

## **Correlation and Prediction of Dense Fluid Transport Coefficients. V. Aromatic Hydrocarbons**

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A previously described method, based on consideration of hard-sphere theory, is used for the simultaneous correlation of the coefficients of self-diffusion, viscosity, and thermal conductivity for benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, and ethylbenzene in excellent agreement with experiment, over extended temperature and pressure ranges. Values are given for the roughness factors  $R_D$ ,  $R_\eta$ , and  $R_\lambda$ , and the characteristic volume,  $V_0$ , is expressed as a function of both carbon number and temperature.

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**KEY WORDS:** benzene; diffusion; ethylbenzene; hard-sphere theory; mesitylene; thermal conductivity; toluene; viscosity; xylene.

### **1. INTRODUCTION**

In previous papers [1, 2], a scheme was developed for the simultaneous correlation of self-diffusion, viscosity, and thermal conductivity coefficient data over a wide range of temperatures and pressures using a consistent set of values for the close-packed volume  $V_0$ . It was shown that the scheme provides a very satisfactory correlation of dense fluid *n*-alkane transport coefficient data [2] and, consequently, that it can be used with confidence to predict transport coefficients for these compounds under other conditions of temperature and pressure. The method has also been applied to simple organic molecular liquids [3] and has been extended to *n*-alkane mixtures [4]. It has been demonstrated that this scheme can lead to predictions of transport property coefficients for these systems, at pressures up to 600 MPa, with an accuracy of  $\pm 6\%$ .

The scheme is based on the assumption that transport coefficients of

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real dense fluids, expressed in terms of the reduced volume  $V/V_0$ , are directly proportional to values given by exact hard-sphere theory [5]. The proportionality factor, described as roughness factor  $R$ , accounts for molecular roughness and departure from molecular sphericity. In order to obtain a consistent set of values for the molecular parameter  $V_0$ , it is important that at least two transport properties are correlated simultaneously. These should be the self-diffusion and viscosity coefficients, which provide the most critical test of any correlation scheme. Ideally, all three properties should be considered together. Universal curves have been determined empirically for each reduced transport coefficient as a function of reduced density [2]. The predictive scheme for diffusion has recently been further developed [6] as a result of a molecular dynamics study by Erpenbeck and Wood [7]. The expression for the reduced diffusion coefficient was modified [6] in line with these new calculations, and as a consequence, methane was found to behave as a rough hard-sphere system.

In this paper the general applicability of the scheme is further tested using a set of simple aromatic hydrocarbons including benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, and ethylbenzene for which experimental data are available up to high pressures.

## 2. THE CORRELATION METHOD

As the method for correlating transport coefficients has been described in detail in the case of *n*-alkanes [2, 6], just the main features of the scheme are reproduced here.

It has been shown [5] that for rough spherical molecules the transport coefficients can be directly related to the smooth hard-sphere transport coefficients. A corresponding relationship between the experimental transport coefficients of rough nonspherical molecules and the smooth hard-sphere values (subscript shs) can therefore be assumed:

$$D_{\text{exp}} = R_D D_{\text{shs}}; \quad \eta_{\text{exp}} = R_\eta \eta_{\text{shs}}; \quad \lambda = R_\lambda \lambda_{\text{shs}} \quad (1)$$

where  $R_D$ ,  $R_\eta$ , and  $R_\lambda$  are the roughness factors for self-diffusion, viscosity, and thermal conductivity, respectively, and are assumed to be independent of both temperature and density.

Exact smooth hard-sphere transport coefficients are given by the product of the values from Enskog theory [8] and the computed corrections to Enskog theory:

$$D_{\text{shs}} = D_E (D/D_E)_{\text{MD}}; \quad \eta_{\text{shs}} = \eta_E (\eta/\eta_E)_{\text{MD}}; \quad \lambda_{\text{shs}} = \lambda_E (\lambda/\lambda_E)_{\text{MD}} \quad (2)$$

Reduced coefficients of self-diffusion  $D^*$ , viscosity  $\eta^*$ , and thermal conductivity  $\lambda^*$  are convenient to use [9].

