

Correlation and Prediction of Dense Fluid Transport Coefficients. I. *n*-Alkanes

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Recent accurate measurements of the self-diffusion coefficient for *n*-hexadecane and *n*-octane and of the viscosity coefficient for *n*-heptane, *n*-nonane, and *n*-undecane over wide pressure ranges have been used to provide a critical test of a previously described method, based on consideration of hard-sphere theory, for the correlation of transport coefficient data. It is found that changes are required to the universal curve for the reduced viscosity coefficient as a function of reduced volume and, also, to the parameters R_D , R_η , and R_λ which were introduced to account for effects of nonspherical molecular shape. The scheme now accounts most satisfactorily for the self-diffusion, viscosity, and thermal conductivity coefficient data for all *n*-alkanes from methane to hexadecane at densities greater than the critical density.

KEY WORDS: diffusion; hard-sphere theory; *n*-alkanes; thermal conductivity; viscosity.

1. INTRODUCTION

In a recent publication [1], a scheme was described for the simultaneous correlation of self-diffusion, viscosity, and thermal conductivity coefficient data for dense-fluid *n*-alkanes. The method was developed from a consideration of the results given by hard-sphere models. A consistent set of values for V_0 , the close-packed volume, was obtained, and these values were expressed as a function of carbon number and temperature. This made it possible to calculate with confidence transport properties for these compounds under other experimental conditions.

At that time, accurate self-diffusion coefficient data were available only for methane [2, 3] and *n*-hexane [4]. It was shown that these measurements

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could be satisfactorily correlated on the basis that the roughness parameter R_D was equal to unity. This was as expected for methane, which behaves as a smooth hard-sphere system with regard to the density dependence of its transport coefficients [5, 6]. However, for *n*-hexane there is no theoretical reason why R_D should equal one, and so accurate self-diffusion coefficient measurements were made for *n*-hexadecane and *n*-octane [7] to determine values of the roughness factor for higher alkanes. It was found that for *n*-hexadecane the data could not be satisfactorily correlated with R_D equal to unity using the reference curve for diffusion and V_0 values given previously [1]. The discrepancies with the experimental measurements varied from +30 to -28%. However, with the same reference curve, when R_D was reduced to about 0.5, the data could be fitted [8] to within their estimated experimental uncertainty, but the V_0 values required to correlate these data were significantly lower than those given earlier [1].

For the viscosity coefficient, recent accurate measurements [9] for *n*-heptane, *n*-nonane, and *n*-undecane using a vibrating-wire viscometer for pressures up to 70 MPa were found to be in reasonable agreement with the predictions of the correlation method [1], but the difference, of about 6%, was systematic.

In view of these shortcomings in the previously described method, the new transport-property measurements have been used to define more closely the reference curves, the characteristic volumes V_0 , and the roughness parameters to produce an improved correlation scheme.

2. THE CORRELATION METHOD

It has previously been shown [10] that in the application of the hard-sphere theories of transport properties, it is convenient to consider reduced coefficients of self-diffusion D^* , viscosity η^* , and thermal conductivity λ^* . These are defined as follows:

$$D^* = \left[\frac{nD_{\text{SHS}}}{n_0 D_0} \right] \left[\frac{V}{V_0} \right]^{2/3} \quad (1)$$

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

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

where subscript zero refers to the low-density coefficient and n is the number density. The exact smooth hard-sphere coefficients, subscript SHS,

are given by the product of the values given by Enskog theory [11] and the computed corrections to Enskog theory:

$$D_{\text{SHS}} = D_{\text{E}}(D/D_{\text{E}})_{\text{MD}}, \quad \eta_{\text{SHS}} = \eta_{\text{E}}(\eta/\eta_{\text{E}})_{\text{MD}}, \quad \lambda_{\text{SHS}} = \lambda_{\text{E}}(\lambda/\lambda_{\text{E}})_{\text{MD}} \quad (4)$$

Values for the reduced coefficients can be calculated for different reduced volumes, V/V_0 , with the use of values for the correction factors which have been computed by molecular dynamics [12, 13]. However, for viscosity and thermal conductivity, and for self-diffusion above the freezing density [14], these corrections have greater uncertainty.

