conductivity ($mW \cdot m^{-1} \cdot {}^{\circ}C^{-1}$)
298.58	141.9
302.74	140.3
306.78	139.3
306.83	139.0
310.73	137.9
315.63	136.3
320.29	134.6
325.72	132.8
329.85	131.8
333.32	130.0
335.41	129.5

The maximum deviation of the measurements from the above equation is one of ±0.2%, whereas the standard deviation is one of ±0.16%. Figure 1 shows a plot of the deviations of the present results from Eq. (1). In the same figure, we have included the only other very accurate set of data for benzene, the high-pressure measurements of Li et al. [5] extrapolated to atmospheric pressure. The accuracy claimed by Li et al. is also ±0.5% and, as can be seen, is well in accord with the accuracy of our measurements.

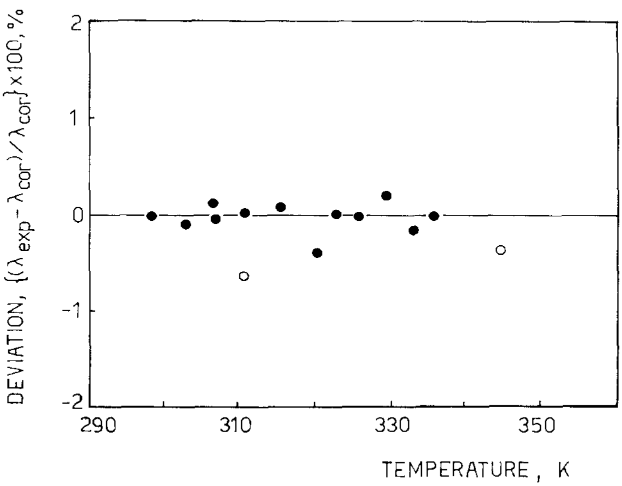

Fig. 1. Deviations of the experimental thermal conductivity values for benzene from Eq. (1). (●) Present work; (○) Li et al. [5].

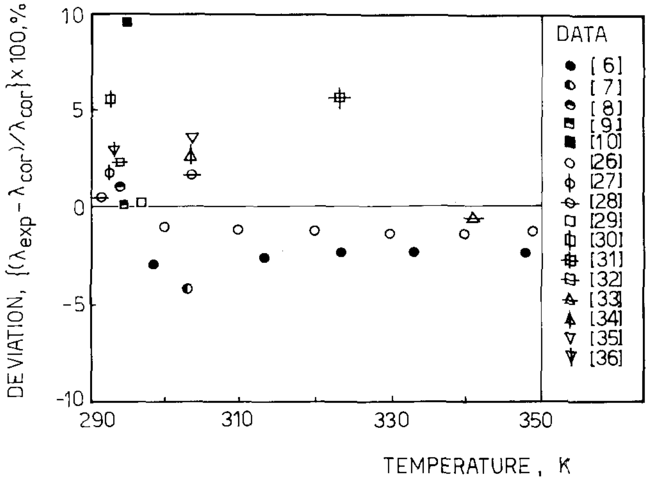

Fig. 2. Deviations of the experimental thermal conductivity values of other investigators, for benzene, from Eq. (1).

Figure 2 shows the deviations from Eq. (1) of the experimental measurements of other investigators, whose claimed accuracy is believed to be inferior to the present measurements. The measurements of Kashiwagi et al. [6], Mallan et al. [7], and Buchmann [8] were performed in transient-type instruments but on a relative basis. The measurements of Horrocks et al. [9] and van der Held and van Drunen [10] were also transient measurements, but they did not have a complete working equation available. All other measurements were performed in various types of steady-state instruments. Only investigators whose measurements depart less than 10% from Eq. (1) are presented. The discordancy of the literature values can be seen.

4. THE VAN DER WALLS MODEL

In the last two decades there has been considerable progress toward the molecular description of the transport properties of fluids [11–13]. A significant factor in this development was the computer simulation studies of transport processes by molecular dynamics [14] and their subsequent use in the development of the van der Waals model for a fluid [11]. This pictures a fluid as an assembly of molecules exerting a weak long-range attractive interaction and undergoing hard-core collisions on impact. At densities greater than about the critical density, the attractive part of the interaction provides a fairly uniform attractive energy surface and the model then becomes equivalent to the hard-sphere theory of transport in fluids. The application of this model to real systems requires a temperature-dependent core size volume V_0. The use of the rigid-sphere model allows the dominant effects in transport phenomena in dense fluids to be analyzed with the aid of the Enskog theory, corrected for correlations between velocities of the molecules from molecular dynamics simulations. Strictly speaking, this model is applicable only to monatomic systems. It has, however, been applied to the interpretation of viscosity coefficient data not only for monatomic fluids [11] but also for diatomic [15] and lower molecular weight hydrocarbons [16, 17], which behave as smoth hard spheres, and for other polyatomic fluids [18] considered as rough hard spheres with coupling of translational and rotational motion. In the case of the thermal conductivity coefficient data, it has been applied to paraffin and some aromatic hydrocarbons [19–21] with considerable success.

