Transport Properties of Nonelectrolyte Liquid Mixtures—III. Viscosity Coefficients for n-Octane, n-Dodecane, and Equimolar Mixtures of n-Octane + n-Dodecane and n-Hexane + n-Dodecane from 25 to 100°C at Pressures Up to the Freezing Pressure or 500 MPa

J. H. Dymond,[1] J. Robertson,[1] and J. D. Isdale[2]

Viscosity coefficients measured with an estimated accuracy of 2% using a new design of self-centering falling body viscometer are reported for n-octane, n-dodecane, and equimolar mixtures of n-octane + n-dodecane and n-hexane + n-dodecane at 25, 50, 75, and 100°C at pressures up to the freezing pressure or 500 MPa. The data for a given composition at different temperatures and pressures are very satisfactorily correlated by a plot of η', defined as $10^4 \eta V^{2/3}/(MT)^{1/2}$ in the cgs system of units or, generally, $9.118 \times 10^7 \eta V^{2/3}/(MRT)^{1/2}$, versus $\log V'$, where $V' = V \cdot V_0(T_R)/V_0(T)$ and V_0 represents the close-packed volume at temperature T and reference temperature T_R. The experimental results are fitted, generally well within the estimated uncertainty, by the equation

$$\ln \eta' = -1.0 + \frac{BV_0}{V - V_0},$$

where B and V_0 are temperature and composition dependent. Values of B and V_0 for the mixtures are simply related to values for the pure liquids. The binary mixing rule of Grunberg and Nissan is investigated. Values of the mixing parameter G are positive, tend to increase with increases in pressure, and also increase with increases in difference in carbon number of the two pure components.

KEY WORDS: Alkane mixtures; Grunberg and Nissan equation; high pressure; n-octane; n-dodecane; viscometer; viscosity.

[1]Chemistry Department, The University, Glasgow G12 8QQ, U.K.
[2]National Engineering Laboratory, East Kilbride, Glasgow G75 0QU, U.K.

1. INTRODUCTION

It is essential to have accurate transport coefficient data over a wide range of temperature and pressure for liquids and liquid mixtures in order to develop methods of correlation and prediction and theories of transport properties. In the first paper of the series [1] we reported accurate measurements at saturation pressure of viscosity coefficients for two-component, three-component, and four-component n-alkane mixtures from 12 to 105°C. The next paper [2] considered the effect of elevated pressure on the viscosity coefficient for the n-hexane + n-hexadecane system at temperatures from 25 to 100°C. For the correlation of viscosity coefficient data for mixtures of given composition at different temperatures over the whole pressure range, a graphical method based on the hard sphere model was shown to be successful. In order to fit the experimental data mathematically, a free-volume form of equation was shown to be very satisfactory.

The present paper investigates the effect of increased pressure on the viscosity coefficient of other n-alkanes and n-alkane mixtures. Using a new design of self-centering falling body viscometer, which is described in Section 2, measurements have been made on n-octane, n-dodecane, and equimolar mixtures of n-octane + n-dodecane and n-hexane + n-dodecane at 25, 50, 75, and 100°C at pressures up to the freezing pressure or 500 MPa. The results given in Section 6 have an estimated accuracy of 2%. They have been used to test the applicability of the graphical method and the free-volume form of equation in Sections 8 and 9.

The data have also been used to study the variation of the mixing parameter G in the Grunberg and Nissan equation [3] with temperature, pressure, and composition. In Section 10 an equation is proposed for G which allows all our viscosity coefficient data on n-alkane mixtures at elevated pressures to be reproduced to within the estimated experimental uncertainty.

2. THE VISCOMETER

Viscosity coefficients were determined experimentally from measurements of the terminal velocity of a self-centering sinker falling axially down the center of a vertical circular tube containing the liquid. The new viscometer is based on the earlier design [2] but incorporates a more effective pressure transmitting device, more reliable electrical leads, and a shorter tube. The viscometer is illustrated in Fig. 1. The sinker and the tube were made from the same nonmagnetic En58J stainless steel. The tube was approximately 12 cm in length with an internal diameter of 7.562 mm and an outside diameter of 2.4 cm. The bore was finished to 0.13 μm and the variation of its diameter was less than 0.005 mm. Sealing was effected by a
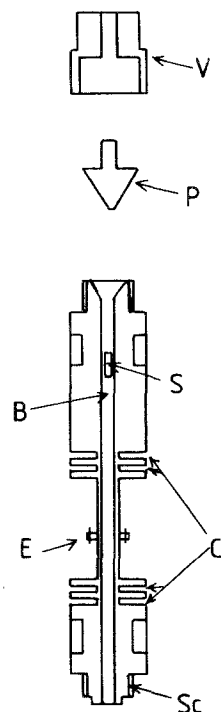
Fig. 1. The high-pressure viscometer: V, viscometer end cap; P, plug; S, sinker; B, viscometer bore; E, electrical connections; C, coil grooves; Sc, screws into the connector on the pressure transmitting device.

plug which was held in place by the viscometer end cap. The other end of the viscometer screwed into the pressure transmitting device shown in Fig. 2. This was basically a length of p.t.f.e. tubing which was sealed at one end by a metal closing seal. The tubing was protected by a surrounding perforated metal shield. The entire assembly fitted into a pressure vessel, and when hydraulic fluid was pumped into the vessel, the tubing contracted and transmitted the pressure to the liquid under study in the viscometer. This arrangement allows a greater relative volume expulsion than the previous method of pressure transmission [2], which used a metallic bellows, and has the further advantages that it could be more easily cleaned and any bubbles in the liquid could be seen and expelled before the viscometer was finally sealed.