The reduced coefficients can also be calculated from experimental data. In the case of spherical molecules where transfer of rotational momentum can occur, Chandler showed [15] that the diffusion and viscosity coefficients were directly proportional to the smooth hard-sphere values. The proportionality coefficients, the translational-rotational coupling factors, were assumed to be temperature independent and, at most, weakly density dependent. This idea has been extended to *n*-alkanes [1, 16] by assuming that the transport coefficients for these compounds are directly proportional to the smooth hard-sphere values, with proportionality factors R_D , R_η , and R_λ for self-diffusion, viscosity, and thermal conductivity, respectively, accounting for effects of nonspherical molecular shape. These factors are assumed to be independent of both temperature and density. Thus, values for the reduced smooth hard-sphere transport coefficients can then be calculated from experiment after substitution of the hard-sphere expressions:

$$D^* = \frac{D_{\text{exp}}^*}{R_D} = 5.030 \times 10^8 \left[\frac{M}{RT} \right]^{1/2} \frac{DV^{-1/3}}{R_D} \quad (5)$$

$$\eta^* = \frac{\eta_{\text{exp}}^*}{R_\eta} = 6.035 \times 10^8 \left[\frac{1}{MRT} \right]^{1/2} \frac{\eta V^{2/3}}{R_\eta} \quad (6)$$

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

The determination of V_0 and the R factor at any temperature for a particular transport property, X , for a given compound is accomplished by curve-fitting. In principle, a plot of $\log X^*$ versus $\log V$ from experiment is simply superimposed on the plot of $\log X^*$ versus $\log (V/V_0)$ from theory, by vertical and horizontal adjustment. The R factor is found from the vertical displacement and V_0 from the horizontal shift. In practice, uncertainties in the computed corrections to Enskog theory make this scheme possible only for diffusion and, here, only up to moderate reduced densities. By

using diffusion data for methane [2, 3], V_0 values were determined and used to define the smooth hard-sphere curves for viscosity and thermal conductivity [17]. Viscosity and thermal conductivity data for higher n -alkanes were then used [1] to build up reference curves for each of these reduced smooth hard-sphere properties, by overlapping the curves given by methane. In this way a simultaneous fit of different transport coefficients can be made with consistent V_0 values. However, the reference curves and molecular parameters were not uniquely defined—some variation was still possible. The reason is that for the higher n -alkanes, in particular, the measurements at individual temperatures corresponded to high V_0/V but they covered only small density ranges. Small variations in the reference curves could be compensated by variation in the R factors and V_0 values in fitting the experimental data.

3. RESULTS

Recent accurate measurements of self-diffusion [7] and viscosity coefficients [9] have been considered, in addition to the earlier data, to define the reference curves more precisely. Optimum values for V_0 and the corresponding R factor which gave the best simultaneous fit to all properties for which data were available were obtained from the curve-fitting procedure described above.

The universal curves were expressed as before in terms of reduced volume V_r , where $V_r = V/V_0$:

$$\log \left(\frac{D_{\text{exp}}^*}{R_D} \right) = \sum_{i=0}^5 a_{D_i} (1/V_r)^i \quad (8)$$

$$\log \left(\frac{\eta_{\text{exp}}^*}{R_\eta} \right) = \sum_{i=0}^7 a_{\eta_i} (1/V_r)^i \quad (9)$$

$$\log \left(\frac{\lambda_{\text{exp}}^*}{R_\lambda} \right) = \sum_{i=0}^4 a_{\lambda_i} (1/V_r)^i \quad (10)$$

The values for the coefficients a_{D_i} , a_{η_i} , and a_{λ_i} are given in Table I. The curves for diffusion and thermal conductivity are the same as before, but that for viscosity had to change because of the variation in the V_0 values that was necessary for the diffusion-data fit.

