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Transport Properties of Nonelectrolyte Liquid Mixtures—II. Viscosity Coefficients for the n-Hexane + n-Hexadecane System at Temperatures from 25 to 100°C at Pressures Up to the Freezing Pressure or 500 MPa

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Viscosity coefficients measured with an estimated accuracy of 2% using a self-centering falling body viscometer are reported for n-hexane, n-hexadecane, and four binary mixtures 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', as suggested by the hard-sphere theories, 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 for all compositions are fitted, generally well within the estimated uncertainty, by the equation

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

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, and viscosity coefficients calculated on the basis of this equation have an estimated accuracy of 3%. The effectiveness of the recently recommended empirical Grunberg and Nissan equation is investigated. It is found that the parameter G is pressure dependent, as well as composition dependent, but is practically temperature independent.

KEY WORDS: viscosity coefficient; viscometer; high pressure; hard-sphere theory; n-hexane; n-hexadecane; Grunberg and Nissan equation.

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1. INTRODUCTION

For the most satisfactory interpretation of transport property data for liquids and liquid mixtures, a rigorous theory based on a sound molecular model is required. At the present time, the only successful molecular theory of transport [1] is for dilute gases composed of structureless spherical particles. For molecular liquids and liquid mixtures, it is necessary to take into account nonspherical molecular shape and the many-body interactions. Even with the advent of fast electronic computers, it has proved possible to calculate viscosity coefficients only for certain model systems [2, 3]. Moreover, even if it were possible to represent molecular interactions in real polyatomic liquids correctly, the computer time involved in the calculation of viscosity coefficients is so great that other methods of prediction and correlation of viscosity coefficients would still be of the greatest importance.

In order to test the effectiveness of empirical and of semitheoretical expressions (that is, those which are based on a molecular model, but which involve certain approximations in their derivation) for representing viscosity coefficient data for liquids and liquid mixtures, it is essential to have accurate experimental data over a wide range of temperature and pressure. However, there are few measurements at elevated pressures, and even at one atmosphere, the data generally cover a very restricted range of temperature. For this reason, in an earlier paper [4], we reported accurate measurements at saturation pressure of viscosity coefficients for hydrocarbon mixtures specifically for two-component, three-component, and four-component n-alkane mixtures from 12 to 105°C. The present paper investigates the effect of elevated pressure.

Viscosity coefficients have been measured for n-hexane, n-hexadecane, and four binary mixtures using a self-centering falling body viscometer (described in Section 2) from 25 to 100°C at pressures up to the freezing pressure or 500 MPa. The results given in Section 6 have an estimated accuracy of 2%. These accurate measurements have been used to test the adequacy of the hard-sphere theories for representing viscosity coefficient data for real single component liquids. As shown in Section 7, the density dependence of the results for n-hexane at any given temperature does follow closely the behavior expected on the basis of the rough hard-sphere model, but only for pressures up to 150 MPa. For the correlation of viscosity coefficient data for mixtures of given composition at different temperatures over the whole available pressure range, a method based on the hard-sphere model and previously applied to data for pseudospherical molecular liquids and rigid ring hydrocarbons is described in Section 8. In order to fit the experimental data mathematically, a free-volume form of equation proposed on the basis of hard-sphere theories is shown in Section 9 to be very satisfactory.

However, in view of the difficulties of developing a successful rigorous theory based on a sound molecular model, it is appropriate also to consider purely empirical relationships for the representation of mixture viscosity coefficients. The Grunberg and Nissan equation [5], a simple relation containing one adjustable parameter, which has been shown by Irving [6] to be most effective in representing atmospheric viscosity coefficient data for liquid mixtures, is shown in Section 10 to reproduce the present data practically to within the estimated experimental uncertainty, provided that the Grunberg constant is allowed to vary with pressure and composition.

2. EXPERIMENTAL: 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 sinker and the tube were made from the same nonmagnetic En 58J stainless steel, thus minimizing compressibility and thermal expansion effects. A section through the viscometer is shown in Fig. 1. The viscometer tube was approximately 23 cm in length, with an external diameter of 2.4 cm and an internal diameter of 7.645 mm. The sinker, illustrated in Fig. 2, had a small cylinder of ferrite embedded in the core. It was 14 mm long and 7.549 mm in diameter, leaving an annulus of 0.048 mm between the tube and the sinker. The diameter of the sinker and the internal diameter of the tube were constant to within ±0.005 mm and deviated from circularity by less than 0.005 mm. This particular type of sinker has been shown to be self-centering [7]. The position of the sinker was detected by the change in inductance it caused as it passed through two pairs of coils wound on the outside of the tube.