A new sinker with a small ferrite core made to the same design as that used previously [2] was 14 mm in length and 7.338 mm in diameter, leaving an annulus of 0.112 mm between the tube and the sinker. The position of the sinker was detected as before by the change in inductance that it caused as it passed through pairs of coils wound on the outside of the tube. These coils were wound from approximately 700 turns of 44 S.W.G. insulated copper wire and had a mean resistance of 57.9 ± 0.8 Ω. They were connected to form
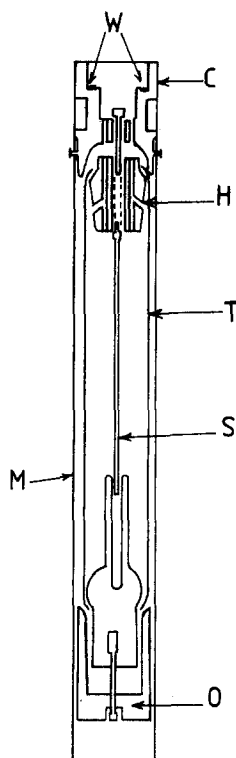
Fig. 2. Arrangement for transmitting pressure to the liquid in the high-pressure viscometer: W, copper washers; C, connector to viscometer; H, holes for the release of air bubbles; T, p.t.f.e. tubing; S, spacer rod; M, perforated metal shield; O, closing seal for tubing.

a bridge circuit. A demodulator working in conjunction with a phase shifter reduced the amplified 300-Hz signal to a dc level which operated a Schmitt trigger when the sinker was midway between the coils. The resultant sharp pulse started a Hewlett–Packard Counter Timer, Type 5223L, as the sinker went through the first pair of coils, and the timer was stopped when the sinker passed through the second pair of coils, thus giving an accurate fall time. This has to be corrected for buoyancy effects of the test liquid on the sinker and for the compressibility and thermal expansion of the component materials. The equation used to calculate viscosity coefficients from fall-time measurements has the form

$$\eta_P = \frac{t(1 - \rho_L/\rho_S')}{A[1 + 2\alpha(T - T_0)][1 - 0.666\beta(P - P_0)]} \tag{1}$$

where η_P is the viscosity coefficient at pressure P, t is the fall time, ρ_L and ρ_S' are the density of the liquid and sinker at pressure P and temperature T, T is the experimental temperature, T_0 is a reference temperature (taken as 25°C), P_0 is the atmospheric pressure, α is the linear coefficient of thermal

expansion, β is the compressibility coefficient, and A is the viscometer constant.

3. MATERIALS

The n-hexane, n-octane, and n-dodecane were purchased from B.D.H. Chemicals Ltd., Poole, England, and had a stated minimum purity of 99 mol%, except n-octane, which was 99.5 mol%. UltraR benzene was purchased from Hopkin and Williams Ltd., Chadwell Heath, England, and hexafluorobenzene was supplied by Fluorochem Ltd., Glossop, England. Benzene had a stated minimum purity of not less than 99.5%, and hexafluorobenzene was not less than 99 mol%. The chemicals were fractionally distilled before use. The refractive index $n(D, 298.15K)$ of n-hexane was 1.37240, that of n-octane was 1.39525, and that of n-dodecane was 1.41959, in close agreement with the literature values of 1.37229 [4], 1.39505 [5], and 1.41949 [5], respectively. For hexafluorobenzene, $n(D, 298.15K)$ was 1.37502 and, for benzene, 1.49797, in good agreement with the reported value [6] of 1.49800.

4. CALIBRATION

Although in principle it is possible to calculate the values of viscosity coefficients directly from the measurements of fall times and from the instrument dimensions, in practice the instrument is calibrated using liquids of known viscosity and density at atmospheric pressure. Values of A were calculated from Eq. (1) for the following liquids: Shell Vitrea No. 21 oil, Shell Tellus 11 oil, n-octane, n-dodecane, benzene, and hexafluorobenzene. Viscosities and densities of Shell Vitrea No. 21 oil were measured by Young [7]. The viscosity coefficients of Shell Tellus 11 oil were measured in suspended level capillary viscometers which had been calibrated by Gallenkamp Ltd., and the densities were measured in a previously calibrated pyknometer of approximately 10-cm^3 capacity. The viscosities of the other liquids were measured using sealed suspended level capillary viscometers [1]. Densities were measured using a sealed Lipkin pyknometer and volume change apparatus [8] with application of the standard corrections. The density of the sinker was determined by weighing it in air and in water. The density ρ'_S of the sinker at temperature T and pressure P was found by correcting the density ρ_{S0}^{25} at $T_0 = 25°C$ and atmospheric pressure by

$$\rho'_S = \frac{\rho_{S0}^{25}}{[1 + 3\alpha(T - T_0)](1 - \beta P)}, \tag{2}$$

where α is the linear coefficient of expansion and β is the compressibility coefficient of the sinker.

Values of A are plotted against viscosity in Fig. 3. A is not a constant but increases by about 9% over the range of viscosities studied. This increase in A at short fall times is due to the onset of nonlaminar flow. Experimentally determined values of A were fitted by an equation of the form

$$A = A_0 \left\{ 1 + \left[\frac{B}{t(1 - \rho_L/\rho'_S)} \right]^N \right\}, \tag{3}$$

where A_0, B, and N were constants to be determined. For this combination of sinker and tube, the values were $A_0 = 8.730$ mPa^{-1}, $B = 0.02405$ s, and $N = 0.5284$. This calibration curve is shown in Fig. 3. The RMS deviation of the 26 points from this line is 1.27% with a maximum deviation of 2.4%.

5. CALCULATION OF VISCOSITY COEFFICIENTS

There are two methods for calculating the viscosity coefficient. The first, the "direct" method, uses Eq. (1) with values of A given by Eq. (3). The second, the "ratio" method, may be used when the viscosity coefficient at atmospheric pressure is accurately known from some other measurements. Application of Eq. (1) at pressure P and at atmospheric pressure gives the corresponding viscosity coefficient ratio in terms of the corresponding ratio of
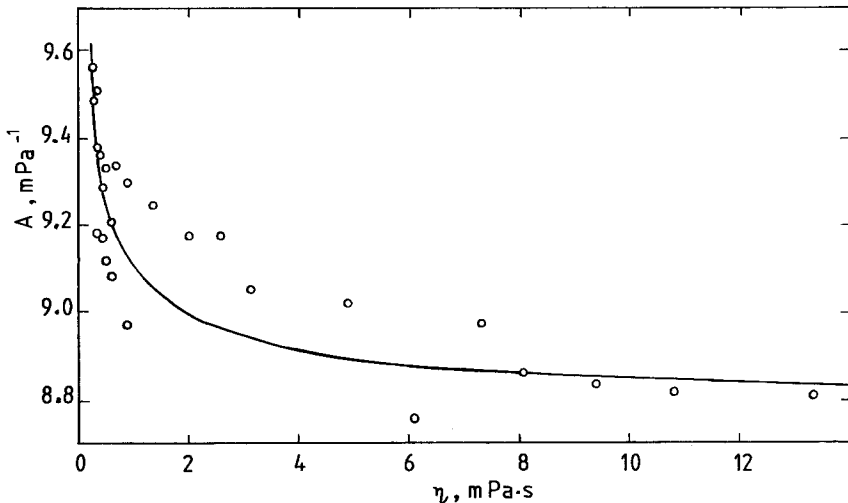

Fig. 3. Calibration curve for the high-pressure viscometer.