Values for V_0 and the R factors for the different compounds at the temperatures of experimental measurement were initially tabulated and then expressed in equation form. In view of the sensitivity of the calculated viscosity and diffusion coefficients to small variations in V_0 , it was necessary to fit these values as closely as possible. V_0 values for the lower

Table I. The Coefficients $a_{\lambda i}$, $a_{\eta i}$, and $a_{D i}$

i	$a_{\lambda i}$	$a_{\eta i}$	$a_{D i}$
0	1.0655	1.0945	3.285
1	-3.538	-9.26324	-31.74261
2	12.120	71.0385	133.0472
3	-12.469	-301.9012	-285.1914
4	4.562	797.6900	298.1413
5	—	-1221.9770	-125.2472
6	—	987.5574	—
7	—	-319.4636	—

n-alkanes, C1 to C4, were fitted by a least-squares regression method, based on the Fischer T test as a function of carbon number C and temperature T with the following result.

CH₄-C₄H₁₀:

$$\begin{aligned}
 10^6 V_0 = & 45.822 - 6.1867T^{0.5} + 0.36879T - 0.007273T^{1.5} \\
 & + C(2.17871T^{0.5} - 0.185198T + 0.00400369T^{1.5}) \\
 & + C^2(6.95148 - 52.6436T^{-0.5}) + C^3(-7.801897 + 42.24493T^{-0.5} \\
 & + 0.4476523T^{0.5} - 0.009573512T) \quad (11)
 \end{aligned}$$

For higher *n*-alkanes where measurements have been made over a narrower temperature range, a simpler form of equation fitted the results.

C₅H₁₂-C₁₆H₃₄:

$$\begin{aligned}
 10^6 V_0 = & 117.874 + 0.15(-1)^C - 0.25275T + 0.000548T^2 \\
 & - 0.0000004246T^3 + (C - 6)(1.27 - 0.0009T)(13.27 + 0.025C) \quad (12)
 \end{aligned}$$

In Table II, values for these characteristic volumes are given at selected temperatures. The R factors were fitted by least-squares regression analysis, as a function of *n*-alkane carbon number, with the following results:

$$R_D = 0.9908 + 0.0119C - 0.00258C^2 \quad (13)$$

$$R_\eta = 0.995 - 0.0008944C + 0.005427C^2 \quad (14)$$

$$\begin{aligned}
 R_\lambda = & -18.8416C^{-1.5} + 41.461C^{-1} - 30.15C^{-0.5} \\
 & + 8.6907 + 0.001337C^{2.5} \quad (15)
 \end{aligned}$$

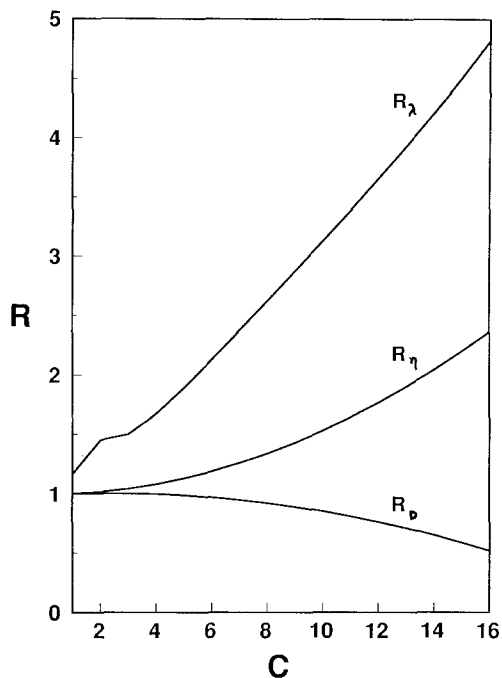


Fig. 1. Dependence of the *R* factors on carbon chain length.

