

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

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Received January 2, 1985

Changes in the high-pressure self-centering falling-body viscometer system, and the new automated data logging system, are described. Viscosity coefficient measurements made with an estimated accuracy of $\pm 2\%$ are reported for isooctane and for equimolar mixtures of isooctane + *n*-octane and isooctane + *n*-dodecane at 25, 50, 75, and 100°C at pressures up to 500 MPa or to the freezing pressure. The pressure dependence of the results is found to be represented equally well by the recent equation of Makita and by a free-volume form of equation. The Grunberg and Nissan equation gives a good fit to the mixture viscosity coefficient data.

KEY WORDS: free volume; Grunberg and Nissan equation; high pressure; isooctane; *n*-dodecane; *n*-octane; viscosity.

1. INTRODUCTION

In order to increase our understanding of the dependence of transport properties on pressure and temperature and, in the case of mixtures, on composition also, it is necessary to have accurate experimental data over a wide range of experimental conditions. In previous papers [1–3], we have reported measurements at elevated pressures of the viscosity coefficients for *n*-hexane + *n*-hexadecane, [1], for *n*-octane, *n*-dodecane, and equimolar mixtures of *n*-octane + *n*-dodecane and *n*-hexane + *n*-dodecane [2], and for

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benzene, perdeuterobenzene, hexafluorobenzene, and an equimolar mixture of benzene + hexafluorobenzene [3] at 25 to 100°C. This paper extends the investigation to branched-chain hydrocarbons with viscosity coefficient measurements on isooctane (2,2,4-trimethylpentane) and equimolar mixtures of isooctane + *n*-octane and isooctane + *n*-dodecane from 25 to 100°C and at pressures up to the freezing pressure or 500 MPa. The principle of operation of the high-pressure self-centering falling-body viscometer remains unaltered, but as described in Section 2 changes have been made to the sinker detection system and a microprocessor-based data logging system has been installed. The measured viscosity coefficients are given in Section 4. It is shown in Section 5 that the data for a given liquid at different temperatures and pressures can be correlated very satisfactorily by a graphical method [4] based on plots of η' , where $\eta' = 9.118 \times 10^7 \eta V^{2/3} / (\text{MRT})^{1/2}$ versus $\log V$. In the subsequent section, a previously proposed [4] free-volume form of equation is applied to the present results. The fit to the data is less satisfactory than in the case of the *n*-alkane liquids and binary mixtures, for which the pressure dependence is smaller, but even so the present viscosity coefficient values can be fitted generally to better than 3%. The recently proposed equation of Kashiwagi and Makita [5] relating viscosity coefficients to pressure is tested in Section 7 and found to give a reasonable fit (better than 10%). Finally, in Section 8, the empirical equation of Grunberg and Nissan [6] is applied to the mixture viscosity coefficient data. It is found that the parameter *G* is practically temperature independent and decreases only slightly with increases in pressure.

2. EXPERIMENTAL

The high-pressure falling-body viscometer has been described in detail elsewhere [2, 7]. The terminal velocity of a self-centering hemispherically nosed sinker, with a small piece of ferrite embedded in it, is measured as it falls axially down a vertical cylindrical tube. In previous measurements [1–3], the change in inductance as the sinker passed through two pairs of coils wound on the outside of the tube was used to start and to stop a timer. This detection system suffered the disadvantages that the four coils had to be wound to be electrically identical, a large number of turns was required necessitating thin wire, which was fragile and suffered from shorted turns, the electrical balance of the AC bridge drifted during use, and six leadouts were required through the pressure vessel end plug. These problems were overcome with the new system designed with two coils, not necessarily identical, having fewer turns and thus allowing the use of

thicker, more robust wire, and with just two leadouts through the end plug. It proved impossible to achieve a large enough signal from a resonance detector system due to the physical constraints on the dimensions of the ferrite core, and so it became necessary to revert to a bridge circuit. The two coils on the viscometer, which form the active arm of the bridge, each consist of 250 turns of 38 SWG insulated copper wire and are connected in series, having a combined resistance of 20.20Ω and inductance of 1.70 mH at 20°C . The three other arms of the bridge are remote from the viscometer. The variable resistor, of noninductive construction, and the variable inductor are used to balance the bridge, with the sinker remote from either coil. The current through the coils is 40 mA rms at a frequency of 300 Hz. This frequency is the highest that can be used before eddy current effects from the sinker body become significant.