These triggering coils were wound from 44 SWG insulated copper wire

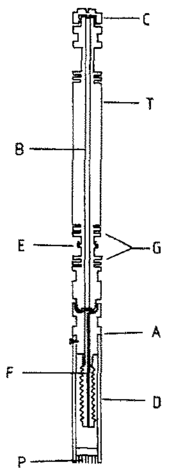
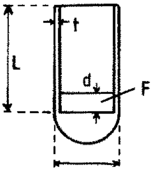


Fig. 1. The viscometer: A, bellows section; B, viscometer bore; C, end cap; D, bellows cage; E, electrical connections; F, filler rod; G, coil grooves; P, pin connectors; T, viscometer tube.



t	0·06L - 0·08L
d	0·20L - 0·26L

Fig. 2. The sinker: F, ferrite core.

with a resistance of 80 ohms and approximately 550 turns on each coil. They were trimmed to the same inductance within 0.2 mH and to the same resistance within 0.5 Ω, and the ends were soldered to pin connections attached to the narrow sections of the viscometer tube. Connecting wires from these collars were led along axial grooves to a pin connector at the end of the bellows support cage. The four coils formed a bridge circuit which was unbalanced by the passage of the ferrite core through each coil in turn. As the sinker with its ferrite core entered the first coil an out-of-balance signal was produced, which was then amplified. The demodulator working in conjunction with the phase shifter then reduced this 300 Hz signal to a dc level, which first rose and then fell as the sinker approached the second coil, reaching zero at the midpoint. At this point, the dc signal operated a Schmitt trigger, which produced a sharp pulse to start a Hewlett Packard Counter Timer, type 5223L. The input level at which the trigger operated was offset slightly from zero to avoid false triggering caused by background noise in the circuit. This process was repeated as the sinker went through the second pair of coils, and this time the pulse from the Schmitt trigger stopped the timer. The viscometer end cap was screwed to one end of the viscometer tube and sealing was effected by 0.1 mm thick copper washers, which were tightly clamped in a recess in the end cap by raised sections of the viscometer tube.

Pressure was transmitted to the liquid by flexible metal bellows attached to one end of the tube. The bellows were of 0.1 mm stainless steel seamless tubing with 12 convolutions, and fully compressed they could expel 25% of the total sample volume. The relative amount of liquid expelled could be increased by decreasing the liquid volume with the addition of fillers, one in the bellows, and the other in the viscometer tube remote from the measuring section. The filler in the bellows section gave an indication of the state of compression of the bellows as, when fully compressed, the filler rod prevented the sinker from leaving the bottom pair of coils. Sealing between the bellows and viscometer tube was effected with copper washers in the same way as between the tube and end cap.

Linear deformation of the bellows was ensured by a brass support cage, which had holes drilled along the side to allow free passage of the pressurizing fluid. This was a mixture of two parts kerosine to one part Tellus 21 oil, which combined a high freezing pressure with good lubricating properties. The pressurizing system consisted of a Madan Airhydro Pump supplied with an air line, pressure intensifier, pressure gauge block with pressure release valve, and a pressure vessel enclosed in an oil bath. Pressure was measured using a manganin pressure gauge, which had been calibrated using a Budenberg Dead Weight Tester, calibrated at the National Physical Laboratory.

The temperature of the pressure vessel was controlled by immersion in a bath containing Marlotherm S heating oil. The bath was insulated with fiberglass on all sides, and heat loss from the surface was minimized by using Alplas insulating spheres. Temperature control with a Grant Instruments controller with mercury contact thermometer was better than ±0.03 K over the whole temperature range. Temperatures were measured using a Hewlett Packard 2801A quartz thermometer which had been checked against a platinum resistance thermometer calibrated by the National Physical Laboratory. This confirmed the accuracy of ±0.02 K quoted for the quartz thermometer.

3. MATERIALS

The n-hexane and n-hexadecane were purchased from B.D.H. Chemicals Ltd., Poole, England, and had a stated minimum purity of 99 mol%. Freezing temperature determinations on the n-hexadecane indicated its purity was 99.6 mol%. Its refractive index *n*(*D*, 298.15 K) was 1.43244. For n-hexane, g.l.c. analysis of the major peak area indicated a purity of 99.7 mol%. The refractive index *n*(*D*, 298.15 K) was 1.37240. Both chemicals were used as received.

4. VISCOMETER CALIBRATION

Fall times recorded in the falling body viscometer were corrected for the 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 densities of the liquid and sinker at pressure P, A is the viscometer calibration constant, T is the experimental temperature, P_0 is atmospheric pressure, T_0 is a reference temperature, taken as 298 K, α is the linear coefficient of thermal expansion, and β is the compressibility coefficient. ρ_s', the corrected sinker density, is calculated from

$$\rho_s' = \rho_{s,T_0} \left| \frac{1}{\{1 + 3\alpha(T - T_0)\}\{1 - \beta(P - P_0)\}} \right| \tag{2}$$

where the symbols are as defined for the previous equation. This equation is obtained by considering the sinker to be a simple cylinder and studying the effect of temperature and pressure on its volume. The viscometer constant, A, was obtained by measuring the fall time of the sinker at atmospheric pressure in liquids of accurately known density and viscosity coefficient. A series of liquids were chosen whose viscosity coefficients at atmospheric pressure covered the full range of viscosity coefficients likely to be encountered with the n-hexane plus n-hexadecane system. Liquids used in the calibration were n-hexane, n-hexadecane, mixtures of n-hexane plus n-hexadecane, and Shell Vitrea 21 calibration oil. The viscosity coefficients of Shell Vitrea 21 at the various temperatures were measured in National Physical Laboratory calibrated U-tube viscometers and the density in a calibrated Lipkin pyknometer. Saturation pressure viscosity coefficients for n-hexane, n-hexadecane, and mixtures of n-hexane plus n-hexadecane were measured in sealed viscometers [4] and the corresponding densities measured in a pyknometer and volume change apparatus as described elsewhere [8]. The variation of the calibration constant A with increasing viscosity is shown in Fig. 3. Below 0.29 mN s m^{-2}, the increase in A is rapid, possibly indicating that the flow was becoming nonlaminar. The experimental results above 0.29 mN s m^{-2} were fitted by an equation of the form