To test the theory without prior estimation of the core volumes V_0, the quantities η^* and λ^* were introduced [22], defined by

$$\eta^* = (\eta/\eta_0)(V/V_0)^{2/3} \tag{2}$$

$$\lambda^* = (\lambda/\lambda_0)(V/V_0)^{2/3} \tag{3}$$

where η_0 and λ_0 are the zero-density viscosity and thermal conductivity at temperature T and V is the molar volume of the fluid. The quantities η^* and λ^* can be evaluated from experimentally accessible quantities as

$$\eta^* = 6.035 \times 10^8 \, \eta V^{2/3} (MRT)^{-1/2} \tag{4}$$

$$\lambda^* = 1.609 \times 10^8 \, \lambda V^{2/3} \frac{(M/R^3T)^{1/2}}{(1 + 0.352 C^0_{v,\mathrm{int}}/R)} \tag{5}$$

where M is the molar mass, $C^0_{v,\mathrm{int}}$ is the internal part of the molar heat capacity at zero density, R is the gas constant, and η and λ are the experimentally measured viscosity and thermal conductivity coefficients (all expressed as SI units). Thus it should be possible to superimpose plots of experimental curves of η^* against $\ln V$ for a single fluid at a series of temperatures merely by imposing relative shifts along the $\ln V$ axis. The amount of shift required will produce the values of V_0 at every temperature. As the core volume, V_0, is characteristic of the fluid, the same procedure, if adopted for the λ^*, should produce the same values for the core volumes V_0.

In the past decade new accurate measurements of the viscosity and thermal conductivity permitted the evaluation of the core volumes. However, as each investigator studied either only the viscosity or only the thermal conductivity, incosistent values of V_0 have been reported in the literature. In this paper the viscosity and the thermal conductivity are examined together, for the first time to our knowledge, in an effort to produce the best predictive scheme for both quantities over a wide range of temperatures and pressures, based on the same core volume values.

5. THE PREDICTIVE SCHEME

For the thermal conductivity of benzene the values reported in Table I have been used. As, however, these measurements refer to atmospheric pressure only, the high-pressure transient hot-wire measurements of Li et al. [5] that have an accuracy of ±0.5% have been included in our analysis. The temperature range covered by these two sets of data is 295–365 K and the pressure range is 0.1–330 MPa.

For the viscosity of benzene the measurements of Dymond et al. [23] were used. The reported accuracy of these measurements is ±2% and they cover a range from 295 to 375 K and from 0.1 to 400 MPa. The internal part of the molar heat capacity at zero density required was calculated from the equation [4],

$$C^0_{v,\mathrm{int}} = -53.196 + 0.44646\,T - 2.143\times10^{-4}\,T^2 \tag{6}$$

The dependence of the quantities λ^* and η^* on the ratio (V/V_0) was found to be best described by the equations,

$$\ln\lambda^* = a_0 + a_1\ln(V/V_0) \tag{7}$$

$$\ln\eta^* = a_3 + \frac{B}{[(V/V_0)-1]} \tag{8}$$

The values of the coefficients a_0 and a_1 in Eq. (7) have been taken from a new study of the normal alkanes [25] extending earlier work [19]. In this study the core volume of hexane at 298 K has been adopted as a reference datum. Thus, values of λ^* for benzene may be represented by Eq. (7) by selecting an optimum value of V_0 for each temperature. Having thus obtained the core volumes, it is possible to seek an optimum representation of the viscosity data through Eq. (8), if B is represented as a single quadratic function of temperature.