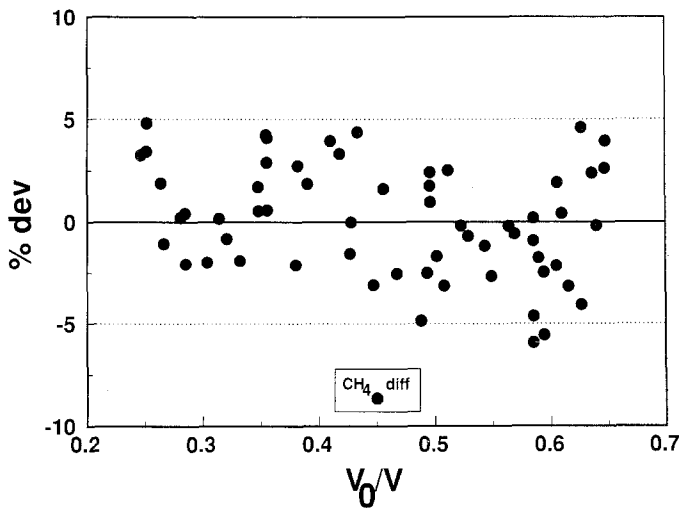


Fig. 2. Percentage deviation $[100(D_{\text{exp}} - D_{\text{calc}})/D_{\text{exp}}]$ of experimental diffusion coefficient data for methane (● [2, 3]) from values calculated using Eqs. (6), (9), (11), and (14) at different reduced densities.

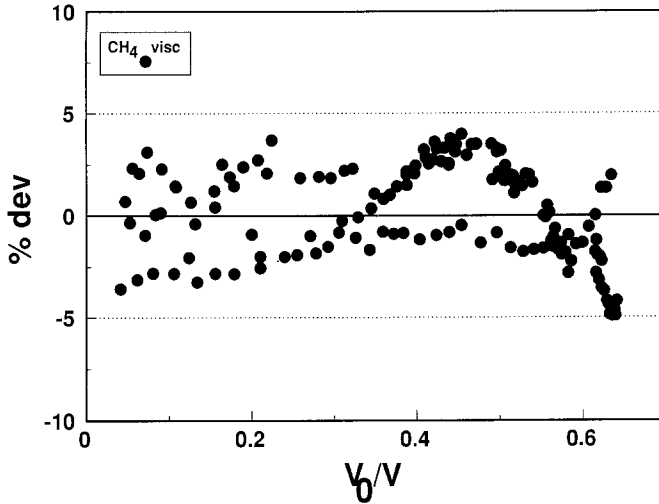


Fig. 3. Percentage deviation $[100(\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{exp}}]$ of experimental viscosity coefficient data for methane (● [18, 19]) from values calculated using Eqs. (5), (8), (11), and (13) at different reduced densities.

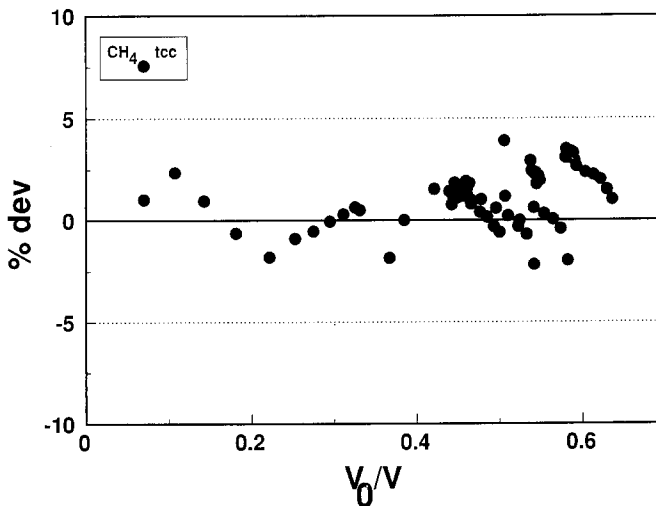


Fig. 4. Percentage deviation $[100(\lambda_{\text{exp}} - \lambda_{\text{calc}})/\lambda_{\text{exp}}]$ of experimental thermal conductivity coefficient data for methane (● [29, 30]) from values calculated using Eqs. (7), (10), (11), and (15) at different reduced densities.