Table I. Viscosity Coefficient and Density of *n*-Octane

Temperature (°C)	Pressure (MPa)	Density (kg · m⁻³)	Viscosity coefficient (mPa · s)
25.08	0.1	698.5	0.509
	53.6	736.5	0.852
	102.5	760.6	1.204
	149.4	778.5	1.666
	202.0	795.0	2.274
	252.1	808.6	3.044
	305.1	821.7	4.059
	353.6	832.8	5.229
	401.5	843.5	6.683
	453.0	854.8	8.670
50.10	0.1	678.1	0.387
	52.4	720.3	0.624
	99.9	745.7	0.879
	150.6	766.1	1.206
	200.2	782.3	1.593
	253.5	797.4	2.099
	302.0	809.8	2.654
	354.3	822.6	3.385
	408.8	835.5	4.314
	455.0	846.4	5.260
	505.5	858.7	6.497
75.14	0.1	657.0	0.3036
	47.5	701.8	0.476
	103.1	734.2	0.702
	153.9	755.3	0.945
	203.4	771.9	1.220
	253.7	786.5	1.555
	303.1	799.6	1.936
	352.1	812.1	2.381
	405.3	825.4	2.946
	452.6	837.3	3.538
	503.0	850.5	4.270
99.97	0.1	635.5	0.2457
	48.8	687.0	0.397
	103.6	721.5	0.574
	162.1	746.9	0.799
	197.7	759.4	0.950
	250.9	775.6	1.206
	302.3	789.7	1.487
	354.4	803.2	1.826
	404.6	815.9	2.206

measured fall times, ratio of density terms, and ratio of A values and a small pressure correction, which leads to a reduction in systematic errors. By considering the different sources of error in these two methods, it is found that the ratio method reduces the uncertainty by a factor of 2 over the direct method. Taking into account the fluctuations in the pressure during a run, which were usually much less than 0.5 MPa, and the temperature variations which were at most 0.03 K, leads to an estimate of the accuracy of the viscosity coefficients of $\pm 2\%$.

6. RESULTS

Measurements of the fall times for the sinker have been made for n-octane, n-dodecane, and equimolar mixtures of n-hexane + n-dodecane and n-octane + n-dodecane at 25, 50, 75, and 100°C at pressures up to the freezing pressure or 500 MPa. At atmospheric pressure, the fall time was measured at least seven times and the mean fall time calculated. The standard deviation of the mean, expressed as a percentage of the mean, was never greater than 0.27% and had an average value of 0.09% (for 32 sets of readings at atmospheric pressure). Standard deviations at higher pressures were generally less than this. The derived viscosity coefficients are presented in Tables I to IV, together with values for the density under corresponding conditions calculated from values of the isothermal secant bulk modulus by which experimental density data have been fitted [9]. The densities have an estimated accuracy of $\pm 0.2\%$.

7. COMPARISON OF VISCOSITY COEFFICIENTS WITH LITERATURE DATA

In order to facilitate comparison with literature values, viscosity coefficient ratios η_P/η_0, where η_0 is the atmospheric pressure value, have been considered. For n-octane, viscosity coefficient ratios at different pressures are compared with the results of Bridgman [10] in Fig. 4. His isotherm at 30°C lies just below the isotherm at 25°C of the present work. There is good agreement between the two isotherms at 75°C, the maximum deviation of 2.2% occurring at pressures around 400 MPa. The results of Brazier and Freeman [11] are not included in Fig. 4 because their values deviate so markedly from both those of Bridgman and the present work. Brazier and Freeman used a rolling ball viscometer. Instruments of this type are often subject to errors caused by slipping and/or spinning of the ball instead of pure rolling. These effects are especially likely at low viscosities and it is significant

Table II. Viscosity Coefficient and Density of *n*-Dodecane

Temperature (°C)	Pressure (MPa)	Density (kg · m^{-3})	Viscosity coefficient (mPa · s)
25.12	0.1	745.3	1.355
	52.9	777.6	2.430
	104.5	800.2	3.921
	119.2	805.7	4.451
50.20	0.1	727.1	0.915
	12.9	737.4	1.065
	52.4	762.7	1.585
	101.0	785.9	2.398
	152.5	805.3	3.535
	195.9	819.3	4.768
	261.9	838.5	7.275
74.95	0.1	708.9	0.667
	9.1	717.1	0.743
	69.4	757.8	1.321
	104.0	774.4	1.726
	152.1	793.1	2.410
	199.7	808.6	3.239
	253.1	823.7	4.414
	304.6	837.1	5.843
	367.0	852.4	8.029
	422.5	865.9	10.44
100.06	0.1	690.4	0.508
	24.1	714.0	0.671
	95.9	759.7	1.228
	154.4	784.1	1.800
	197.9	798.8	2.321
	256.2	816.0	3.170
	308.7	830.2	4.110
	352.4	841.7	5.060
	408.0	856.1	6.495
	452.9	868.0	7.856
	501.6	881.4	9.609

that Brazier and Freeman's calibration graph has large uncertainties in this region. Serious disagreement was found previously [2] in the case of *n*-hexane at temperatures above 25°C between the results of Brazier and Freeman and other workers [2, 10, 12].

