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Correlation and Prediction of Dense Fluid Transport Coefficients. III. *n*-Alkane Mixtures

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Viscosity and thermal conductivity coefficients for binary, ternary, and quaternary *n*-alkane mixtures are predicted over extended ranges of temperature and pressure, in excellent agreement with experiment, by extension of a method recently described for the correlation of *n*-alkane transport coefficients. The outstanding advantage of this approach is that there are no adjustable parameters. Furthermore, in contrast with other mixture viscosity equations, this scheme does not require experimental viscosity coefficient data for the pure components under the same conditions of temperature and pressure.

KEY WORDS: hard-sphere theory; *n*-alkane mixtures; thermal conductivity; viscosity.

1. INTRODUCTION

The need for reliable prediction of the viscosity of multicomponent mixtures has led to more than 50 equations being proposed [1] for viscosities of binary liquid mixtures. Extensive tests of the effectiveness of such equations have shown [2] that for 35 selected nonpolar + nonpolar systems, there were several equations with one or two adjustable coefficients which fitted the data almost equally satisfactorily. They all produced a significantly better data fit than equations with no disposable parameters. However, some mixture data were needed in order to determine these parameters. In addition, viscosity coefficients are required for the pure components at each temperature. It should be noted that, in these tests of the applicability of mixture equations, and in more recent investigations [3–8], only atmospheric pressure viscosities were considered.

Over the past 10 years, we have undertaken a program of viscosity

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coefficient measurement [9] for hydrocarbons and their binary mixtures up to elevated pressures (500 MPa) in order to determine a reliable method for viscosity correlation and prediction over this extended range of experimental conditions. It was found that a free-volume form of equation fitted the data for different mixtures generally to within ±5%, though the deviations increased to about 10% at the highest pressures. However, experimental viscosities were necessary for each mixture to determine values for the two parameters, which were both temperature and composition dependent. An improved fit was given by the purely empirical Grunberg and Nissan equation [10], which contains only one adjustable parameter. This reproduced the experimental data practically to within the estimated experimental uncertainty. However, some mixture data were necessary to determine the Grunberg parameter. It was found that this parameter was temperature independent for *n*-alkane mixtures but varied with pressure and composition. In addition, calculation of mixture viscosities from the Grunberg and Nissan equation required viscosities for the pure components under the same conditions of temperature and pressure as for the mixture.

In view of the severe limitations in applying these equations for the prediction of mixture viscosities, we have extended to mixtures the scheme that was described recently [11] for correlation and prediction of self-diffusion, viscosity, and thermal conductivity coefficients of *n*-alkanes.

2. THE CORRELATION METHOD

As the method for correlating *n*-alkane transport coefficients has been described in detail [11], just the main features are reproduced here before describing the extension to *n*-alkane mixtures.

The basic assumption is that the *n*-alkane transport coefficients are directly proportional to the smooth hard-sphere coefficients. Proportionality factors, R_η and R_λ for viscosity and thermal conductivity, respectively, are introduced to account for effects of nonspherical molecular shape. It is assumed that these factors are independent of both temperature and density.

Instead of the transport coefficients themselves, it is convenient to consider reduced coefficients of viscosity η^* and thermal conductivity λ^*, defined as follows:

$$\eta^* = \left[\frac{\eta_{\text{SHS}}}{\eta_0}\right]\left[\frac{V}{V_0}\right]^{2/3} \quad (1)$$

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

where subscript zero refers to the low density coefficient and n is the number density. Subscript SHS is the smooth hard-sphere coefficient, V is the molar volume, and V_0 is the volume of close packing.

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

$$\eta^* = \frac{\eta^*_{\text{exp}}}{R_\eta} = 6.035 \times 10^8 \left[\frac{1}{\text{MRT}}\right]^{1/2} \frac{\eta V^{2/3}}{R_\eta} \tag{3}$$

$$\lambda^* = \frac{\lambda^*_{\text{exp}}}{R_\lambda} = 1.936 \times 10^7 \left[\frac{M}{RT}\right]^{1/2} \frac{\lambda V^{2/3}}{R_\lambda} \tag{4}$$

The determination of V_0 and the R factor at any temperature for a particular transport property, P, for a given compound is accomplished by curve-fitting. In principle, a plot of log P^* versus log V from experiment is simply superimposed on universal plots of log P^* versus $\log(V/V_0)$ from exact hard-sphere theory by vertical and horizontal adjustment. The R factor is found from the vertical displacement, and V_0 from the horizontal shift. In practice, as the smooth hard-sphere coefficients cannot be calculated exactly, these universal curves for viscosity and thermal conductivity were developed from consideration of hard-sphere theory and also using experimental data for higher *n*-alkanes [11].