The out-of-balance signal from the bridge is amplified and passed through an AC to DC converter. With the bridge initially balanced, a small DC offset is applied at this stage to eliminate any remaining imbalance not taken up by the resistor and inductor. The passage of the sinker through each coil causes an increase in the out-of-balance signal which is amplified and fed to the detector system. This is based on a microprocessor, with the program stored in an EPROM. As the sinker passes through each coil, the DC signal increases and is a maximum when the ferrite core of the sinker is at the center of the coil. The DC level is sampled digitally by the microprocessor system and the maximum detected. When this occurs a signal is sent to start or stop a counter/timer. The microprocessor contains internal self-check routines, and subroutines in the program eliminate false triggering due to spurious peaks.

Since the coils are wired in series and the detector system is looking for a maximum, not a predetermined level, the coils do not need to be identical and there are only two leadouts. The use of an autozeroing amplifier in the detector system means that once the bridge is balanced at a given temperature and pressure, it will remain stable for long periods. With the previous system it was frequently necessary to rebalance the bridge during long fall-time measurements, which was undesirable due to the possibility of setting a false balance point.

The power levels used in the new bridge are significantly lower than used previously and there are only two coils of 250 turns each, as opposed to four coils of 440 turns each. Thus heating effects and magnetic forces on the sinker are insignificant.

Viscosity coefficients are related to the fall time t by the equation

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

where η_p is the viscosity coefficient at pressure P , ρ_L and ρ_S' are the densities of liquid and sinker at pressure P and temperature T , T is the experimental temperature, and T_0 is a reference temperature (taken as 25°C). P_0 is the atmospheric pressure, β is the compressibility coefficient, and A is the viscometer constant.

Values of A were calculated for the new sinker/tube combination from Eq. (1) from measurements on Shell Vitrea No. 21 oil, *n*-hexadecane, *n*-hexane, isooctane, and equimolar mixtures of isooctane + *n*-octane and isooctane + *n*-dodecane at atmospheric pressure and different temperatures. The viscosity coefficients were measured in suspended-level viscometers and have an estimated accuracy of $\pm 0.5\%$. The viscometer constant varies with the Reynolds number as shown in Fig. 1, increasing by about 5% over this range of viscosities. The calibration curve is given by

$$A = 46.6 \left\{ 1 + \left[\frac{0.03}{t(1 - \rho_L/\rho_S')} \right]^{0.5} \right\} \quad (2)$$

where t is in seconds and A has units of mPa^{-1} .

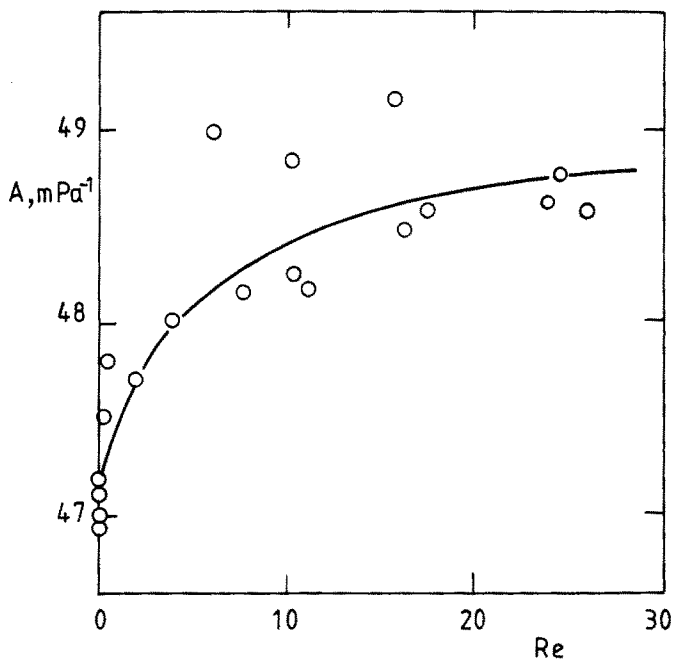


Fig. 1. Calibration curve for the high-pressure viscometer.

Viscosity coefficients at elevated pressures were determined from the ratio of the high-pressure coefficient to the atmospheric-pressure value obtained by applying Eq. (1) to each pressure, and the atmospheric-pressure viscosity coefficient determined as above. This method gives an estimated accuracy of $\pm 2\%$ in the high-pressure viscosity coefficients.