For *n*-dodecane, the results of the present work are compared in Fig. 5 with those of Hogenboom et al. [13], who claim an accuracy of between 2 and 5%. The two sets of results agree very well. Their values at 37.78°C lie about

Table III. Viscosity Coefficient and Density of 0.500-mol Fraction *n*-Octane in
n-Octane + *n*-Dodecane Mixture

Temperature (°C)	Pressure (MPa)	Density (kg · m⁻³)	Viscosity coefficient (mPa · s)
25.05	0.1	725.9	0.869
	25.7	744.1	1.151
	74.8	770.9	1.810
	103.4	783.3	2.286
	150.1	800.5	3.255
	197.9	815.6	4.569
	238.6	827.3	5.992
50.07	0.1	706.9	0.623
	25.4	728.2	0.818
	96.1	768.2	1.482
	153.5	790.2	2.215
	197.6	804.2	2.912
	252.4	819.4	4.017
	302.9	832.4	5.310
	353.0	844.8	6.908
	395.6	855.3	8.589
75.02	0.1	687.7	0.472
	51.0	730.4	0.781
	94.1	754.5	1.083
	149.6	777.5	1.555
	197.3	793.3	2.054
	248.9	808.1	2.708
	301.1	821.6	3.516
	351.0	833.7	4.453
	404.4	846.4	5.664
	455.1	858.5	7.069
	502.0	869.9	8.602
100.02	0.1	668.0	0.370
	49.7	712.0	0.612
	99.6	741.0	0.886
	152.6	763.7	1.229
	202.6	780.9	1.608
	251.2	795.3	2.045
	300.0	808.5	2.554
	349.5	820.9	3.171
	401.2	833.5	3.919
	452.5	845.9	4.798
	505.5	858.9	5.858

Table IV. Viscosity Coefficient and Density of 0.501-mol Fraction n-Hexane in n-Hexane + n-Dodecane Mixture

Temperature (°C)	Pressure (MPa)	Density (kg · m⁻³)	Viscosity coefficient (mPa · s)
24.95	0.1	713.8	0.719
	49.7	746.4	1.181
	102.2	771.3	1.802
	152.2	790.0	2.570
	177.7	798.3	3.065
	203.6	806.2	3.605
74.97	0.1	673.7	0.403
	52.1	717.0	0.667
	96.3	741.8	0.923
	150.4	764.7	1.293
	210.0	781.9	1.711
	248.5	795.9	2.178
	302.5	810.3	2.811
	355.7	823.7	3.569
	403.4	835.3	4.378
	455.1	847.9	5.411
100.01	0.1	652.8	0.3214
	51.8	701.9	0.533
	98.0	729.2	0.743
	150.8	752.0	1.019
	203.3	770.1	1.339
	250.8	784.4	1.675
	303.4	799.2	2.112
	351.8	812.3	2.579

midway between our isotherms at 25 and 50°C, and their 79.44°C data fall marginally below the 75°C isotherm. (Their viscosity at 79.44°C and 280 MPa appears to have been misprinted as 4.47 MPa s instead of 4.74 MPa s.) The isotherms at 100 and 98.89°C are practically coincident. The maximum difference between the present results and those of Hogenboom et al. corrected to the same temperature is estimated to be less than 2%.

8. CORRELATION OF VISCOSITY COEFFICIENT DATA

It is possible to correlate the experimental data by a method suggested [14] by consideration of the hard-sphere results. A quantity η' is defined as $10^4 \eta V^{2/3}/(MT)^{1/2}$ in the cgs system of units or, more generally, by

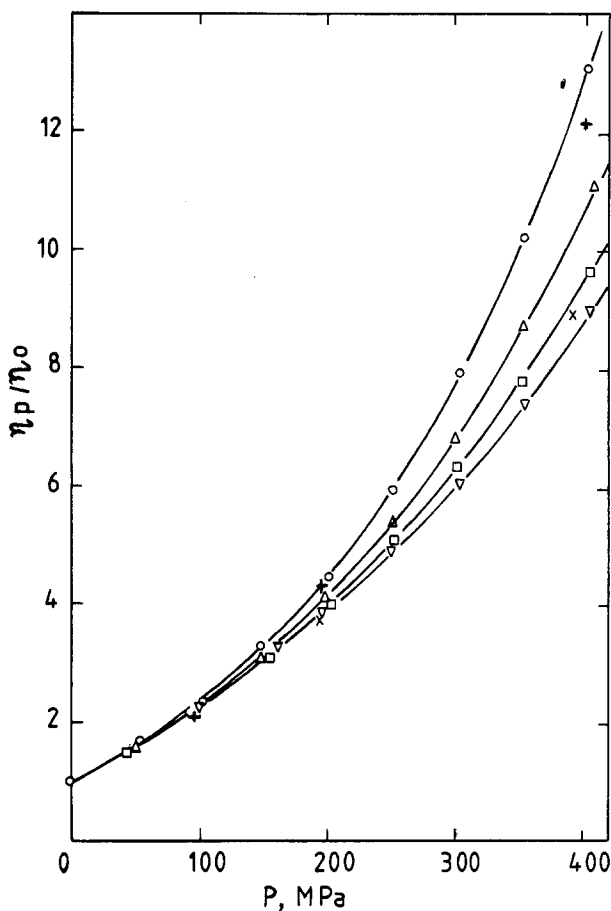$$\eta' = 9.118 \times 10^7 \frac{\eta V^{2/3}}{(MRT)^{1/2}}. \tag{4}$$

Fig. 4. Comparison of present viscosity coefficient ratios for *n*-octane (O, 25.08°C; △, 50.10°C; □, 75.14°C; ∇, 99.97°C) with literature values (+, 30°C; ×, 75°C [10]).

Plots of η' versus $\log V$ for a given mixture at different temperatures should be superimposable by lateral movements upon the curve obtained for any reference temperature T_R. The amount by which $\log V$ has to be adjusted leads to a value for $V_0(T)/V_0(T_R)$ and hence gives a measure of the effect of temperature changes on the close-packed volume, V_0. Results previously obtained [14] showed that η' versus $\log V$ plots were superimposable not only over the density range for which the rough hard-sphere theory applies but over the whole density range.