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

$$\log_{10}\left[\frac{\eta^*_{\text{exp}}}{R_\eta}\right] = \sum_{i=0}^{7} a_{\eta i}(1/V_r)^i \tag{5}$$

$$\log_{10}\left[\frac{\lambda^*_{\text{exp}}}{R_\lambda}\right] = \sum_{i=0}^{4} a_{\lambda i}(1/V_r)^i \tag{6}$$

Values for the coefficients $a_{\eta i}$ and $a_{\lambda i}$ are given in Table I.

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

i	$a_{\eta i}$	$a_{\lambda i}$
0	1.0945	1.0655
1	−9.2632	−3.5380
2	71.0385	12.1200
3	−301.9012	−12.4690
4	797.6900	4.562
5	−1221.9770	—
6	987.5574	—
7	−319.4636	—

V_0 values for the lower n-alkanes, C_1 to C_4, were fitted using a least-squares regression analysis, as a function of carbon number C and temperature T with the following results.

CH_4–C_4H_{10}:

$$\begin{aligned}10^6 V_0 = {} & 45.822 - 6.1867T^{0.5} + 0.36879T - 0.007273T^{1.5} \\ & + C(2.17871T^{0.5} - 0.185198T + 0.00400369T^{1.5}) \\ & + C^2(6.95148 - 52.6436T^{-0.5}) + C^3(-7.801897 \\ & + 42.24493T^{-0.5} + 0.4476523T^{0.5} - 0.009573512T)\end{aligned} \tag{7}$$

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

Table II. Summary of Conditions for Binary n-Alkane Viscosity Data (X_1 is the Mole Fraction of the First Named Component)

Mixture	X_1	n	T (K)	P_{max} (MPa)	Ref. No.
$C_1 + C_6$	0.359 0.498 0.749	42	293–390	41	13
$C_6 + C_8$	0–1	9	298	0.1	14
	0–1	27	293–308	0.1	15
$C_6 + C_9$	0–1	9	298	0.1	14
$C_6 + C_{10}$	0–1	9	298	0.1	14
	0–1	27	293–308	0.1	15
$C_7 + C_6$	0.36441 0.66741	65	293–323	72	16
	0–1	9	298	0.1	14
	0–1	25	293–323	0.1	15
$C_7 + C_8$	0–1	9	298	0.1	14
	0–1	36	293–313	0.1	15
$C_7 + C_9$	0.46043 0.74916	66	293–323	72	16
	0–1	9	298	0.1	14
$C_7 + C_{10}$	0.48629 0.76815	53	293–323	72	17
	0–1	9	298	0.1	14
	0–1	36	293–313	0.1	15
$C_7 + C_{11}$	0.50979 0.78448	67	293–323	75	18
$C_7 + C_{12}$	0–1	3	298	0.1	14
	0–1	36	293–313	0.1	15
$C_7 + C_{14}$	0–1	3	298	0.1	14
	0–1	36	293–313	0.1	15

Table II. *(Continued)*

Mixture	X_1	n	T (K)	P_{max} (MPa)	Ref. No.
$C_8 + C_9$	0–1	9	298	0.1	14
$C_8 + C_{10}$	0–1	9	298	0.1	14
	0–1	36	293–313	0.1	15
$C_9 + C_{10}$	0–1	9	298	0.1	14
$C_9 + C_{12}$	0–1	3	298	0.1	14
$C_9 + C_{14}$	0–1	3	298	0.1	14
$C_9 + C_{16}$	0–1	3	298	0.1	14
$C_{10} + C_1$	0.6876	96	292–431	42	19
	0.4425				
	0.3100				
	0.1533				
$C_{10} + C_5$	0–1	9	298	0.1	20
$C_{10} + C_{12}$	0–1	3	298	0.1	14
$C_{10} + C_{14}$	0–1	3	298	0.1	14
$C_{10} + C_{16}$	0–1	3	298	0.1	14
$C_{12} + C_6$	0.5	24	298–373	456	21
	0.7481	16	288–323	0.1	22
	0.4998				
	0.2499				
	0–1	27	298–328	0.1	20
	0–1	3	298	0.1	14
$C_{12} + C_8$	0.5	38	298–373	506	21
	0–1	3	298	0.1	14
$C_{12} + C_{14}$	0–1	3	298	0.1	14
$C_{12} + C_{16}$	0–1	3	298	0.1	14
$C_{14} + C_6$	0–1	10	298	0.1	23
	0–1	3	298	0.1	14
$C_{14} + C_8$	0–1	10	303, 308	0.1	24
	0–1	3	298	0.1	14
	0–1	36	293–313	0.1	15
$C_{16} + C_6$	0–1	27	283–378	0.1	25
	0.2	159	298–373	503	3
	0.4				
	0.6				
	0.8				
	0–1	20	298	0.1	23
	0–1	3	298	0.1	14
$C_{16} + C_7$	0–1	4	298	0.1	26
	0–1	3	298	0.1	14
$C_{16} + C_8$	0–1	15	318–338	0.1	4
	0–1	3	298	0.1	14
$C_{16} + C_{14}$	0–1	11	298	0.1	23
	0–1	3	298	0.1	14
	0–1	36	298	0.1	15