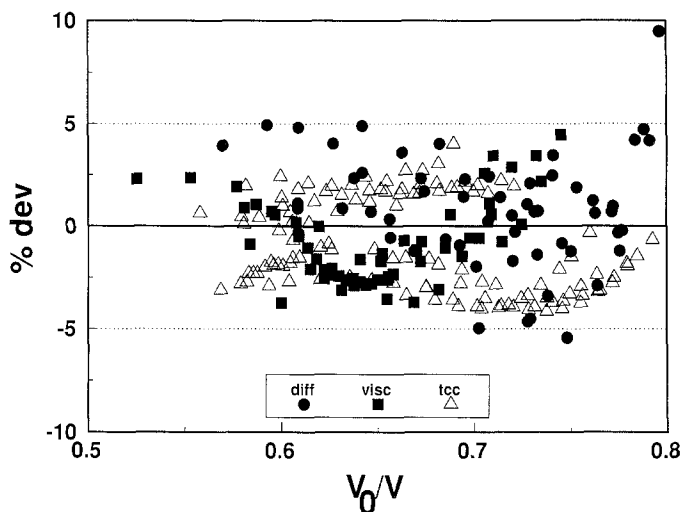


Fig. 5. Percentage deviation $[100(X_{\text{exp}} - X_{\text{calc}})/X_{\text{exp}}]$ of experimental data for the transport coefficient, X , for *n*-hexane from values calculated at different reduced densities. Diffusion, ● [4]; viscosity, ■ [23–25]; thermal conductivity, △ [35, 36].

For thermal conductivity, measurements which showed a critical enhancement were not considered. The dependence of R_D , R_η , and R_λ on the length of the alkane chain is shown in Fig. 1. The variation is smooth, except for ethane thermal conductivity, where the optimum value for R_λ is somewhat higher than expected.

Table III. Comparison of Self-Diffusion Coefficients Calculated by the Present Method with Experimental Values

Compound	<i>P</i> range (MPa)	No. of points				Ref. No(s).
		Total	Deviation from expt.			
			5–10%	> 10%		
CH ₄	1.5–222	61	2	—	2,3	
C ₆ H ₁₄	0.1–394	59	2	—	4	
C ₈ H ₁₈	0.1–364	10	1	—	7	
C ₁₆ H ₃₄	0.1–280	20	2	—	7	
Total		150	7	—		

The correlation scheme for the self-diffusion, viscosity, and thermal conductivity coefficients for the *n*-alkanes is summarized in Eqs. (5)–(15). The success with which this method fits the experimental data is demonstrated in Tables III, IV, and V and in Figs. 2–5. In the case of self-diffusion, Table III, agreement is very satisfactory, with only a few points deviating by more than 5%. The root mean-square percentage deviation is 3.0%. For methane, where measurements cover the temperature range from 110 to 323 K, the deviations are random, as shown in Fig. 2.

The viscosity measurements extend generally to higher pressures. Table IV includes the new data for *n*-heptane, *n*-nonane, and *n*-undecane [9]. With an increased number of experimental points, the fit is an improvement over the earlier scheme [1], with only 5 of over 1100 points now differing by more than 10%. Uncertainties in density at the highest pressures will contribute to these deviations. The overall root mean-square percentage deviation is 2.8%. More experimental data are available for methane than any other *n*-alkane. The deviation plot is shown in Fig. 3, and indicates a fairly random distribution of points.

Table IV. Comparison of Viscosity Coefficients Calculated by the Present Method with Experimental Values

Compound	<i>P</i> range (MPa)	Total	No. of points		Ref. No(s).
			Deviation from expt.		
			5–10%	>10%	
CH ₄	0.6–1002	149	—	—	18, 19
C ₂ H ₆	0.3–32	99	1	—	20
C ₃ H ₈	1.7–32	60	2	—	21
C ₄ H ₁₀	1.5–34	73	—	—	22
C ₅ H ₁₂	—	—	—	—	—
C ₆ H ₁₄	0.1–420	135	—	—	23–26
C ₇ H ₁₆	0.1–110	112	1	—	9, 24, 26
C ₈ H ₁₈	0.1–506	126	6	2	24, 26, 27
C ₉ H ₂₀	0.1–70	28	—	—	9
C ₁₀ H ₂₂	0.1–110	169	6	—	24, 26, 28–30
C ₁₁ H ₂₄	0.1–61	28	—	—	9
C ₁₂ H ₂₆	0.1–453	113	19	2	24, 26, 27
C ₁₃ H ₂₈	—	—	—	—	—
C ₁₄ H ₃₀	0.1	10	2	1	24
C ₁₅ H ₃₂	—	—	—	—	—
C ₁₆ H ₃₄	0.1–273	25	5	—	27
Total		1127	42	5	