For ease of operation and to maintain a regular check on the temperature and pressure, a data logging system based on a controller, a modified desktop computer, and a programmable scanner has been installed. Analogue signals from the metal-sheathed platinum resistance thermometers and from the manganin-wire resistance gauge are routed via the scanner to a digital voltmeter and thence to the controller. The measured fall times are read from the counter/timer over the IEEE bus to the controller. When all the appropriate constants for the liquid under test are stored in the controller, viscosity coefficients and densities can be output direct from the input data.

3. MATERIALS

The *n*-octane and *n*-dodecane were purchased from BDH Chemicals Ltd., Poole, U.K., and had stated minimum purities of 99.5 and 99 mol %, respectively. Gold-label isooctane (2,2,4-trimethylpentane) was purchased from Aldrich Chemical Co. Ltd., Gillingham, U.K., with a stated purity of >99 mol %. The refractive index n (D , 298.15 K) of *n*-octane was 1.39525 and that of *n*-dodecane was 1.41959, in close agreement with the literature values of 1.39505 [8] and 1.41949 [8]. The measured densities at 298.15 K for isooctane, *n*-octane, and *n*-dodecane were 687.82, 698.60, and 745.43 $\text{kg} \cdot \text{m}^{-3}$, respectively, compared with literature values of 687.77 [9], 698.61 [10], and 745.37 $\text{kg} \cdot \text{m}^{-3}$ [11].

4. RESULTS

Measurements of the sinker fall time have been made for isooctane and for equimolar mixtures of isooctane + *n*-octane and isooctane + *n*-dodecane at 25, 50, 75, and 100°C, at pressures up to the freezing pressure or 500 MPa. The calculated viscosity coefficients are given in Tables I to III, together with values for the density under the same conditions, calculated from values of the isothermal secant bulk modulus by which experimental density data have been fitted [12]. The densities have an estimated accuracy of $\pm 0.2\%$. No literature viscosity coefficient values have been found for the mixtures studied here, and for isooctane the only measurements in this temperature range are at atmospheric pressure [13, 14] and agree with the present measurements.

Table I. Viscosity Coefficient and Density of Isooctane

Temperature (°C)	Pressure (MPa)	Density (kg · m ⁻³)	Viscosity coefficient (mPa · s)
24.99	0.1	687.82	0.4718
	26.4	711.0	0.641
	50.7	728.2	0.814
	100.5	755.3	1.237
	200.4	792.2	2.482
	311.9	821.1	4.855
	406.5	841.4	8.230
	499.4	859.8	13.62
49.99	0.1	666.67	0.3587
	25.1	692.1	0.492
	52.2	713.5	0.634
	101.6	742.5	0.942
	196.8	780.0	1.758
	310.5	811.1	3.273
	406.8	833.0	5.241
	503.1	853.3	8.399
75.01	0.1	644.44	0.2818
	25.8	675.2	0.390
	50.7	697.5	0.499
	101.5	730.1	0.750
	200.5	770.5	1.396
	307.0	800.3	2.468
	412.5	824.9	4.035
	501.4	844.5	5.628
99.98	0.1	621.21	0.2270
	25.6	657.3	0.323
	51.0	682.9	0.411
	101.2	717.6	0.613
	198.4	759.0	1.089
	300.1	788.9	1.901
	403.6	815.0	2.974
	500.5	838.8	4.264

Table II. Viscosity Coefficient and Density of an Equimolar Mixture of Isooctane + *n*-Octane

Temperature (°C)	Pressure (MPa)	Density (kg · m ⁻³)	Viscosity coefficient (mPa · s)
25.05	0.1	692.50	0.4882
	26.7	714.4	0.639
	50.9	730.7	0.799
	97.5	755.7	1.151
	200.2	794.0	2.263
	293.2	819.2	3.879
	402.3	844.1	6.887
	492.3	863.1	10.85
50.04	0.1	673.15	0.3739
	26.9	698.0	0.506
	52.8	717.3	0.634
	98.3	743.9	0.873
	198.3	784.2	1.637
	303.0	814.1	2.821
	424.7	842.4	4.982
	496.8	857.8	6.850
74.92	0.1	651.50	0.2958
	28.4	682.9	0.403
	50.9	702.2	0.493
	100.8	734.0	0.711
	197.5	774.4	1.248
	302.8	805.2	2.073
	399.7	828.7	3.115
	496.2	850.8	4.586
100.03	0.1	627.22	0.2374
	27.1	662.2	0.328
	52.8	686.8	0.416
	101.3	720.0	0.591
	199.6	762.8	1.026
	300.2	792.9	1.619
	400.5	817.9	2.411
	497.5	840.7	3.416