C_5H_{12}–$C_{16}H_{34}$:

$$10^6 V_0 = 117.874 + 0.15(-1)^C - 0.25275T + 0.000548T^2 - 0.00000042464T^3 + (C-6)(1.27 - 0.0009T)(13.27 + 0.025C) \qquad (8)$$

For *n*-pentane, it was suggested [11] that Eq. (8) could be used to calculate V_0. However, very recent measurements [12] of the viscosity of *n*-pentane at 303.2 and 323.2 K at pressures up to 250 MPa indicate that V_0 needs to be slightly larger in order to give an optimum fit to these data.

The R factors were fitted by least-squares regression analysis as a function of *n*-alkane carbon number, with the following results:

$$R_\eta = 0.995 - 0.0008944C + 0.005427C^2 \qquad (9)$$

$$R_\lambda = -18.8416C^{-1.5} + 41.461C^{-1} - 30.15C^{-0.5} + 8.6907 + 0.001337C^{2.5} \qquad (10)$$

For extension to *n*-alkane mixtures, it is assumed that the mixture behaves as a single-component liquid, with molecular parameters given by the mole fraction average of the values for the individual components. Thus

$$V_{0,\mathrm{m}} = \sum_{i=1}^{i} x_i V_{0,i} \qquad (11)$$

$$R_{\eta,\mathrm{m}} = \sum_{i=1}^{i} x_i R_{\eta,i} \qquad (12)$$

$$R_{\lambda,\mathrm{m}} = \sum_{i=1}^{i} x_i R_{\lambda,i} \qquad (13)$$

3. RESULTS

Table II lists the sources of data for binary *n*-alkane mixture viscosities used in this study with their corresponding temperature and pressure ranges, and the success with which this method fits these experimental data is demonstrated in Table III. The method can also be extended to multicomponent mixtures as illustrated in Table IV for the cases of ternary and quaternary mixture viscosities. For the mixtures where measurements have been made at atmospheric pressure, or up to 70 MPa, there is excellent agreement, with few experimental points deviating by more than 5%. This is illustrated for *n*-heptane + *n*-undecane viscosities [18] in Fig. 1. The measurements which were made with a vibrating-wire viscometer have an

Table III. Comparison of Calculated Viscosity Coefficients with Experimental Values for Binary *n*-Alkane Mixtures

Mixture	*n*	(5–10)%	>10%	Ref. No(s).
$C_1 + C_6$	42	20	5	13
$C_6 + C_8$	36	—	—	14, 15
$C_6 + C_9$	9	—	—	14
$C_6 + C_{10}$	36	—	—	14, 15
$C_7 + C_6$	99	—	—	14–16
$C_7 + C_8$	45	—	—	14, 15
$C_7 + C_9$	75	—	—	15, 16
$C_7 + C_{10}$	98	—	—	14, 15, 17
$C_7 + C_{11}$	67	—	—	18
$C_7 + C_{12}$	39	—	—	14, 15
$C_7 + C_{14}$	39	—	—	14, 15
$C_8 + C_9$	9	—	—	14
$C_8 + C_{10}$	45	—	—	14, 15
$C_9 + C_{10}$	9	—	—	14
$C_9 + C_{12}$	3	—	—	14
$C_9 + C_{14}$	3	—	—	14
$C_9 + C_{16}$	3	—	—	14
$C_{10} + C_1$	96	13	—	19
$C_{10} + C_5$[a]	9	—	—	20
$C_{10} + C_{12}$	3	—	—	14
$C_{10} + C_{14}$	3	—	—	14
$C_{10} + C_{16}$	3	—	—	14
$C_{12} + C_6$	70	7	5	14, 20–22
$C_{12} + C_8$	41	2	7	14, 21
$C_{12} + C_{14}$	3	—	—	14
$C_{12} + C_{16}$	3	—	—	14
$C_{14} + C_6$	13	1	—	14, 23
$C_{14} + C_8$	49	—	—	14, 15, 24
$C_{16} + C_6$	209	24	7	3, 14, 23, 25
$C_{16} + C_7$	7	—	—	14, 26
$C_{16} + C_8$	18	—	—	4, 14
$C_{16} + C_{14}$	50	—	—	14, 15, 23
Total	1234	67	24	

[a] Using new V_0 value for C_5 [12].