Table V. Comparison of Thermal Conductivity Coefficients Calculated by the Present Method with Experimental Values

Compound	<i>P</i> range (MPa)	No. of points			Ref. No(s).
		Total	Deviation from expt.		
			5–10%	>10%	
CH ₄	0.3–70	73	—	—	31, 32
C ₂ H ₆	0.3–70	91	5	—	33
C ₃ H ₈	1.0–70	70	4	—	34
C ₄ H ₁₀	1.0–50	10	—	—	35
C ₅ H ₁₂	1.8–283	48	—	—	36
C ₆ H ₁₄	0.1–644	120	—	—	37–39
C ₇ H ₁₆	0.1–500	95	—	—	38–41
C ₈ H ₁₈	0.1–592	112	1	—	37, 39, 42
C ₉ H ₂₀	0.1–503	84	—	—	42, 43
C ₁₀ H ₂₂	0.1–200	40	—	—	38
C ₁₁ H ₂₄	0.1–403	67	—	—	42, 43
C ₁₂ H ₂₆	0.1–200	42	—	—	44
C ₁₃ H ₂₈	24–468	57	—	—	45
C ₁₄ H ₃₀	0.1	21	—	—	42
C ₁₅ H ₃₂	—	—	—	—	—
C ₁₆ H ₃₄	0.1	10	—	—	46
Total		940	10	—	

For thermal conductivity an increase in data points has brought the total to over 900. Of these, only 1% deviate by more than 5%, which is a most satisfactory situation. The root mean-square percentage deviation is 2.4%. As shown for methane in Fig. 4, the deviations are generally well within 5%.

A method for checking that the V_0 values are optimum is to plot the deviations of all the experimental transport coefficients from the calculated values on the one graph. This is shown in the case of *n*-hexane in Fig. 5. The overall data fit would not be improved by varying V_0 . The reason is that variation in V_0 leads to changes in opposite directions in the calculated self-diffusion and viscosity coefficients.

4. CONCLUSIONS

New self-diffusion and viscosity coefficient data for *n*-alkanes are used to provide a critical test of a correlation method for the simultaneous fit of thermal conductivity, viscosity, and diffusion, based on consideration of the

exact hard-sphere theory of transport properties. It is found that changes are required to the universal curve for the reduced viscosity coefficient. New equations are given for the factors R_D , R_η , and R_λ in terms of the carbon chain length, to account for effects of nonspherical molecular shape, and equations are given for the characteristic volume V_0 .

This new scheme provides a significantly improved method for the correlation, and accurate ($\pm 6\%$) prediction, of dense fluid n -alkane transport coefficient data.