Table III. Viscosity Coefficient and Density of an Equimolar Mixture
of Isooctane + *n*-Dodecane

Temperature (°C)	Pressure (MPa)	Density (kg · m ⁻³)	Viscosity coefficient (mPa · s)
25.00	0.1	721.99	0.8601
	26.0	741.1	1.159
	51.4	756.2	1.505
	103.1	780.3	2.379
	1500	798.0	3.425
	201.3	815.0	4.941
	241.4	827.6	6.482
49.99	0.1	703.99	0.6179
	27.9	726.8	0.846
	52.9	743.3	1.075
	98.5	767.2	1.563
	197.2	803.8	3.088
	303.2	832.4	5.785
	397.2	854.0	9.590
74.88	0.1	684.41	0.4691
	26.2	708.9	0.636
	51.9	728.2	0.814
	98.4	755.3	1.179
	196.6	794.2	2.228
	304.7	823.9	3.997
	402.9	845.7	6.398
	503.4	865.6	10.13
99.70	0.1	663.25	0.3678
	25.9	691.5	0.507
	54.5	715.2	0.660
	104.3	745.3	0.976
	199.2	783.3	1.737
	297.8	811.3	2.863
	400.1	835.6	4.530
	502.5	858.3	6.872

5. CORRELATION OF VISCOSITY COEFFICIENT DATA

Experimental viscosity coefficient data for liquids and liquid mixtures have been correlated very satisfactorily [2, 4] by a method suggested by consideration of the results for hard spheres. A quantity η' is defined as $10^4 \eta V^{2/3}/(MT)^{1/2}$ in the cgs system of units or, more generally, as

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

Plots of η' versus $\log V$ for a given liquid at different temperatures are superimposable laterally on the curve obtained for a given reference tem-

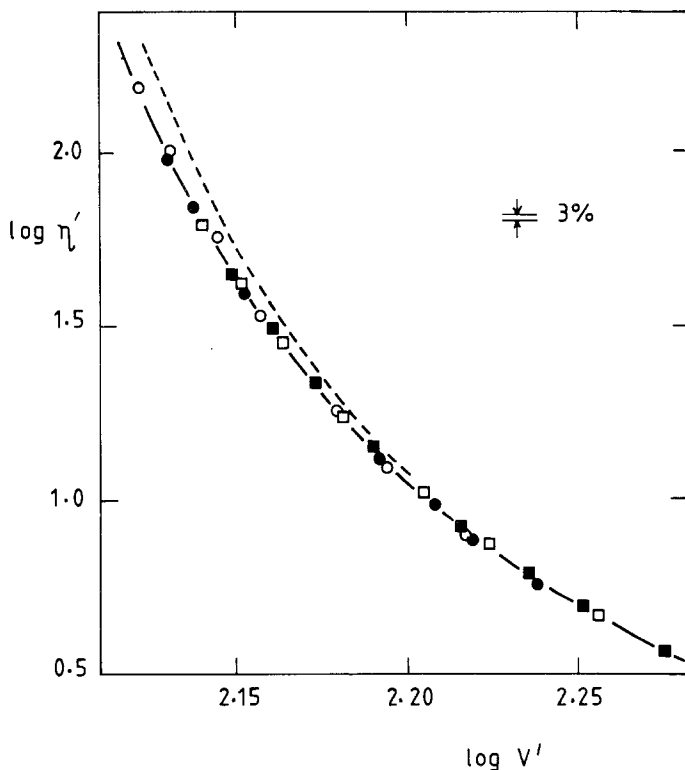


Fig. 2. Correlation of experimental viscosity coefficient data for the equimolar mixture of isooctane + *n*-octane at different temperatures and pressures based on the 25°C isotherm. η' is defined by Eq. (3); $V' = V \cdot V_0(T_R)/V_0(T)$. (○) 25°C; (●) 50°C; (□) 75°C; (■) 100°C; (---) curve for isooctane.

perature, T_R , over the whole density range. The amount by which $\log V$ has to be adjusted leads to a value for $V_0(T)/V_0(T_R)$, where $V_0(T)$ represents the close-packed volume at temperature T .