These are defined as follows:

$$D_{\text{exp}}^* = R_D D_{\text{shs}}^* = R_D \left[ \frac{n D_{\text{shs}}}{n_0 D_0} \right] \left[ \frac{V}{V_0} \right]^{2/3} \quad (3)$$

$$\eta_{\text{exp}}^* = R_\eta \eta_{\text{shs}}^* = R_\eta \left[ \frac{\eta_{\text{shs}}}{\eta_0} \right] \left[ \frac{V}{V_0} \right]^{2/3} \quad (4)$$

$$\lambda_{\text{exp}}^* = R_\lambda \lambda_{\text{shs}}^* = R_\lambda \left[ \frac{\lambda_{\text{shs}}}{\lambda_0} \right] \left[ \frac{V}{V_0} \right]^{2/3} \quad (5)$$

where subscript zero refers to the low-density hard-sphere coefficient in the first-order approximation and  $n$  is the number density.

Values for the reduced smooth hard-sphere transport coefficients can be calculated from experiment after substitution of the hard-sphere expressions which give:

$$D_{\text{shs}}^* = \frac{D_{\text{exp}}^*}{R_D} = 5.030 \times 10^8 \left[ \frac{M}{RT} \right]^{1/2} \frac{DV^{-1/3}}{R_D} \quad (6)$$

$$\eta_{\text{shs}}^* = \frac{\eta_{\text{exp}}^*}{R_\eta} = 6.035 \times 10^8 \left[ \frac{1}{MRT} \right]^{1/2} \frac{\eta V^{2/3}}{R_\eta} \quad (7)$$

$$\lambda_{\text{shs}}^* = \frac{\lambda_{\text{exp}}^*}{R_\lambda} = 1.936 \times 10^7 \left[ \frac{M}{RT} \right]^{1/2} \frac{\lambda V^{2/3}}{R_\lambda} \quad (8)$$

The determination of  $V_0$  and the  $R$  factor at any temperature for a particular transport property is accomplished by a well-established curve-fitting procedure. A plot of  $\log P^*$  versus  $\log V$  from experiment is superimposed on universal plots of  $\log P^*$  versus  $\log(V/V_0)$  from hard-sphere theory by vertical and horizontal adjustment from which the  $R$  factor and  $V_0$  values are, respectively, obtained. The universal curves for the transport properties were developed from a consideration of both hard-sphere theory and experimental data for higher  $n$ -alkanes. However, recent accurate calculations of the corrections to Enskog theory for hard-sphere diffusion [7] have resulted in a revision of the hard-sphere based correlation for dense fluid self-diffusion coefficients [6]. The expression formerly given for the reduced diffusion coefficient as a function of reduced volume has been adjusted in line with these new molecular dynamics values. This results in values for the correction to the Enskog diffusion coefficient in excellent agreement with those given by Alder et al. [10]. This modification has been discussed in detail elsewhere [6].

**Table I.** The Coefficients  $a_{D_i}$ ,  $a_{\eta_i}$ , and  $a_{\lambda_i}$ 

$i$	$a_{D_i}$	$a_{\eta_i}$	$a_{\lambda_i}$
0	3.33076	1.0945	1.0655
1	-31.74261	-9.26324	-3.538
2	133.0472	71.0385	12.120
3	-285.1914	-301.9012	-12.469
4	298.1413	797.6900	4.562
5	-125.2472	-1221.9770	—
6	—	987.5574	—
7	—	-319.4636	—

The resulting universal curves are expressed in terms of reduced volume  $V_r$ , where  $V_r = V/V_0$ :

$$\log \left[ \frac{D_{\text{exp}}^*}{R_D} \right] = \sum_{i=0}^5 a_{D_i} (1/V_r)^i \quad (9)$$

$$\log \left[ \frac{\eta_{\text{exp}}^*}{R_\eta} \right] = \sum_{i=0}^7 a_{\eta_i} (1/V_r)^i \quad (10)$$

$$\log \left[ \frac{\lambda_{\text{exp}}^*}{R_\lambda} \right] = \sum_{i=0}^4 a_{\lambda_i} (1/V_r)^i \quad (11)$$

The values for the coefficients  $a_{D_i}$ ,  $a_{\eta_i}$ , and  $a_{\lambda_i}$  are given in Table I.