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REFERENCES

1. M. J. Assael, J. H. Dymond, and V. Tselekidou, *Int. J. Thermophys.* **11**:8 (1990).
2. K. R. Harris, *Physica* **94A**:448 (1978).
3. K. R. Harris and N. J. Trappeniers, *Physica* **104A**:262 (1980).
4. K. R. Harris, *J. Chem. Soc. Faraday Trans. 1* **78**:2265 (1982).
5. A. J. Easteal and L. A. Woolf, *Physica* **124B**:173 (1984).
6. J. H. Dymond, *Physica* **75**:100 (1974).
7. J. H. Dymond and K. R. Harris, Unpublished results.
8. J. H. Dymond, P. M. Patterson, K. R. Harris, and L. A. Woolf, *High Temp. High Press.* (in press).
9. M. A. Assael and M. Papadaki, *Int. J. Thermophys.* **12**:801 (1991).
10. J. H. Dymond, in *Proc. 6th Symp. Thermophys. Prop.* (ASME, New York, 1973), p. 143.
11. D. Enskog, *Kungl. Svensk. Vet.-Ak. Handl.* **4**:63 (1922).
12. B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.* **53**:3813 (1970).
13. A. J. Easteal, L. A. Woolf, and D. L. Jolly, *Physica* **121A**:286 (1983).
14. R. J. Speedy, *Mol. Phys.* **62**:509 (1987).
15. D. Chandler, *J. Chem. Phys.* **62**:1358 (1975).
16. J. H. Dymond and M. A. Awan, *Int. J. Thermophys.* **10**:941 (1989).
17. J. H. Dymond, *Physica* **144B**:267 (1987).
18. D. E. Diller, *Physica* **108A**:143 (1981).
19. P. S. van der Gulik, R. Mostert, and H. R. van den Berg, *Physica* **151A**:153 (1988).
20. D. E. Diller and J. M. Saber, *Physica* **108A**:143 (1981).
21. D. E. Diller, *J. Chem. Eng. Data* **27**:240 (1982).
22. D. E. Diller and L. J. van Poolen, *Int. J. Thermophys.* **6**:43 (1985).
23. J. H. Dymond, K. J. Young, and J. D. Isdale, *Int. J. Thermophys.* **1**:345 (1980).
24. B. Knapstead, P. A. Skjolsvik, and H. A. Oye, *J. Chem. Eng. Data* **34**:37 (1989).
25. M. J. Assael, M. Papadaki, M. Dix, S. M. Richardson, and W. A. Wakeham, *Int. J. Thermophys.* **12**:231 (1991).
26. H. Kashiwagi and T. Makita, *Int. J. Thermophys.* **3**:289 (1982); private communication (1985).
27. J. H. Dymond, J. Robertson, and J. D. Isdale, *Int. J. Thermophys.* **2**:133 (1981).

28. A. L. Lee and R. T. Ellington, *J. Chem. Eng. Data* **10**:346 (1965). [Densities calculated from the Tait equation of J. H. Dymond and R. Malhotra, *Int. J. Thermophys.* **8**:541 (1987).]
29. J. H. Dymond and K. J. Young, *Int. J. Thermophys.* **2**:237 (1981).
30. M. J. Assael and M. Papadaki, Unpublished results.
31. U. V. Mardolcar and C. A. Nieto de Castro, *Ber. Bunsenges. Phys. Chem.* **91**:152 (1987).
32. H. M. Roder, *Int. J. Thermophys.* **6**:119 (1985).
33. H. M. Roder and C. A. Nieto de Castro, *High Temp. High. Press.* **17**:453 (1985).
34. H. M. Roder and C. A. Nieto de Castro, *J. Chem. Eng. Data* **27**:12 (1982).
35. C. A. Nieto de Castro, R. Tufeú, and B. Le Neindre, *Int. J. Thermophys.* **4**:11 (1983).
36. A. M. F. Palavra, W. A. Wakeham, and M. Zalaf, *Int. J. Thermophys.* **8**:305 (1987).
37. S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **88**:32 (1984).
38. M. J. Assael, E. Charitidou, C. A. Nieto de Castro, and W. A. Wakeham, *Int. J. Thermophys.* **8**:663 (1987).
39. Y. Tanaka, Y. Itani, H. Kubota, and T. Makita, *Int. J. Thermophys.* **9**:331 (1988).
40. J. Menashe and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **85**:340 (1981).
41. Y. Nagasaka and A. Nagashima, *Ind. Eng. Chem. Fundam.* **20**:216 (1981).
42. J. Calado, J. M. N. Fareleira, C. A. Nieto de Castro, and W. A. Wakeham, *Int. J. Thermophys.* **4**:193 (1983).
43. J. Menashe and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **86**:541 (1982).
44. H. Kashiwagi, M. Oishi, Y. Tanaka, H. Kubota, and T. Makita, *Int. J. Thermophys.* **3**:101 (1982).
45. M. Mustafa, M. Sage, and W. A. Wakeham, *Int. J. Thermophys.* **3**:217 (1982).
46. M. J. Assael, E. Charitidou, and L. Karagiannidis, *Int. J. Thermophys.* **12**:491 (1991).