Application of this method to the present results for isooctane and for equimolar mixtures of isooctane + n -octane and isooctane + n -dodecane shows that these data, too, can be very satisfactorily correlated on the basis of a single curve for each system. The 25°C isotherm was taken as the reference. The results are shown in Fig. 2 for the equimolar mixture of isooctane + n -octane, together with the corresponding curve for isooctane, which has a somewhat steeper dependence on the molar volume at high densities. The resulting curve for the equimolar isooctane + n -dodecane mixture is practically identical to that for the isooctane + n -octane mixture and can be superimposed upon it by taking the ratio of V_0 for the mixture with n -dodecane to V_0 for the mixture with n -octane to be 1.275 at 25°C. For each system, the deviation of the points from the reference curve is less than 3%. Values derived for $V_0(T)/V_0(T_R)$ for isooctane and its mixtures are given in Table IV. The ratios for isooctane agree to within 0.1% with values previously obtained for n -octane [2] and there is little difference on going to the mixtures.

6. FREE-VOLUME FORM OF EQUATION

It has been shown [1, 2, 4] that the equation

$$\ln \eta' = A + \frac{BV_0}{V - V_0} \quad (4)$$

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

Liquid	T (°C)			
	25	50	75	100
Isooctane	1.000	0.986	0.977	0.968
Isooctane + n -octane ($x = 0.5$)	1.000	0.986	0.970	0.964
Isooctane + n -dodecane ($x = 0.5$)	1.000	0.984	0.973	0.962
n -Octane + n -dodecane ^a ($x = 0.5$)	1.000	0.984	0.973	0.966

^a From Ref. 2.

with $A = -1.0$ very satisfactorily reproduces experimental viscosity coefficient data for relatively rigid-ring hydrocarbons, *n*-hexane, *n*-octane, *n*-dodecane, and *n*-hexadecane and for binary *n*-alkane mixtures. For the mixtures, V_0 values varied linearly with the mole fraction at each temperature. B also varied with the composition and temperature, but the values for mixtures were related simply to the values obtained for the pure liquids.

The present results for systems involving a branched hydrocarbon have been used as a further test of the applicability of this equation. A was taken as -1.0 as before, with values of V_0 and B derived from the data, first, by optimization to give the best fit and, second, with V_0 values for isooctane adjusted to give a smooth temperature variation. V_0 for the equimolar mixtures was taken to be the average of the values for the pure components, and B values were then optimized to give a least-squares fit. It was found that the data fit obtained using the temperature-smoothed V_0 values for isooctane given in Table V was only slightly inferior to that

Table V. Values of V_0 and B

Liquid	T (°C)	V_0 ($\text{cm}^3 \cdot \text{mol}^{-1}$)	B	B [Eq. (5)]
Isooctane	25.0	101.2	1.958	
	50.0	99.8	1.977	
	75.0	98.4	2.011	
	100.0	97.0	2.045	
				$a = -0.6$
Isooctane + <i>n</i> -octane ($x = 0.5$)	25.0	99.7	2.000	2.006
	50.0	98.0	2.025	2.031
	75.0	96.3	2.054	2.071
	100.0	94.6	2.121	2.117
				$a = 0.3$
Isooctane + <i>n</i> -dodecane ($x = 0.5$)	25.0	124.9	2.114	2.106
	50.0	122.2	2.157	2.163
	75.0	119.5	2.227	2.238
	100.0	116.8	2.316	2.301
Isooctane + <i>n</i> -octane ^a ($x = 0.5$)	25.0	98.6	2.067	
	50.0	95.9	2.154	
	75.0	94.0	2.197	
	100.0	93.0	2.217	

^a Optimized values of V_0 and B .

obtained using optimized V_0 values. As shown in Fig. 3, the agreement with experimental data using Eq. (4) with V_0 and B values for isooctane from Table V was generally within $\pm 5\%$, the larger deviations occurring at the higher pressures. The pattern of negative deviations at intermediate pressures and positive deviations at the highest pressure has been observed for other hydrocarbon systems [2]. For the equimolar isooctane + n -dodecane mixture the data fit obtained using averaged V_0 values of the pure components, with V_0 for n -dodecane from Ref. 2, was little different from the fit using optimized V_0 values: The corresponding B values were fitted to the equation