When this method is applied to the viscosity coefficient data reported in Section 6, it is found that the results can be correlated very satisfactorily on the basis of a single curve for each of the pure liquids and the mixtures. A

typical plot is shown in Fig. 6 for the equimolar mixture of n-octane + n-dodecane. The 25°C isotherm was selected as the reference curve. At the highest pressures at 100°C, the experimental points lie to the left of the curve, but it is thought that the densities in this region may be high by about 0.3%. Otherwise the deviation of points from the reference curve is less than 3%. Values derived for $V_0(T)/V_0(T_R)$ for the pure liquids and the mixtures are given in Table V. The ratios lie between those found [2] for n-hexane and n-hexadecane which, relative to 25°C as reference temperature, are 0.974 and 0.954, respectively, at 100°C.
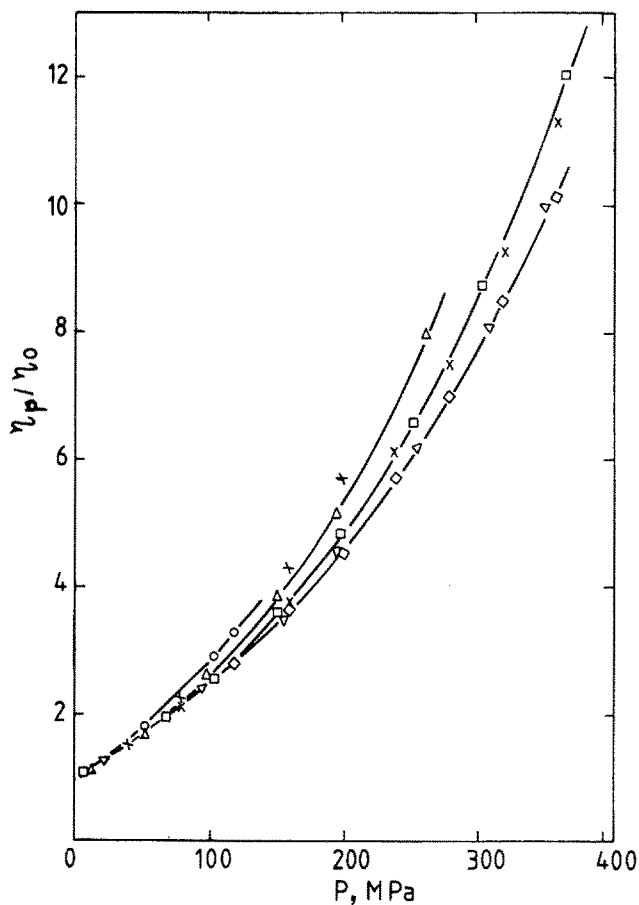
Fig. 5. Comparison of present viscosity coefficient ratios for n-dodecane (○, 25.12°C; △, 50.20°C; □, 74.95°C; ▽, 100.06°C) with literature values (+, 37.78°C; ×, 79,44°C; ◇, 98.89°C [13]).
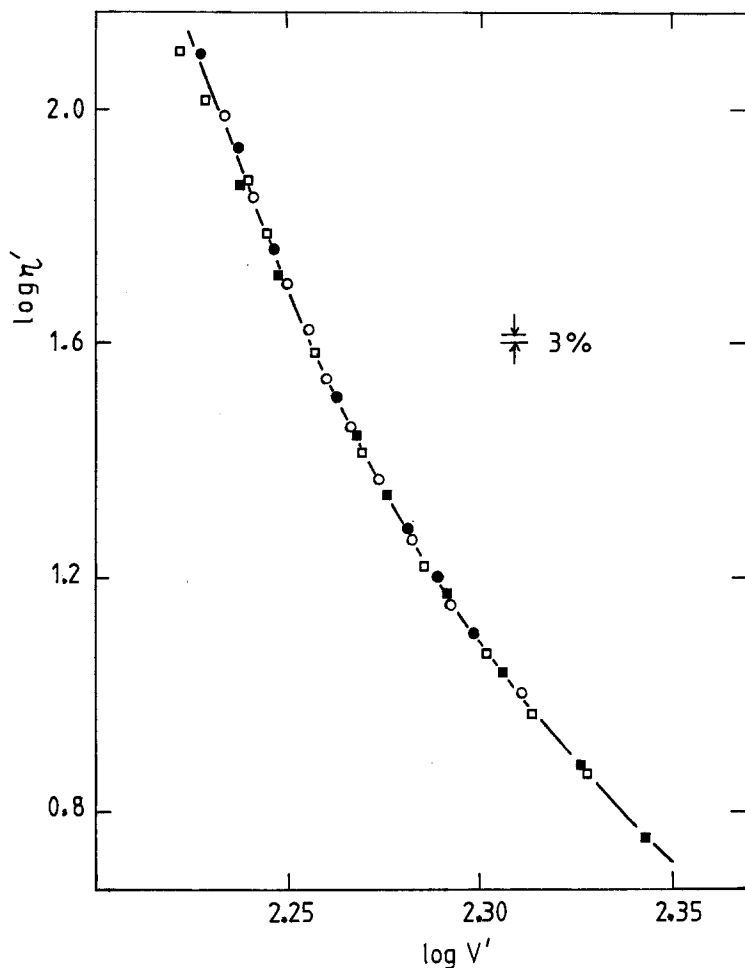
Fig. 6. Correlation of experimental viscosity coefficient data for the equimolar
n-octane + n-dodecane mixture at different temperatures and pressures based on
the 25°C isotherm. η' is defined by Eq. (4), $V' = V \cdot V_0(T_R)/V_0(T)$. O, 25°C; ●,
50°C; □, 75°C; ■, 100°C.

9. FREE-VOLUME FORM OF EQUATION

Dymond and Brawn [14] have shown that the free-volume form of the
equation

$$\ln\eta' = A + \frac{BV_0}{V - V_0}, \tag{5}$$

which satisfactorily represents the smooth hard-sphere viscosity coefficient

data with $A = -0.762$ and $B = 1.335$, also reproduces experimental data for pseudospherical molecules and relatively rigid ring hydrocarbons. For these compounds, A was found to be temperature independent and could be taken as -1.0. Viscosity data for n-hexane, n-hexadecane, and their mixtures were also fitted [2] very satisfactorily by Eq. (5) with $A = -1.0$. Values of V_0 varied linearly with mole fraction at each temperature. B also varied with composition and temperature, but the values for mixtures were simply related to those of the pure liquids.

The present measurements have been used as a further test of this equation. In order that the parameters should have significance, A was taken as -1.0 and V_0 for the pure liquids and the mixtures was calculated from the V_0 values derived previously [2] for n-hexane and n-hexadecane assuming a linear dependence on equivalent carbon number as illustrated in Fig. 7. The B values derived from a least-squares fit are summarized in Table VI, together with values of V_0.