The final relations that produce the best fit for both the thermal conductivity and the viscosity data were

$$\ln\lambda^* = 3 - 2.211\ln(V/V_0) \tag{9}$$

$$\ln\eta^* = 0.715 + \frac{B}{[(V/V_0)-1]} \tag{10}$$

Table II. Typical Values of the Function B and the Core Volume as a Function of Temperature [Eqs. (11) and (12)]

Temperature (K)	B	$10^{-6} V_0$ ($m^3 \cdot mol^{-1}$)
310	1.594	59.44
320	1.654	58.46
330	1.717	57.49
340	1.782	56.52
350	1.850	55.55
360	1.921	54.58
370	1.994	53.60

with

$$V_0 = 8.9576 \times 10^{-5} - 9.722 \times 10^{-8} T \tag{11}$$

$$B = 0.9543 - 1.7924 \times 10^{-3} T + 1.2438 \times 10^{-5} T^2 \tag{12}$$

Typical values of V_0 and B for various temperatures are shown in Table II. Figure 3 shows the deviations of the experimental values of the thermal conductivity of benzene from the values obtained with this scheme. It can be seen that the mximum deviation is ±1.3%, while 90% of the data have a maximum deviation of less than ±1%. Figure 4 shows the deviations of

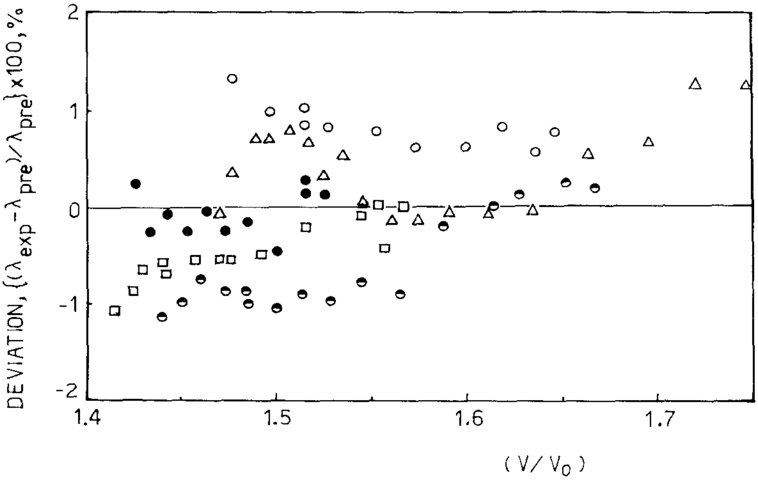

Fig. 3. Deviations of the experimental thermal conductivity values for benzene from the predictive scheme [Eqs. (4)–(6) and (9)–(12)]. (1) ○, Present work. (2) ●, 310.15 K; □, 320.65 K; ◓, 344.15 K; △, 360.15 K [5].

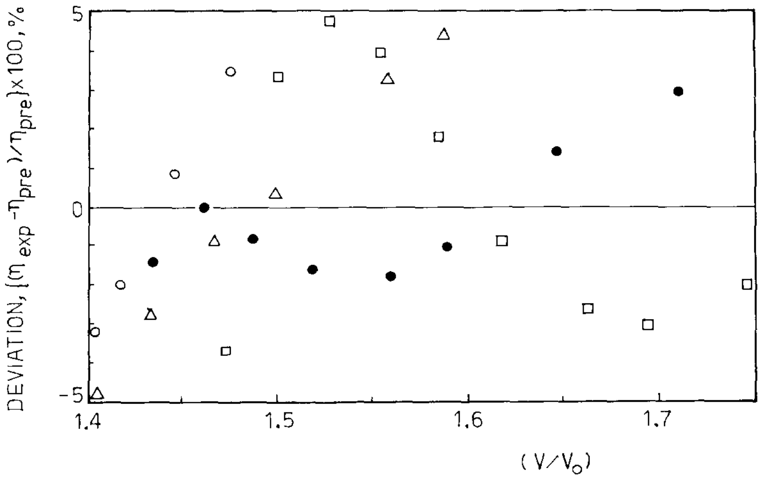

Fig. 4. Deviations of the experimental viscosity values for benzene from the predictive scheme [Eqs. (4)–(6) and (9)–(12)]. (○) 298.38 K; (△) 323.31 K; (●) 348.29 K; (□) 373.15 K [23].

the experimental values of the viscosity of benzene from the values obtained in this scheme. It can be seen that the maximum deviation is ±5%, while 90% of the data have a maximum deviation of less than ±4%. Thus the power of this predictive scheme becomes obvious when such a wide temperature and pressure range is considered.

6. CONCLUSIONS

New absolute measurements of the thermal conductivity of benzene are reported. The measurements have an estimated accuracy of ±0.5 %. A proposed scheme developed alowed the thermal conductivity and the viscosity of benzene, over a temperature range 295–375 K and for pressures up to 400 MPa, to be represented by two equations containing just two parameters characteristic of the fluid at each temperature. The accuracy of the proposed scheme is ±1.3% for the thermal conductivity and ±5% for the viscosity.

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