$$B = x_1 B_1 + x_2 B_2 + ax_1 x_2 (B_1 - B_2) \quad (5)$$

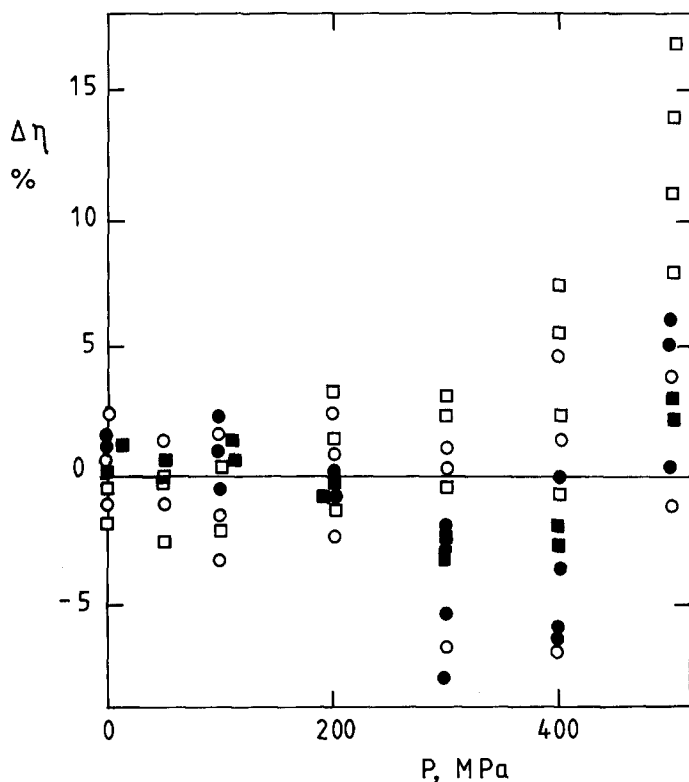


Fig. 3. Comparison of experimental viscosity coefficients with values calculated on the basis of Eq. (4) for (●) isooctane, for (○) equimolar isooctane + n -dodecane mixtures, and for equimolar isooctane + n -octane mixtures using (□) averaged V_0 values and (■) optimized V_0 values at different temperatures. $\Delta\eta = 100[\eta_{\text{calc}} - \eta_{\text{exp}}]/\eta_{\text{exp}}$.

where $B_1 > B_2$, with B for n -dodecane given earlier [2], and x_i is the mole fraction of component i . As shown in Table V, the B values with $a = 0.3$ are in close agreement with the optimized B values. The data fit using Eq. (4) with averaged V_0 and B from Eq. (5) is shown in Fig. 3 to be very satisfactory. It is of interest to note that the value for a (0.2) used previously [2] for the n -octane + n -dodecane system also gives a satisfactory description of the present data.

For the equimolar isooctane + n -octane mixture, with averaged V_0 values it was found that the optimized B values can be represented by Eq. (5) with $a = -0.6$. V_0 and B values for n -octane were taken from Ref. 2. The data fit thus obtained is satisfactory at pressures up to 400 MPa but the calculated values are high by an average of 13% at 500 MPa. Although this might be accounted for partly by the relatively greater effect of small uncertainties in the density at this high pressure, it does indicate a limitation in the use of Eq. (4) with $A = -1.0$ and V_0 values taken as the average of the V_0 for the pure components. In fact, for this system a significantly improved fit to the data can be obtained even with $A = -1.0$ using the optimized V_0 and B values included in Table V. The results, shown in Fig. 3, have a maximum deviation of 3%.

7. PRESSURE DEPENDENCE OF DATA

The satisfactory methods of correlation and representation of the viscosity data described above require accurate density data. It is highly desirable to have an accurate representation of the data as a function of pressure, and the equation which has proved most successful to date is that of Kashiwagi and Makita [5]. The high-pressure viscosity coefficient is related to the viscosity at 0.1 MPa, η_0 , by an equation similar to the Tait equation:

$$\ln(\eta/\eta_0) = E \ln[(D + P)/(D + 0.1)] \quad (6)$$

where P is the pressure (MPa) and D and E are temperature-dependent parameters. This equation has previously been found [5] to give a good representation of data at pressure up to 110 MPa. With the present data, which cover a much wider pressures range, optimization of D and E values produces a data fit within $\pm 9\%$. The derived parameters are given in Table VI, and the comparison with experimental data is shown in Fig. 4. The deviations are found to be systematic, the calculated values being too high at pressures from 100 to 400 MPa and too low at 500 MPa. For predictive purposes, Eq. (6) has the disadvantage that values of D and E do not vary smoothly with changes in temperature. However, it is found [15]