### 3. RESULTS

This correlation scheme for the self-diffusion, viscosity, and thermal conductivity coefficients has been applied to seven simple aromatic hydrocarbons: benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, and ethylbenzene. The temperature and pressures ranges of the data used in this analysis are indicated in Table II. Transport coefficient measurements up to high pressures are available for most of these compounds. There are experimental measurements on all three transport properties for both benzene [11–25] and toluene [15, 18, 21, 24, 26–32].

Considering each compound separately and for each property  $P$  at a given temperature, plots of  $\log P_{\text{exp}}^*$  versus  $\log V$  [Eqs. (6–8)] are compared with the universal curves of  $\log (P_{\text{exp}}^*/R_P)$  [Eqs. (9–11)]. Values for  $V_0$  and  $R_P$  are derived from the points of superposition. The roughness factor,  $R_P$ , is found to be temperature independent. Slight adjustments are

Table II. Data Used in the Analysis

Compound	Prop.	$n$	T range (K)	$P_{\max}$ (MPa)	Ref. No.
Benzene	$D$	13	298-333	70	11
		35	300-440	400	12
		23	280-320	100	13
		9	328-333	155	14
	$\eta$	5	290-380	0.1	15
		6	295-335	0.1	16
		8	280-400	0.1	17
		28	303-323	70	18
		28	295-375	400	19
		35	300-440	400	20
		65	295-350	115	21
		51	294-432	48	22
	$\lambda$	11	295-340	0.1	23
		11	298-332	0.1	24
		59	310-360	330	25
Toluene	$D$	14	273-326	150	26
	$\eta$	7	285-400	0.1	15
		6	297-350	0.1	27
		32	303-340	70	18
		40	295-380	520	28
		48	303-348	252	29
		76	295-350	115	21
	$\lambda$	13	305-350	0.1	30
		11	299-365	0.1	24
		94	273-373	250	31
49	305-350	590	32		
<i>o</i> -Xylene	$\eta$	69	295-350	115	21
	$\lambda$	12	295-360	0.1	33
		16	305-360	43	34
<i>p</i> -Xylene	$\eta$	6	295-400	0.1	15
		57	295-350	115	21
	$\lambda$	11	295-360	0.1	33
17		305-360	41	34	
<i>m</i> -Xylene	$\eta$	23	303-323	70	18
		71	295-350	115	21
	$\lambda$	11	290-360	0.1	33
16		305-360	40	34	
Ethylbenzene	$\eta$	73	295-350	115	21
	$\lambda$	28	300-360	50	35
Mesitylene	$D$	15	298-313	290	36
	$\eta$	6	295-400	0.1	15
		27	295-327	52	37

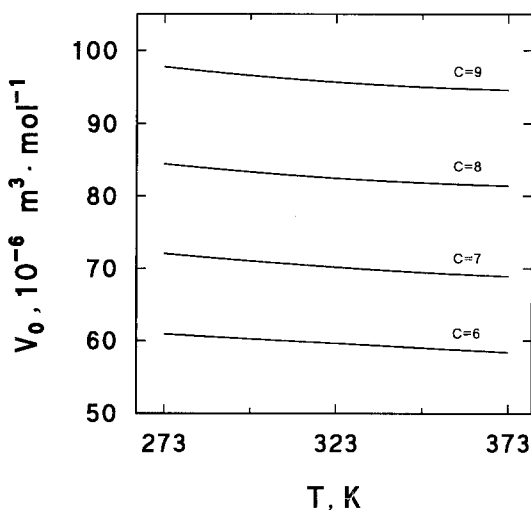
**Table III.** Typical Values of the Characteristic Volume,  $V_0$  ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ), as a Function of Temperature and Carbon Number for the Aromatic Compounds in this Study