Viscosity coefficients calculated using Eq. (5) with $A = -1.0$, and V_0 and B values of column 3 in Table VI, agree with the experimental data to better than $\pm 5\%$ except at the highest pressures, about 500 MPa, where the calculated values are greater than the experimental results by about 10%. These deviations appear to be systematic, as shown in Fig. 8. However, in addition to the $\pm 2\%$ estimated uncertainty in the measured viscosity coefficient, a difference of 0.2% in the density will produce a change of about 1.5% in the calculated viscosity coefficient at atmospheric pressure and about 4.5% at the highest pressures. This data fit can thus be considered very satisfactory, especially since Eq. (5) contains only one adjustable parameter.

The B values for n-octane and n-dodecane lie between those of n-hexane and n-hexadecane at a given temperature, as illustrated in Fig. 9. The deviations from a linear relationship decrease as the temperature is increased. For the mixtures, B is more positive than the values calculated from B for the pure liquids on the basis of a linear dependence on mole fraction and can be

Table V. Values of $V_0(T)/V_0(T_R)$

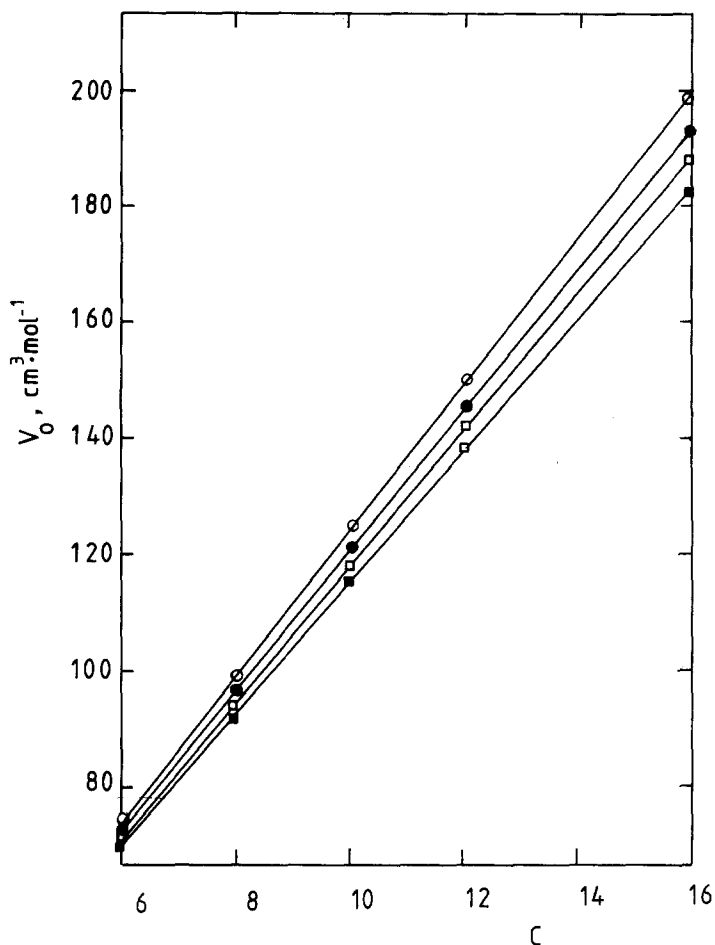|	T (°C)			
Liquid	25	50	75	100
n-Octane	1.000	0.987	0.977	0.968
n-Dodecane	1.000	0.984	0.973	0.961
n-Octane + n-dodecane				
($x = 0.5$)	1.000	0.984	0.973	0.966
n-hexane + n-dodecane				
($x = 0.5$)	1.000	—	0.974	0.964

Fig. 7. Dependence of V_0 on equivalent carbon number C for n-alkanes at different temperatures, where $C = x_1C_1 + x_2C_2$ and C_i is the number of carbon atoms in molecule i. $\bigcirc$, 25°C; $\bullet$, 50°C; $\square$, 75°C; $\blacksquare$, 100°C.

represented by the equation

$$B = x_1B_1 + x_2B_2 + ax_1x_2(B_1 - B_2),\qquad(6)$$

where $B_1 > B_2$. Application of this equation with $a = 0.6$, as previously found for the n-hexane + n-hexadecane system, gives values for B in close agreement with the values derived from the present data for n-hexane +

n-dodecane, as shown in Table VI. For *n*-octane + *n*-dodecane, which are closer in chain length, $a = 0.2$ gives better agreement. It thus appears that the magnitude of a is related to the difference in nature of the pure components.

10. THE GRUNBERG AND NISSAN EQUATION

The Grunberg and Nissan equation [3] relates the viscosity coefficient of a mixture η_M to the viscosity coefficients of the pure components η_1 and η_2 according to

$$\ln\eta_M = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1 x_2 G, \qquad (7)$$

where G is a characteristic constant for each mixture. This equation has been applied [2] to data for the *n*-hexane + *n*-hexadecane system at elevated pressure, and G was found to have a definite composition and pressure dependence, although the temperature dependence was insignificant. In Fig. 10, the results for the equimolar *n*-hexane + *n*-hexadecane mixture are compared with values derived for G from the present measurements for equimolar mixtures of *n*-octane + *n*-dodecane and *n*-hexane + *n*-dodecane. If the viscosities are accurate to $\pm 2\%$, then G is subject to an uncertainty of 0.1