Table VI. Values of D and E

Liquid	T (°C)	D (MPa)	E
Isooctane	25	284	3.253
	50	200	2.445
	75	169	2.151
	100	139	1.890
<i>n</i> -Octane	25	311	3.142
	50	270	2.634
	75	208	2.116
	100	164	1.774
<i>n</i> -Dodecane	25	255	3.092
	50	219	2.585
	75	242	2.727
	100	204	2.334
Isooctane + <i>n</i> -octane ($x = 0.5$)	25	332	3.371
	50	220	2.419
	75	186	2.072
	100	141	1.733
Isooctane + <i>n</i> -dodecane ($x = 0.5$)	25	232	2.795
	50	248	2.837
	75	213	2.485
	100	165	2.056
<i>n</i> -Octane + <i>n</i> -dodecane ($x = 0.5$)	25	255	2.893
	50	264	2.844
	75	234	2.494
	100	187	2.071

that the calculated viscosity coefficients are relatively insensitive to changes in D providing that E is optimized, and further investigations are being made on the applicability of Eq. (6).

8. THE GRUNBERG AND NISSAN EQUATION

The Grunberg and Nissan equation [6] relates the viscosity coefficient of a mixture η_M to the viscosity coefficients of the pure components η_1 and η_2 according to

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

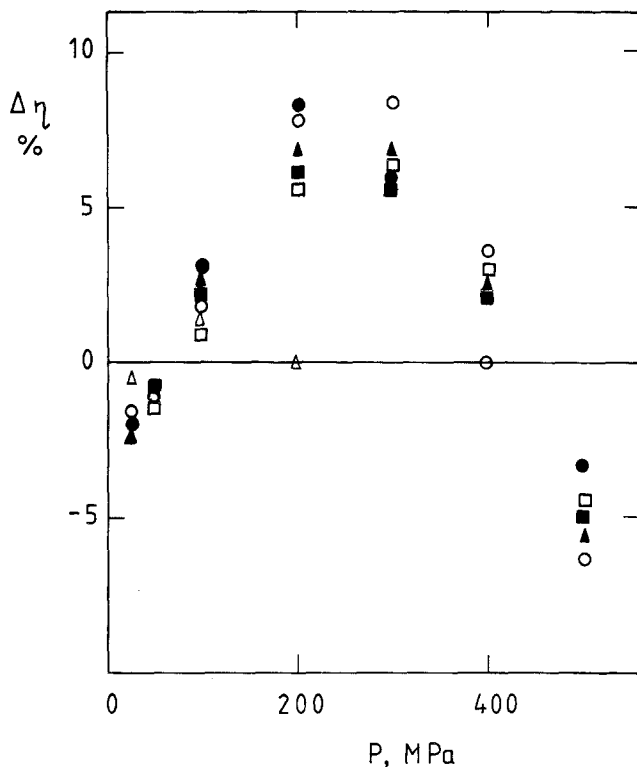


Fig. 4. Comparison of experimental viscosity coefficients with values calculated on the basis of Eq. (6) with values of D and E from Table VI for isooctane at 25°C (○) and 75°C (●), equimolar isooctane + n -octane mixtures at 25°C (□) and 75°C (■), and equimolar isooctane + n -dodecane mixtures at 25°C (△) and 75°C (▲). $\Delta\eta = 100[\eta_{\text{calc}} - \eta_{\text{exp}}]/\eta_{\text{exp}}$.

where G is a characteristic constant for each mixture. This equation has been applied [2] to binary n -alkane mixtures at elevated pressures, and G was found to have a definite composition and pressure dependence. G was positive and increased with the difference in carbon number of the pure components. The temperature dependence of G was found to be small, becoming insignificant as the carbon numbers of the two pure components became closer. The pressure dependence of G for the equimolar mixture of n -octane + n -dodecane [2] is compared with that obtained for the equimolar mixtures of isooctane + n -octane and isooctane + n -dodecane in Fig. 5. On the basis of an uncertainty of $\pm 2\%$ in the measured viscosity coefficient, G is known to ± 0.1 . As with the n -alkane mixtures, G increases