Carbon No.	$T$ (K)			
	298	323	348	373
6	60.24	59.61	58.99	58.38
7	71.04	70.17	69.45	68.89
8	83.33	82.45	81.81	81.39
9	96.61	95.69	95.03	94.62

made for each compound so that  $R_p$  has a constant value and  $V_0$  is property independent and decreases smoothly with increasing temperature. The resulting  $V_0$  values were fitted as a function of temperature and carbon number of the compound using a least-squares regression method to give:

$$10^6 V_0 = -3324.7C^{-2} + 529.47C^{-1} + T(9.48786C^{-2} - 8.55176 \times 10^{-2}C + 6.03463 \times 10^{-3}C^2) + T^2(-1.5797 \times 10^{-3} + 3.9901 \times 10^{-4}C - 2.2309 \times 10^{-5}C^2) \quad (12)$$

Selected values of the characteristic volume are listed in Table III and the smooth decrease in  $V_0$  with increasing temperature is illustrated in Fig. 1.

**Fig. 1.** The volume of close-packing,  $V_0$ , as a function of temperature and carbon number.

**Table IV.** Comparison of Calculated Self-Diffusion Coefficients with Experiment; %dev = 100 (exp - calc)/calc

Compound	$R_D$	$n$	(5-10)%	> 10%
Benzene	0.958	80	7	3
Toluene	0.920	14	1	—
Mesitylene	0.910	15	3	1
Total		109	11	4

No definite trend was observed in the  $R_\eta$  values in going from benzene to mesitylene. There was insufficient  $R_D$  data to predict values for any other compound. However, the  $R_\lambda$  values were found to vary linearly with carbon number:

$$R_\lambda = 1.528 + 0.212 (C - 6) \quad (13)$$

The success with which this method fits the experimental data listed in Table II is demonstrated in Tables IV, V, and VI and also in Figs. 2, 3, and 4. In the case of self-diffusion (Table IV), the agreement is quite acceptable. For benzene diffusion, as shown in Fig. 2, the measurements of Harris [11], McCool et al. [13], and Collings and Woolf [14] are fitted to within  $\pm 5\%$ . The results of Parkhurst and Jonas [12], however, show a large scatter with three points deviating by more than 10%.

In the case of viscosity (Table V), the agreement is very satisfactory, with less than 3% of 767 data points deviating by more than 5%. The deviation plot for benzene is illustrated in Fig. 3, where it can be seen that

**Table V.** Comparison of Calculated Viscosity Coefficients with Experiment; %dev = 100 (exp - calc)/calc

Compound	$R_\eta$	$n$	(5-10)%	> 10%
Benzene	0.960	226	8	1
Toluene	1.030	209	9	—
<i>o</i> -Xylene	1.050	69	—	—
<i>p</i> -Xylene	1.033	63	1	—
<i>m</i> -Xylene	0.950	94	—	—
Ethylbenzene	1.010	73	—	—
Mesitylene	0.900	33	—	—
Total		767	18	1

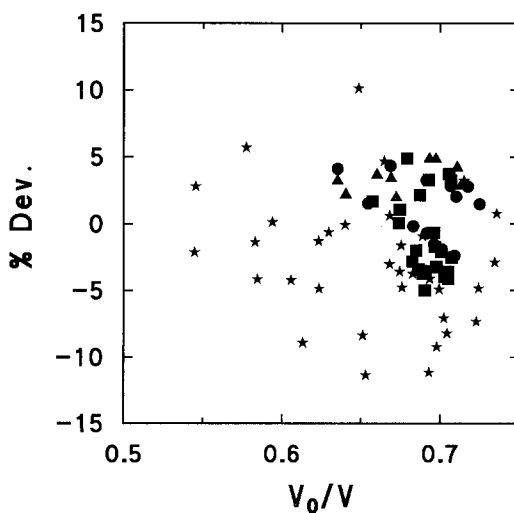
**Table VI.** Comparison of Calculated Thermal Conductivity Coefficients with Experiment; %dev = 100 (exp - calc)/calc

Compound	$R_\lambda$	$n$	(5-10)%	>10%
Benzene	1.528	81	—	—
Toluene	1.740	167	—	—
<i>o</i> -Xylene	1.952	28	—	—
<i>p</i> -Xylene	1.952	28	—	—
<i>m</i> -Xylene	1.952	27	—	—
Ethylbenzene	1.952	28	—	—
Total		358	—	—

only one point, which is at the highest density, deviates by over 10%. It is to be expected that uncertainties in density at the highest pressures contribute to the overall error.