$$A = A_0 \left| 1 + \left\{ \frac{B_0}{t(1 - \rho_L/\rho_s')} \right\}^N \right| \tag{3}$$

where A is the calibration constant, A_0 is the calibration constant at infinite viscosity, and B_0 and N are coefficients from the fitting procedure. The solid line in Fig. 3 represents Eq. (3) with the values $A_0 = 7.994$, $B_0 = 6.441 \times 10^{-5}$, and $N = 0.2$. Agreement with experiment is within ±1.5% in the range of viscosity 0.29 to 25 mN s m^{-2}. Below 0.29 mN s m^{-2}, the results were fitted to the equation $A = 9.635 - 0.210t$. Agreement with experiment was within ±0.5%. The calibration for this viscometer tube/sinker combination thus covers the range 0.16 to 25 mN s m^{-2} (1.6 to 235 s).

Subsequent independent experiments on oils with fall times of 369 and 386 s at atmospheric pressure gave experimental A values of 8.37 and 8.41,

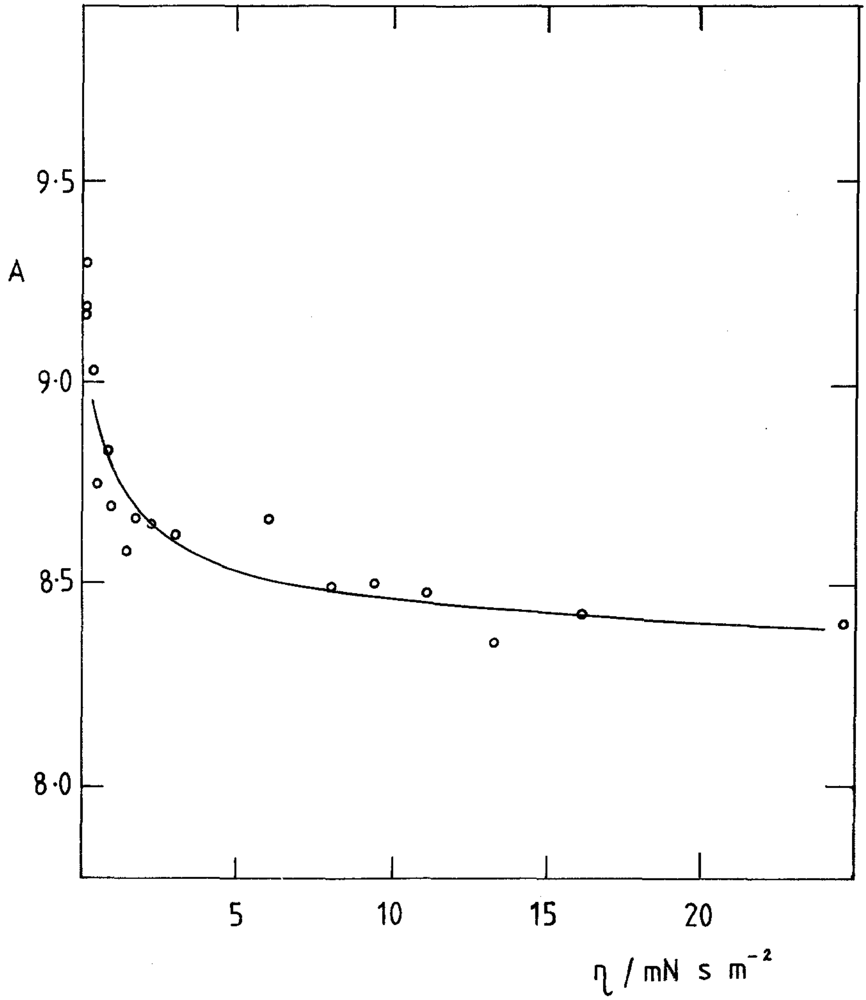


Fig. 3. The viscometer calibration constant, A.

respectively. These agreed with the calculated A value of 8.36 for both from the above calibration to 0.1 and 0.6%, respectively, confirming the calibration at high viscosity coefficient.

5. ACCURACY OF VISCOSITY COEFFICIENT MEASUREMENTS

Measurements of fall time t, liquid density ρ_L, sinker density ρ_s', viscometer constant A, temperature T, and pressure P have to be made, and the degree of accuracy with which each can be measured will determine the contribution to the total uncertainty in a viscosity coefficient. For mixtures, there is the additional possible uncertainty in the composition. An analysis of each of these factors leads to the conclusion that the measured viscosity coefficients should be accurate to ±2%.

6. EXPERIMENTAL RESULTS

Measurements of the fall times for the sinker have been made for n-hexane, n-hexadecane, and the mixtures with mole fraction n-hexadecane of 0.200, 0.400, 0.600, 0.800, at 25, 50, 75, and 100°C, at pressures up to the freezing pressure or 500 MPa. The derived viscosity coefficients are presented in Tables I–VI, together with values for the densities under the corresponding conditions calculated from the experimental data reported for this system [8]. Figure 4 illustrates the typical pressure dependence of the results.