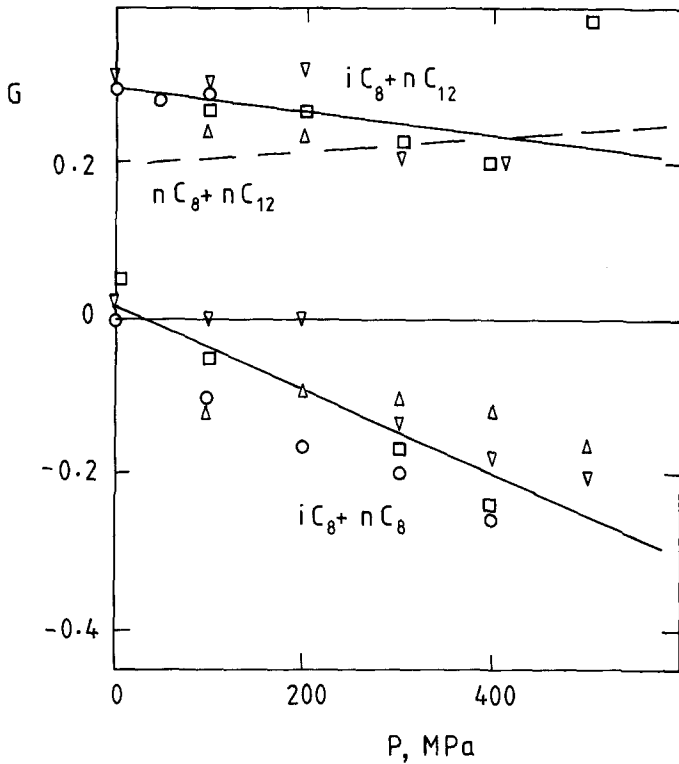


Fig. 5. Grunberg G as a function of pressure for various equimolar mixtures. (○) 25°C; (△) 50°C; (□) 75°C; (▽) 100°C; (---) n -octane + n -dodecane [2].

with the difference in carbon number of the components. However, the pressure dependence is negative with these mixtures containing isooctane as a component and becomes less negative when the n -alkane has a high carbon number. There is no definite temperature dependence of G .

These results suggest that for equimolar isooctane + n -alkane mixtures, the Grunberg G value at pressure P , $G_{0.5}^P$ may be found from the value at atmospheric pressure by means of the expression

$$G_{0.5}^P = G_{0.5}^0 - HP / (C_1 + 1 - C_2) \quad (8)$$

where C_i is the carbon number of component i ($C_1 > C_2$) and H is a constant which, from the systems studied, has the value $5.2 \times 10^{-4} \text{ MPa}^{-1}$.

Using Eq. (8), values of $G_{0.5}^P$ were calculated for isooctane + n -octane taking $G_{0.5}^0$ as 0.01 and for isooctane + n -dodecane with $G_{0.5}^0$ equal to 0.30. In Table VII, a summary is given of the comparison of experimental

Table VII. Summary of Comparison of Experimental Viscosities with Viscosities Calculated Using Grunberg G Values from Eq. (8)

Liquid	Number of points	Maximum percentage deviation	rms percentage deviation
Isooctane + <i>n</i> -octane ($x = 0.5$)	32	2.34	1.26
Isooctane + <i>n</i> -dodecane ($x = 0.5$)	25	3.48	1.19

viscosities with values calculated using the Grunberg and Nissan equation. At rounded pressures from 0.1 to 500 MPa at 25, 50, 75, and 100°C, the root mean square deviation of the calculated viscosities from the measured values was 1.3% for 57 points. All viscosity coefficients were reproduced to within 2.4% (apart from the 500-MPa value at 75°C for isooctane + *n*-dodecane, which differs by 3.5%), a very satisfactory result.

9. CONCLUSIONS

Viscosity coefficients for isooctane and equimolar mixtures of isooctane + *n*-octane and isooctane + *n*-dodecane have been measured with an estimated accuracy of better than 2% using a falling-body viscometer with a modified detection system for the sinker, at 25, 50, 75, and 100°C at pressures up to the freezing pressure or 500 MPa.

Previously proposed methods for correlation and representation of the data are shown to apply satisfactorily to these branched systems, in addition to the straight-chain systems reported earlier. The recently proposed Kashiwagi and Makita equation for relating high-pressure viscosity coefficients to the pressure produces a reasonable data fit, although the deviations are systematic and the optimized parameters do not vary smoothly with changes in temperature. For the mixtures, the Grunberg and Nissan equation reproduces the data to within 2.4%. This approach requires accurate values for the pure components.

ACKNOWLEDGMENTS

This paper is published by permission of the Director, National Engineering Laboratory, Department of Trade and Industry (U.K.). Support from the Science and Engineering Research Council through the

CASE Awards Scheme and from the Mechanical and Electrical Engineering Requirements Board of the Department of Trade and Industry is acknowledged.

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