It can be seen in Table VI that, for thermal conductivity, the comparison with experiment is very good; all of the data fit to within  $\pm 5\%$ . Furthermore, the deviations for benzene are well within 3% (Fig. 4).

It is important for the quality of the fit to ensure that the  $V_0$  values used are optimum values. This may be verified by comparing all the devia-



**Fig. 2.** Percentage deviation  $[100(D_{\text{exp}} - D_{\text{calc}})/D_{\text{calc}}]$  of the experimental diffusion coefficient data for benzene from calculated values at different reduced densities,  $V_0/V$ . ● [11]; ★ [12]; ■ [13]; ▲ [14].



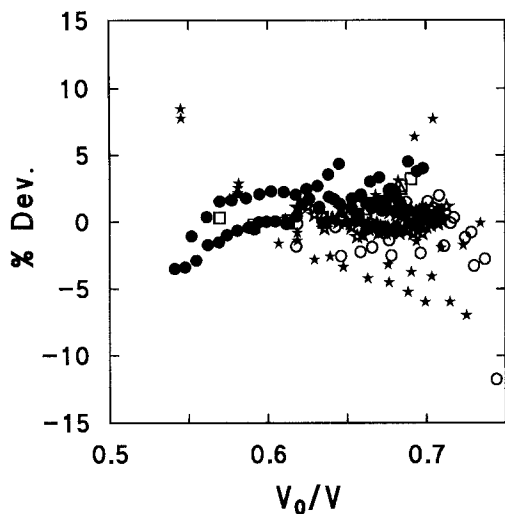


Fig. 3. Percentage deviation  $[100(\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{calc}}]$  of the experimental viscosity coefficient data for benzene from calculated values at different reduced densities,  $V_0/V$ . ■ [15];  $\triangle$  [16];  $\square$  [17];  $\blacktriangle$  [18];  $\circ$  [19];  $\star$  [20];  $\star$  [21];  $\bullet$  [22].

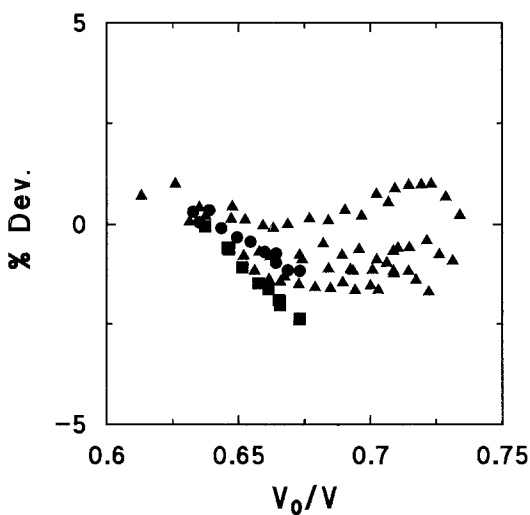


Fig. 4. Percentage deviation  $[100(\lambda_{\text{exp}} - \lambda_{\text{calc}})/\lambda_{\text{calc}}]$  of the experimental thermal conductivity coefficient data for benzene from calculated values at different reduced densities,  $V_0/V$ .  $\bullet$  [23];  $\blacksquare$  [24];  $\blacktriangle$  [25].

tions of the experimental transport coefficients for a particular compound from those calculated. An inspection of Figs. 2, 3, and 4 establishes that the overall data fit for benzene would not be improved by varying  $V_0$ ; an alteration in  $V_0$  leads to changes in opposing directions in the calculated self-diffusion and viscosity coefficients.

#### 4. CONCLUSIONS

Self-diffusion, viscosity, and thermal conductivity coefficient data for benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, and ethylbenzene have been very satisfactorily correlated using a scheme developed for *n*-alkanes based on a consideration of the hard-sphere theory of transport properties. The recently modified universal curve for the reduced diffusion coefficient was employed. Values are given for the factors  $R_D$ ,  $R_\eta$ , and  $R_\lambda$  for each compound and an equation is presented for the characteristic volume  $V_0$  as a function of carbon number and temperature.

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