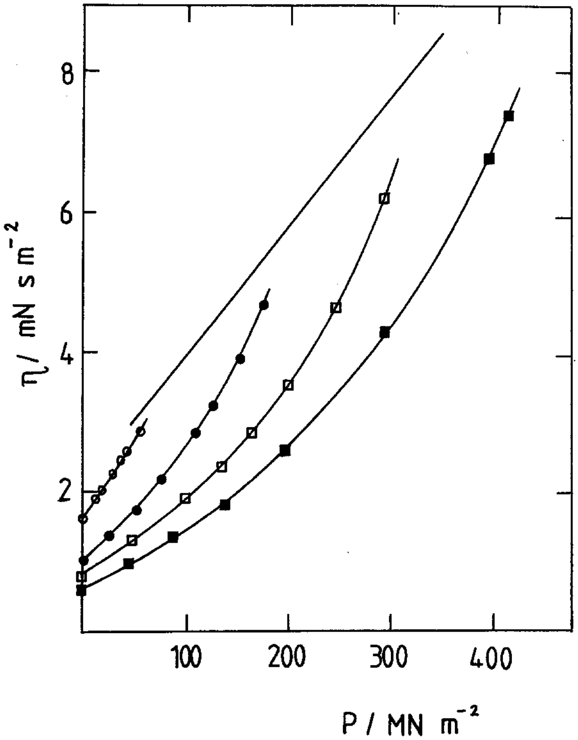


Fig. 4. Experimental viscosity coefficients for the mixture with 0.600 mole fraction n-hexadecane. O, 298.2 K; ●, 323.2 K; □, 348.2 K; ■, 373.2 K.

6.1. Comparison of Viscosity Coefficient Results with Literature Values

The ratio of viscosity coefficient at pressure η_p to the viscosity coefficient at atmospheric pressure η_0 has been measured for n-hexane by Brazier and Freeman [9] at 273, 303, and 333 K up to 400 MPa, by Bridgman [10] at 303

Table I. Viscosity Coefficients for n-Hexane

Temperature (K)	Pressure (MPa)	Density (kg m^{-3})	Viscosity coefficient (mN s m^{-2})
298.29	0.1	655.1	0.2976
	21.1	673.8	0.3628
	42.2	689.6	0.4265
	59.8	701.0	0.4850
	82.6	713.9	0.560
	102.2	723.7	0.634
	203.4	762.0	1.077
	298.7	788.1	1.636
	358.2	802.0	2.100
323.15	0.1	631.7	0.2357
	48.4	677.0	0.3665
	101.5	709.5	0.511
	144.5	729.0	0.645
	198.4	748.4	0.820
	252.0	764.3	1.045
	301.7	777.1	1.279
	350.7	788.5	1.533
	402.0	799.7	1.829
348.38	0.1	606.8	0.1912
	49.8	658.5	0.3084
	100.9	693.0	0.4246
	155.0	719.2	0.561
	204.5	737.9	0.697
	248.9	752.0	0.833
	299.3	765.9	1.008
	349.8	778.5	1.205
	401.1	790.2	1.421
373.36	0.1	580.7	0.1601
	52.5	645.2	0.2672
	102.2	680.3	0.3675
	153.1	705.3	0.4743
	202.7	724.2	0.587
	250.0	739.5	0.705
	300.0	753.9	0.842
	350.1	767.3	0.995
	400.7	780.4	1.158
	419.6	785.2	1.236

Table II. Viscosity Coefficients for n-Hexane (1) + n-Hexadecane (2) with $x_2 = 0.200$

Temperature (K)	Pressure (MPa)	Density (kg m^{-3})	Viscosity coefficient (mN s m^{-2})
298.22	0.1	698.9	0.584
	1.4	700.1	0.599
	9.0	707.0	0.646
	18.5	714.7	0.709
	41.4	730.2	0.877
	61.2	741.2	1.023
	80.9	750.8	1.184
	103.9	760.9	1.403
323.19	0.1	678.1	0.4426
	1.6	679.9	0.4508
	8.4	687.3	0.4868
	48.5	720.2	0.701
	98.7	747.0	1.002
	127.9	759.0	1.206
	152.5	768.0	1.392
	204.5	785.0	1.857
	230.4	792.9	2.145
348.07	0.1	656.4	0.3501
	3.1	659.9	0.3632
	9.4	667.0	0.3902
	48.3	701.5	0.552
	101.1	733.6	0.804
	152.7	756.4	1.082
	202.5	774.0	1.401
	248.7	788.0	1.736
	296.0	800.9	2.138
	351.1	814.8	2.680
	401.8	827.1	3.310
	450.4	838.6	3.982
	482.2	846.2	4.399
373.12	0.1	634.5	0.2803
	48.6	685.6	0.4572
	101.8	720.3	0.660
	151.6	743.2	0.874
	201.4	761.4	1.109
	249.5	776.3	1.368
	302.2	790.8	1.709
	351.5	803.3	2.061
	398.3	814.8	2.446
	447.7	826.6	2.896
	501.9	839.6	3.498

Table III. Viscosity Coefficients for n-Hexane (1) + n-Hexadecane (2) with $x_2 = 0.400$