Table VI. Values of V_0 and B

Liquid	T (°C)	V_0 (cm$^3 \cdot$ mol^{-1})	B	B [Eq. (6)]
n-Octane	25.0	98.2	2.095	
	50.0	96.2	2.130	
	75.0	94.2	2.181	
	100.0	92.2	2.250	
n-Dodecane	25.0	148.6	2.215	
	50.0	144.6	2.300	
	75.0	140.6	2.405	
	100.0	136.6	2.490	
				$a = 0.6$
n-Hexane + *n*-dodecane	25.0	110.8	2.165	2.162
($x = 0.5$)	75.0	105.8	2.293	2.303
	100.0	103.3	2.384	2.369
				$a = 0.2$
n-Octane + *n*-dodecane	25.0	123.4	2.159	2.1616
($x = 0.5$)	50.0	120.4	2.225	2.224
	75.0	117.4	2.301	2.304
	100.0	114.4	2.423	2.382

for an equimolar mixture. For these binary *n*-alkane mixtures, *G* is positive and increases with the difference in carbon number of the pure components. The values tend to increase with an increase in pressure and the rate of increase becomes larger with the difference in carbon number. For a given system, *G* tends to decrease with increasing temperature, but the effect is small and becomes even less significant as the carbon numbers of the two pure components become closer.
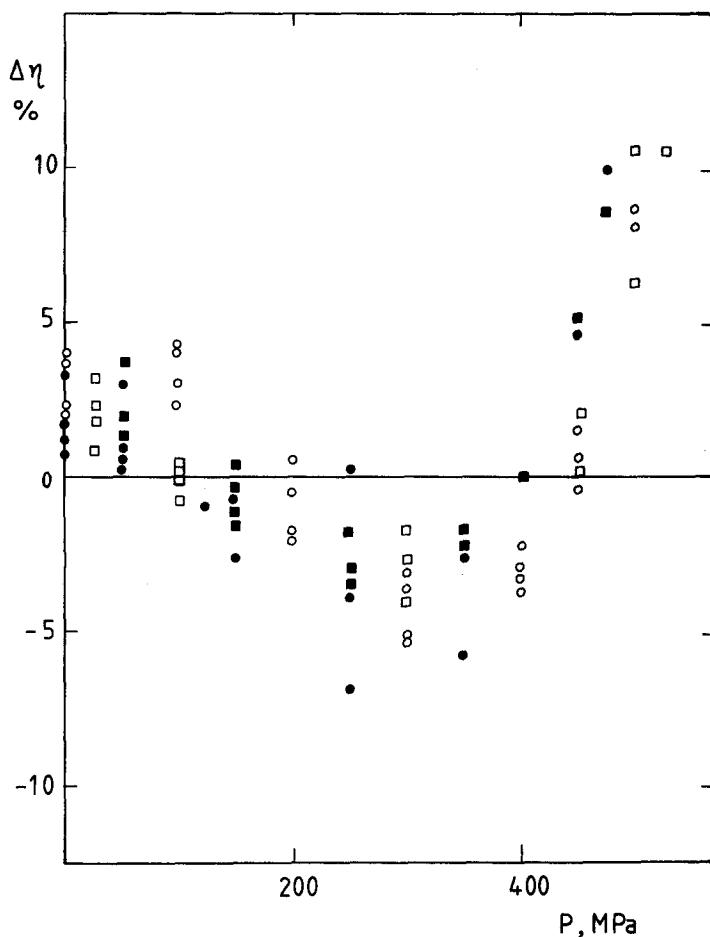

Fig. 8. Comparison of experimental viscosity coefficients with values calculated on the basis of Eq. (5) for (O) *n*-octane, (●) *n*-dodecane, (□) *n*-octane + *n*-dodecane, and (■) *n*-hexane + *n*-dodecane at different temperatures.
$\Delta\eta = 100 \, [\eta_{\text{calc}} - \eta_{\text{exp}}) \, / \, \eta_{\text{exp}}]$.
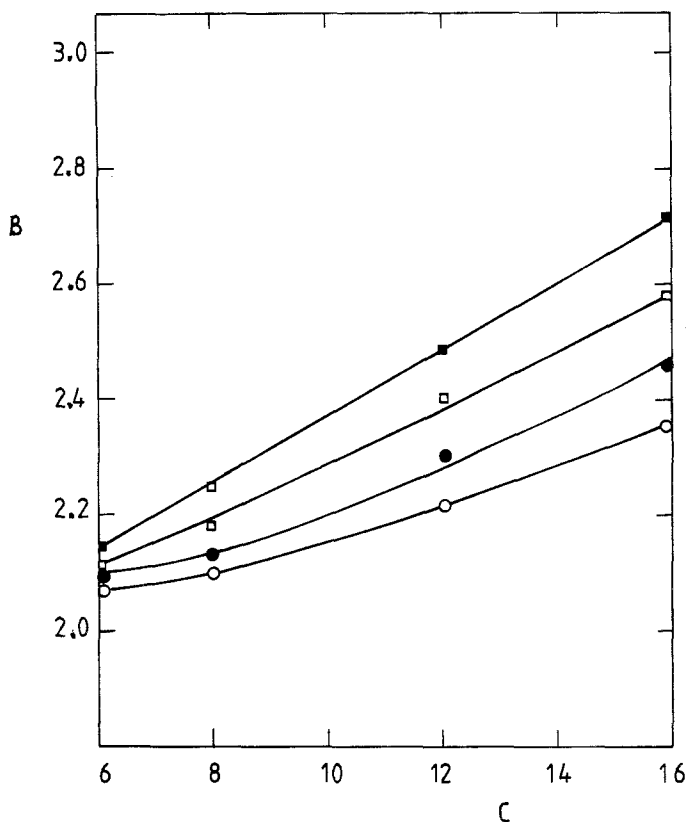
Fig. 9. Dependence of B on carbon number for pure n-alkanes at different temperatures. $\bigcirc$, 25°C; $\bullet$, 50°C; $\square$, 75°C; $\blacksquare$, 100°C.

These facts suggest that the Grunberg G value $G_{0.5}^p$ for the equimolar mixture at pressure P may be found from the value at atmospheric pressure $G_{0.5}^o$ by means of the expression

$$G_{0.5}^p = G_{0.5}^o + (C_1 - C_2)HP, \tag{8}$$

where C_i is the carbon number of component i ($C_1 > C_2$) and H is a constant. The systems studied give the value $H = 4 \times 10^{-5}$ MPa^{-1}. Isdale [15] has shown that the Grunberg G value G_{x1}^o at atmospheric pressure and mole fraction x_1 of the higher molecular weight component is related to $G_{0.5}^o$ by

$$G_{x1}^o = G_{0.5}^o (1.343 - 0.685x_1). \tag{9}$$

Equations (8) and (9) suggest that the Grunberg G at pressure P for mole fraction x_1, G_{x1}^p, can be represented by the relation

$$G_{x1}^p = G_{0.5}^o (1.343 - 0.685x_1) + (C_1 - C_2) (4 \times 10^{-5})P, \qquad (10)$$

where P is in MPa.