Table IV. Comparison of Calculated Viscosity Coefficients with Experimental Values for Ternary and Quaternary *n*-Alkane Mixtures ($P = 0.1$ MPa)

Mixture	*n*	>5%	T (K)	Ref. No.
$C_6 + C_8 + C_{16}$	10	—	288–378	3
$C_6 + C_{14} + C_{16}$	15	—	298	28
$C_6 + C_8 + C_{12} + C_{16}$	5	—	288–378	3
$C_6 + C_{10} + C_{12} + C_{16}$	10	—	303, 308	24
$C_7 + C_9 + C_{12} + C_{16}$	10	—	303, 308	24

estimated accuracy of 0.5%. Viscosities for the mixtures dodecane + hexane, dodecane + octane, and hexadecane + hexane were measured up to 500 MPa using the falling-body viscometer with an estimated uncertainty of ±3%. However, at the highest pressures, a difference of 0.2% in density, which is the estimated experimental uncertainty, will give rise to a change of about 2% in the calculated viscosity. It is therefore not unexpected that there should be a higher number of points which show a discrepancy of more than 5% for these mixtures. Differences greater than 10% occur at the highest temperature and pressures as shown in Fig. 2. It should be noted that over this wide pressure range the high-pressure viscosities are up to 16 times the atmospheric pressure values.

For the binary mixtures where one component is a gas under the experimental conditions, it is interesting to note that the closest fit of the experimental data is obtained for the system where the components have the greatest difference in size. Thus, for the decane + methane system, which is illustrated in Fig. 3, approximately the same fraction of the points is reproduced within 5% as for hexadecane + hexane. However, for methane + hexane less than one-half of the points are fitted to within 5%. Measurements on methane + ethane mixtures [27] for methane mole frac-

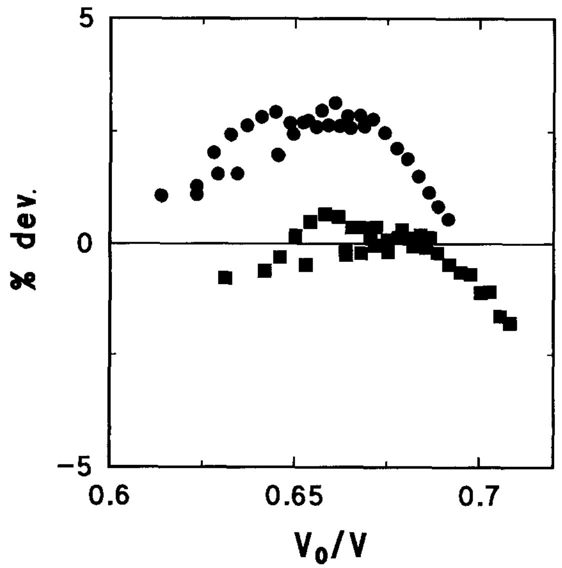

Fig. 1. Percentage deviation $[100(\eta_{exp}-\eta_{calc})/\eta_{calc}]$ of experimental data for the viscosity coefficients for the mixture $C_7H_{16}+C_{11}H_{24}$ [18] from values calculated at different reduced densities, V_0/V; $P_{max}=70$ MPa; $293\ K \leqslant T \leqslant 323\ K$. $X_1=0.50979$ (■); $X_1=0.78448$ (●).