Temperature (K)	Pressure (MPa)	Density (kg m^{-3})	Viscosity coefficient (mN s m^{-2})
298.12	0.1	726.4	0.991
	4.6	730.0	1.027
	10.6	734.5	1.108
	19.6	740.9	1.227
	32.0	749.0	1.396
	40.7	754.2	1.500
	50.7	759.8	1.646
	61.9	765.6	1.806
	70.8	769.8	1.978
	82.0	774.8	2.161
323.33	0.1	707.0	0.703
	5.3	711.9	0.750
	10.5	716.4	0.785
	26.2	728.7	0.928
	50.7	744.6	1.151
	75.0	757.5	1.414
	101.5	769.6	1.730
	121.5	777.8	2.005
	153.8	789.9	2.479
	172.1	796.2	2.762
	199.2	805.4	3.297
348.29	0.1	687.1	0.522
	9.2	696.4	0.581
	51.1	729.5	0.865
	101.4	757.0	1.284
	153.0	778.1	1.769
	202.7	794.8	2.388
	249.7	808.7	3.033
	298.4	822.0	3.834
	341.7	833.3	4.717
373.24	0.1	667.0	0.4147
	5.2	673.2	0.4445
	10.5	679.3	0.4753
	49.8	714.6	0.686
	103.3	746.7	1.015
	152.3	767.8	1.353
	203.7	785.5	1.797
	251.9	799.6	2.254
	303.3	813.2	2.852
	351.3	825.0	3.502
	402.3	837.1	4.323
	451.7	848.7	5.225
	478.3	855.0	5.888
	502.8	860.8	6.334

and 348 K up to 980 MPa, and by Isdale et al. [11] at 298, 323, 348, and 373 K up to 500 MPa. The present viscosity coefficient results were converted to viscosity coefficient ratios, and a comparison was made with the other data. As shown in Fig. 5, the present results at 298 K agree with those of Isdale et

Table IV. Viscosity Coefficients for n-Hexane (1) + n-Hexadecane (2) with $x_2 = 0.600$

Temperature (K)	Pressure (MPa)	Density (kg m^{-3})	Viscosity coefficient (mN s m^{-2})
298.15	0.1	745.4	1.518
	4.3	748.9	1.648
	9.0	752.6	1.737
	15.7	757.5	1.881
	21.6	761.4	2.011
	31.6	767.5	2.248
	36.9	770.5	2.277
	41.8	773.1	2.493
	46.2	775.3	2.595
	57.2	780.4	2.862
323.13	0.1	726.8	1.028
	25.8	747.1	1.379
	52.1	762.8	1.749
	77.6	775.3	2.190
	111.0	789.2	2.891
	126.9	795.3	3.247
	153.2	804.9	3.915
	178.4	813.8	4.678
348.31	0.1	708.0	0.754
	4.9	712.5	0.798
	8.7	716.0	0.833
	49.8	746.4	1.265
	102.0	773.8	1.881
	137.1	788.2	2.358
	167.3	799.0	2.874
	202.6	810.4	3.563
	249.9	824.1	4.666
	297.1	836.7	6.219
373.18	0.1	689.0	0.568
	4.3	693.4	0.595
	9.6	698.6	0.640
	49.9	731.2	0.960
	91.4	755.5	1.317
	140.9	777.7	1.824
	202.2	799.2	2.597
	298.9	826.1	4.282
	400.0	850.1	6.791
	418.4	854.2	7.398

al. to well within the combined uncertainty of 4% and lie between the results given by Brazier and Freeman and by Bridgman at 303 K, although the difference between these sets of results and the present curve is only 4% at 300 MPa. At 348 K, the results reported here agree with those of Isdale et al. to within 1% over the whole pressure range. The results of Bridgman are higher, by as much as 7.3%, at 350 MPa, as illustrated in Fig. 6. However, his

Table V. Viscosity Coefficients for n-Hexane (1) + n-Hexadecane (2) with $x_2 = 0.800$

Temperature (K)	Pressure (MPa)	Density (kg m^{-3})	Viscosity coefficient (mN s m^{-2})
298.09	0.1	759.6	2.236
	4.3	762.8	2.327
	10.2	767.1	2.531
	19.8	773.3	2.868
	30.1	779.2	3.275
	34.3	781.4	3.400
	39.5	784.0	3.552
323.21	0.1	741.7	1.409
	5.0	745.7	1.488
	9.8	749.4	1.586
	39.0	768.5	2.167
	61.4	780.2	2.690
	79.0	788.4	3.156
	101.3	797.7	3.882
	123.4	806.2	4.714
	142.9	813.4	5.483
	156.6	818.3	6.014
348.09	0.1	723.9	0.988
	4.5	727.8	1.034
	9.7	732.2	1.102
	48.9	759.4	1.628
	99.4	784.7	2.549
	148.2	803.7	3.661
	201.8	821.1	5.184
	246.8	834.2	6.733
	300.4	849.0	9.344
373.17	0.1	705.6	0.729
	48.2	744.7	1.208
	100.1	773.5	1.834
	158.5	797.2	2.714
	202.2	811.6	3.515
	251.0	825.7	4.627
	302.1	839.0	6.163
	351.4	850.8	7.850
	401.0	862.3	9.859
	446.1	872.5	12.139

estimate of the accuracy of his measurements suggests that an uncertainty of between 2 and 5% can be assigned to his viscosity coefficients. The results of Brazier and Freeman at 333 K lie so far below the present measurements and the results of Bridgman at 348 K that they must be considered to be in error. Agreement with Isdale et al. for the other isotherms (323 and 373 K) is within 2% over the whole pressure range.