   Values of G were calculated for all the n-alkane mixtures using Eq. (10). G for the equimolar mixture at atmospheric pressure was taken as 1.06 for n-hexane + n-hexadecane, 0.48 for n-hexane + n-dodecane, and 0.18 for n-octane + n-dodecane. In Table VII, a summary is given of the comparison of experimental viscosities with the viscosities calculated using the Grunberg and Nissan equation with G from Eq. (10). For these three systems, the root mean square deviation of the calculated viscosities from the experimental values was 1.3% for 124 points at rounded pressures from 0.1 to 500 MPa at 25, 50, 75, and 100°C. All viscosity coefficients were reproduced to within 3.5%, a very satisfactory result.
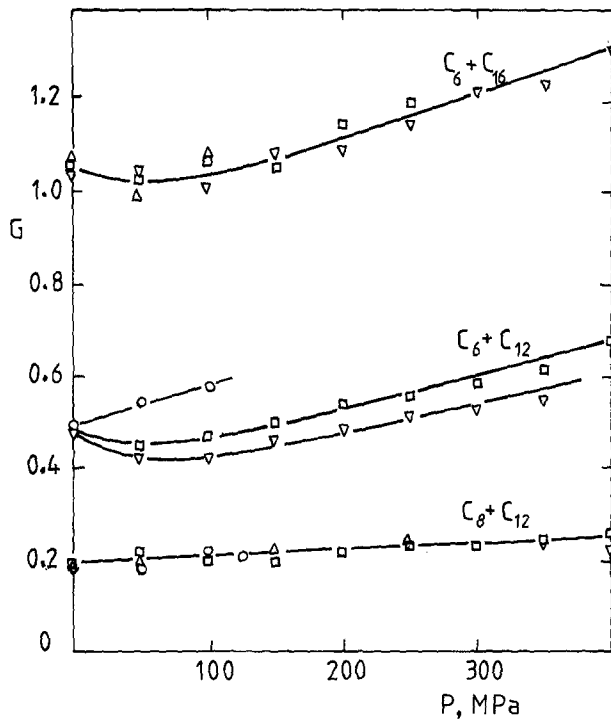

Fig. 10. Grunberg G as a function of pressure for various equimolar mixtures. O, 25°C; △, 50°C; □, 75°C; ▽, 100°C.

Table VII. Summary of Comparison of Experimental Viscosities with Viscosities Calculated Using Grunberg G Values from Eq. (10)

Mixture	Number of points	Maximum percentage deviation	RMS percentage deviation
0.501-mol fraction n-hexane			
in n-hexane + n-dodecane	20	2.13	0.95
0.500-mol fraction n-octane			
in n-octane + n-dodecane	28	0.56	0.27
n-Hexane + n-hexadecane system			
0.200-mol fraction n-hexadecane	19	3.37	1.36
0.400-mol fraction n-hexadecane	19	3.34	1.93
0.600-mol fraction n-hexadecane	19	2.40	1.65
0.800-mol fraction n-hexadecane	19	2.32	1.29

11. CONCLUSION

Viscosity coefficients for n-octane, n-dodecane, and equimolar mixtures of n-hexane + n-dodecane and n-octane + n-dodecane have been measured with an estimated accuracy of $\pm 2\%$ using a modified falling body viscometer from 25 to 100°C at pressures from 0.1 to 500 MPa. Results for a given composition at different temperatures can be correlated very satisfactorily by superimposing plots of $\log \eta'$ versus $\log V$, where $\eta' = 9.118 \times 10^7$ $\eta V^{2/3}/(MRT)^{1/2}$. This provides the basis for a useful method for accurate prediction of viscosity coefficients under other conditions of temperature and pressure.

The previously proposed free-volume form of equation gives a very satisfactory fit to the present data. The parameter V_0 for the pure liquids and mixtures is obtained from the values for n-hexane and n-hexadecane on the basis of a linear dependence on equivalent carbon number. B values are simply related to the values given by n-hexane and n-hexadecane.

The empirical Grunberg and Nissan equation reproduces all the viscosity coefficient data for the mixtures of n-alkanes at high pressure to within 3.5% using a simple expression for the composition and pressure dependence of the parameter G. G is effectively temperature independent. This approach has the advantage of not requiring values of the molar volume, but it does require values for the viscosity coefficient of the pure components.

ACKNOWLEDGMENTS

REFERENCES

1. J. H. Dymond and K. J. Young, *Int. J. Thermophys.* **1**:333 (1980).
2. J. H. Dymond, K. J. Young, and J. D. Isdale, *Int. J. Thermophys.* **1**:347 (1980).
3. L. Grunberg and A. H. Nissan, *Nature (Lond.)* **164**:799 (1949).
4. Int. Data Ser., Selec. Data Mix. Ser. A, 100 (1973).
5. Am. Petrol. Inst. Res. Proj. 44 (Texas A&M University, College Station, (1942).
6. H. L. Clever and K. −Y. Hsu, *J. Chem. Thermodyn.* **7**:435 (1975).
7. K. J. Young, Ph.D. thesis (University of Glasgow, Glasgow, (1980).
8. J. H. Dymond, K. J. Young, and J. D. Isdale, *J. Chem. Thermodyn.* **11**:887 (1979).
9. J. Robertson, Unpublished work (1980).
10. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **61**:57 (1926).
11. D. W. Brazier and G. R. Freeman, *Can. J. Chem.* **47**:893 (1969).
12. J. D. Isdale, J. H. Dymond, and T. A. Brawn, *High Temp. High Press.* **11**:571 (1979).
13. D. L. Hogenboom, W. Webb, and J. A. Dixon, *J. Chem. Phys.* **46**:2586 (1967).
14. J. H. Dymond and T. A. Brawn, *Proc. 7th Symp. Thermophys. Prop.* A. Cezairliyan, ed, (Am. Soc. Mech. Eng., New York, 1977), p. 660.
15. J. D. Isdale, In *Proceedings of the Symposium on Transport Properties of Fluids and Fluid Mixtures: Their Measurement, Estimation, Correlation and Use* (National Engineering Laboratory, East Kilbride, 1979).