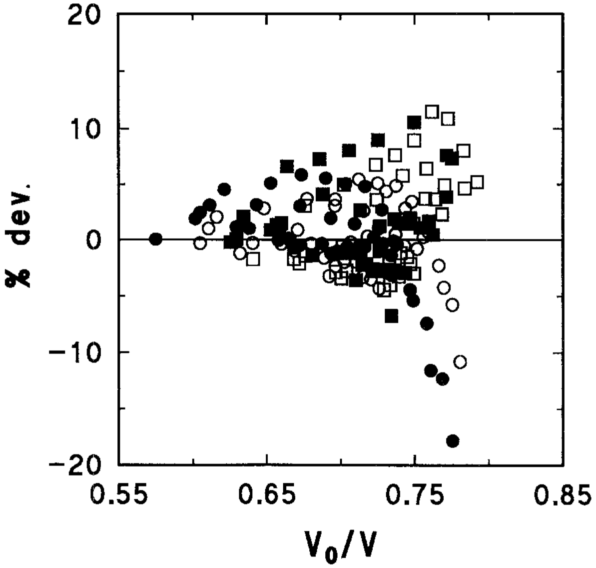

Fig. 2. Percentage deviation $[100(\eta_{\exp}-\eta_{\mathrm{calc}})/\eta_{\mathrm{calc}}]$ of experimental data for the viscosity coefficients for the mixture $C_{16}H_{34}+C_6H_{14}$ [3] from values calculated at different reduced densities, V_0/V; $P_{\max}=503$ MPa; 298 K $\leqslant T \leqslant$ 373 K. $X_1=0.2$ (●); $X_1=0.4$ (○); $X_1=0.6$ (■); $X_1=0.8$ (□).

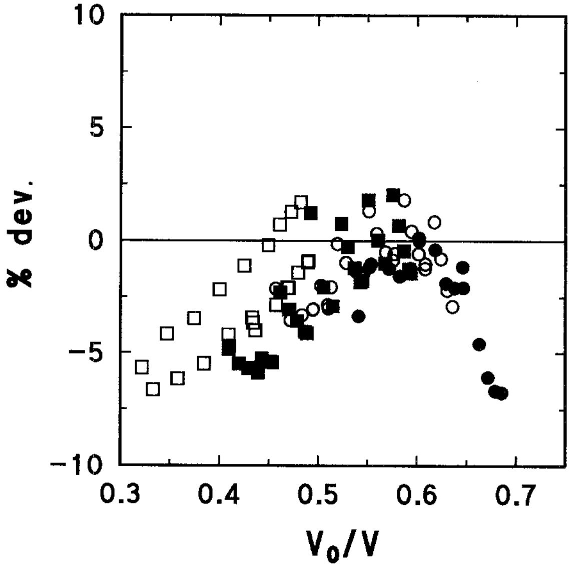

Fig. 3. Percentage deviation $[100(\eta_{\exp}-\eta_{\mathrm{calc}})/\eta_{\mathrm{calc}}]$ of experimental data for the viscosity coefficients for the mixture $C_{10}H_{22}$ + CH_4 [19] from values calculated at different reduced densities, V_0/V; $P_{\max}=42$ MPa; 292 K $\leqslant T \leqslant$ 431 K. $X_1=0.6876$ (●); $X_1=0.4425$ (○); $X_1=0.31$ (■); $X_1=0.1533$ (□).

Table V. Comparison of Calculated Thermal Conductivity Coefficients with Experimental Values for Binary and Ternary *n*-Alkane Mixtures ($P = 0.1$ MPa)

Mixture	*n*	>5%	*T* (K)	Ref. No.
$C_7 + C_{11}$	18	—	288–345	29
$C_7 + C_{16}$	18	—	289–344	29
$C_{11} + C_{16}$	18	—	294–344	29
$C_7 + C_{11} + C_{16}$	18	—	293–344	29

tions of 0.3452, 0.68526, and 0.50217 are fitted within 5% at temperatures from 300 down to 150, 170, and 140 K, respectively. At lower temperatures, V_0 values need to be increased by 1% to reduce the difference to less than 5%.

For ternary and quaternary *n*-alkane mixtures, viscosity coefficient measurements are available only at atmospheric pressure and here the data are all fitted to within 5%.

There are few thermal conductivity measurements on *n*-alkane mixtures. A comparison of the values calculated using the present scheme with these data is summarized in Table V. All experimental points are fitted to within 5%.

4. CONCLUSION

A method for correlating viscosity and thermal conductivity coefficients for *n*-alkanes, based upon universal curves for the reduced transport coefficients, has been extended to *n*-alkane mixtures. Parameters for the mixtures are given by the mole fraction average of the values for the pure substances. Calculated viscosity coefficients and thermal conductivity coefficients for binary, ternary, and quaternary *n*-alkane mixtures are in close agreement with experimental values. The fact that there are no adjustable parameters and that experimental values for the pure components under the same conditions of temperature and pressure are not required makes this a highly recommended approach for the accurate prediction of transport properties of liquid *n*-alkane mixtures over wide ranges of temperature and pressure.

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