The viscosity coefficient of n-hexadecane has been measured at 293.2, 298.2, 310.9, and 372.0 K from 0.1 MPa to the freezing pressure for each isotherm in an *ASME Pressure Viscosity Report* [12]. At 298.2 K and 0.1 MPa, the report gives a value of 2.988 mN s m^{-2}, while this research has a value of 3.078 mN s m^{-2}, a difference of 2.9%. Other literature values at 298 K and 0.1 MPa are 3.062 mN m s^{-2} [13] and 3.087 mN s m^{-2} [14], which

Table VI. Viscosity Coefficient for n-Hexadecane

Temperature (K)	Pressure (MPa)	Density (kg m^{-3})	Viscosity coefficient (mN s m^{-2})
298.08	0.1	770.3	3.078
	0.7	770.7	3.109
	4.5	773.6	3.276
	15.1	780.7	3.758
	27.9	787.8	4.395
323.09	0.1	753.1	1.845
	0.8	753.6	1.872
	4.3	756.4	1.956
	27.3	771.1	2.581
	52.4	785.8	3.387
	78.6	797.9	4.354
	103.4	808.0	5.504
	139.1	821.2	7.494
348.11	0.1	735.9	1.242
	0.9	736.6	1.253
	4.1	739.3	1.310
	50.6	771.1	2.166
	102.5	796.3	3.418
	154.2	815.7	5.070
	204.9	831.8	7.200
	273.1	851.0	11.102
373.24	0.1	718.7	0.895
	51.1	757.5	1.551
	103.1	785.0	2.394
	201.8	821.4	4.631
	330.1	855.5	9.462
	398.8	871.2	13.331
	425.1	877.1	15.075

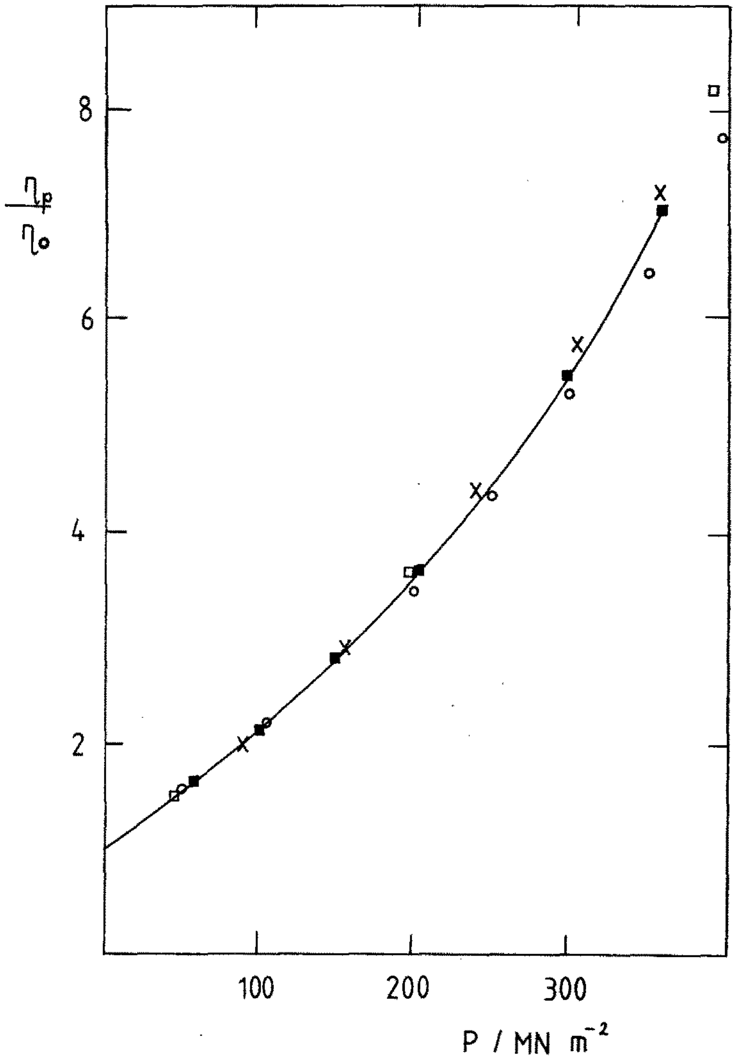


Fig. 5. Comparison of present viscosity coefficient ratios for n-hexane at 298.2 K (■) with literature values at 298.2 K (×, Ref. [11]) and 303.2 K (□, Ref. [10]; ○, Ref. [9]).

suggests that the ASME value is too low by at least 2.5%. Since this is outside their estimate of the error, the most probable cause is that their calibration is slightly out at this viscosity. However, if ratios of the viscosity coefficient under elevated pressure to the atmospheric values are taken and compared with corresponding viscosity coefficient ratios obtained from this research, agreement is within 2.3%, which is within the combined uncertainty of 4%. At

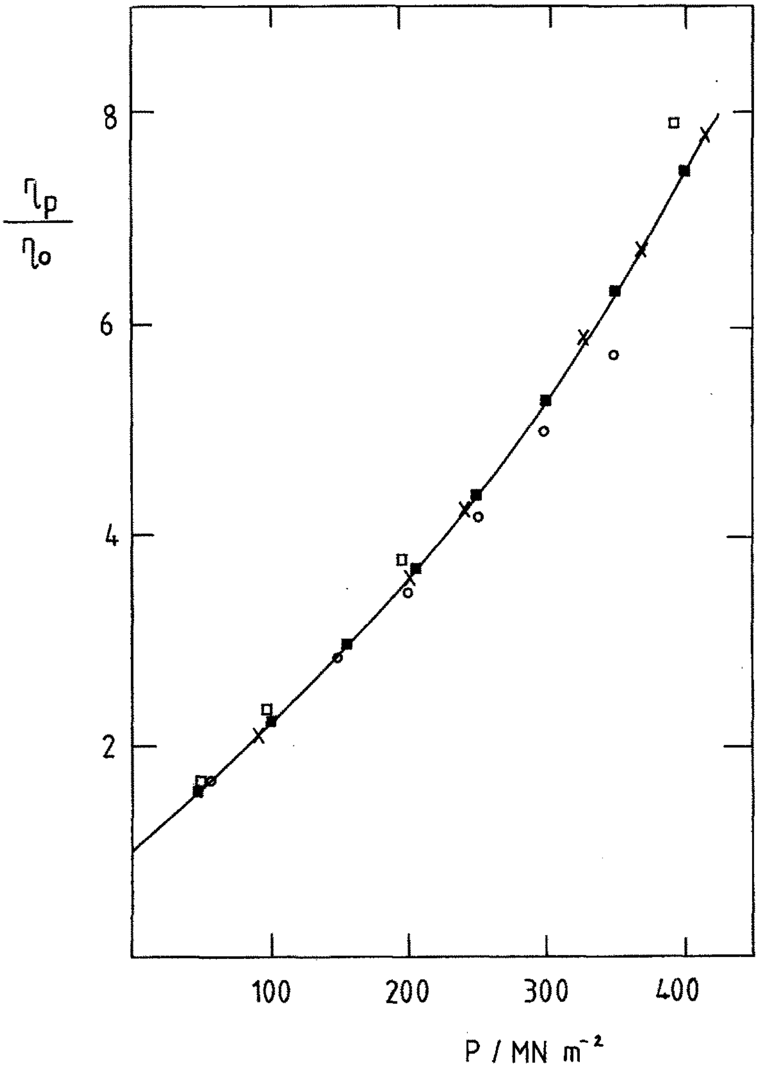


Fig. 6. Comparison of present viscosity coefficient ratios for n-hexane at 348.2 K (■) with literature values at 348.2 K (×, Ref. [11]; □, Ref. [10]) and 333.2 K (○, Ref. [9]).

372.0 K, ASME results in the range of pressure 286–450 MPa extrapolated to 373.2 K agree with the present results to within 6%. In this pressure range, the ASME results for n-hexadecane have a possible uncertainty of 2–5%. The agreement at 373 K is therefore within the combined experimental uncertainty.

7. HARD-SPHERE THEORIES OF VISCOSITY COEFFICIENTS

For transport properties in dense fluids, it is the repulsive intermolecular forces that predominate. The attractive forces provide a fairly uniform attractive potential energy surface in which the molecules move. The simplest model is the hard-sphere model, and this has the great advantage that rigorous expressions can be obtained for the transport coefficients. For the viscosity coefficient, Enskog theory [15] relates the dense fluid coefficient, subscript E, to the dilute hard-sphere value η_0, by the expression

$$\frac{\eta_E}{\eta_0} = \frac{1}{g(\sigma)} + 0.8\frac{b_0}{V} + 0.761\, g(\sigma)\left(\frac{b_0}{V}\right)^2 \tag{4}$$

where V is the molar volume, $b_0 = 2\pi N\sigma^3/3$ for spheres of diameter σ, and the radial distribution function $g(\sigma)$ is given by

$$g(\sigma) = \left(\frac{pV}{NkT} - 1\right)\frac{V}{b_0} \tag{5}$$

$g(\sigma)$ can be calculated from the Carnahan-Starling expression [16],

$$g(\sigma) = (1 - 0.5\xi)(1 - \xi)^{-3} \tag{6}$$

where $\xi = b_0/4V$.

In the first approximation, η_0 is given by [17]

$$\eta_0 = \frac{5}{16\sigma^2}\left(\frac{mkT}{\pi}\right)^{1/2} \tag{7}$$

for spheres of mass per molecule m.

These results thus depend only on the core size σ. They have to be corrected for the effects of correlated molecular motion using the exact hard-sphere results obtained [2] in computer simulation studies. For rough hard spherical molecules (RHS), where there is the possibility of translational-rotational coupling, Chandler [18] showed that, for densities above twice critical,

$$\eta_{\mathrm{RHS}} \simeq C\eta_{\mathrm{SHS}} \tag{8}$$

where η_{SHS} represents the smooth hard-sphere value, and C is the translational rotational coupling constant, which is practically density and temperature independent.

To test the applicability of this model, it is convenient to express the computed smooth hard-sphere viscosity coefficients at densities corresponding to twice critical and above by an equation in (V/V_0). It was shown in an

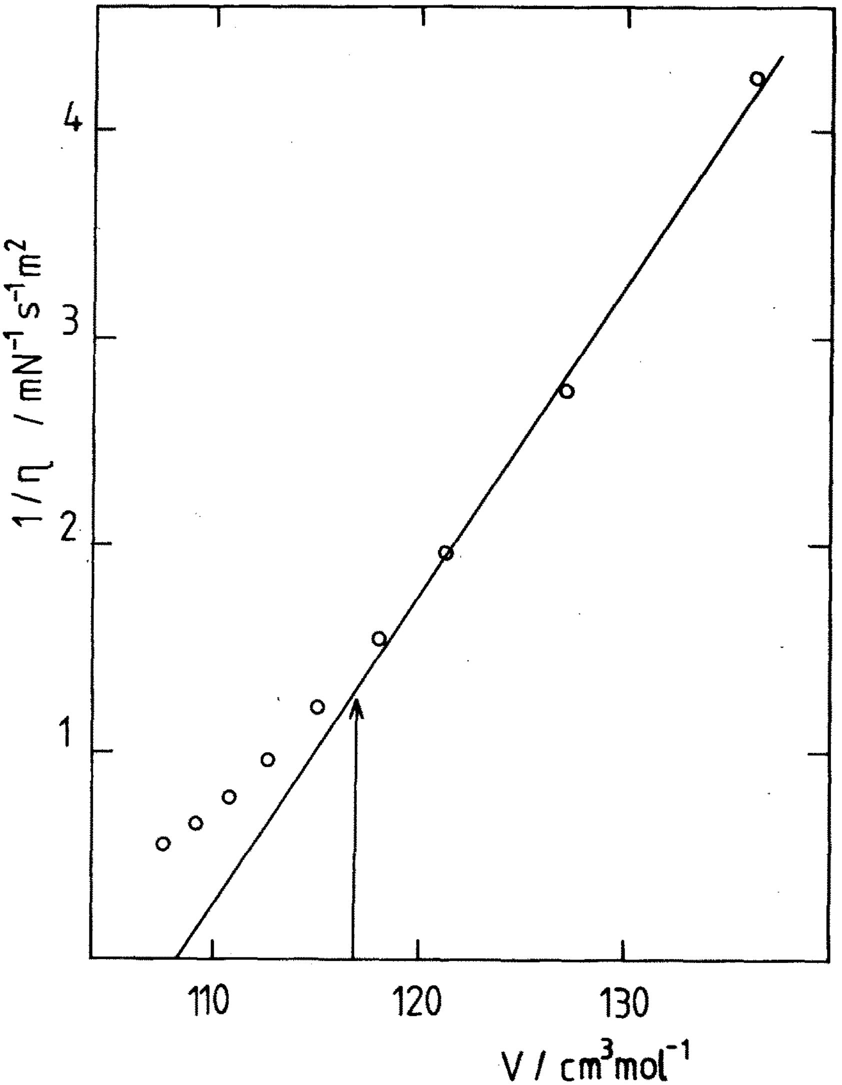


Fig. 7. Molar volume dependence of the fluidity of n-hexane at 323.2 K. Present results, O. Solid line: predictions of the rough hard-sphere theory with $C = 1.48$. The vertical line denotes the limiting volume for which the hard-sphere system remains fluid.

earlier paper [19] that within the uncertainty of computed corrections to Enskog theory,

$$\eta_0/\eta_{\mathrm{SHS}} = 0.2195\ (V/V_0 - 1.384) \tag{9}$$

Substitution of the hard-sphere expression for η_0 leads to the result

$$1/\eta_{\mathrm{RHS}} \simeq 1.324 \times 10^8\ (V - 1.384\ V_0)/CV_0^{1/3}(MRT)^{1/2} \tag{10}$$

More recent computer simulation studies [20] suggest that the numerical factors may differ slightly from those given in this equation, but the important point is that the rough hard-sphere model predicts a linear dependence of fluidity on molar volume.

Although n-hexane is not a hard spherical molecule, this model has been applied [21] to tracer diffusion studies in which n-hexane is one of the components. It is therefore of interest to see how well the viscosity coefficient measurements follow the predicted behavior. As shown in Fig. 7, it is found that the reasonably linear portion of the plot of fluidity versus molar volume extends only to a molar volume corresponding to a pressure of about 150 MPa, whereas the present data extend to 400 MPa, and n-hexane is liquid to still higher pressures. Indeed, the serious limitation of this model is that it predicts a fluid-solid phase change at pressure just in excess of 150 MPa, in contradiction to observation. A second limitation is that the translational-rotational coupling constant cannot at present be calculated by any method, but only derived from experimental viscosity coefficient data.

8. CORRELATION METHODS

However, it is possible to correlate experimental data by a method suggested [22] from 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 as

$$\eta' = 9.118 \times 10^7\ \eta\ V^{2/3}/(MRT)^{1/2} \tag{11}$$

For the density region where the rough hard-sphere theory is applicable, η' will be proportional to $(\eta_{\mathrm{SHS}}/\eta_0)\ (V/V_0)^{2/3}$ and thus will depend only upon (V/V_0). Plots of η' versus log V using data for a given compound at different temperatures should be superimposable 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. For real molecules, where the repulsive energy is soft, this ratio will be greater than unity for temperature T less than T_R. Results thus obtained using experimental data for carbon tetrachloride [23, 24] and tetramethylsilane [25] showed [22] 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. Furthermore, it was found that the method gave an excellent correlation of the

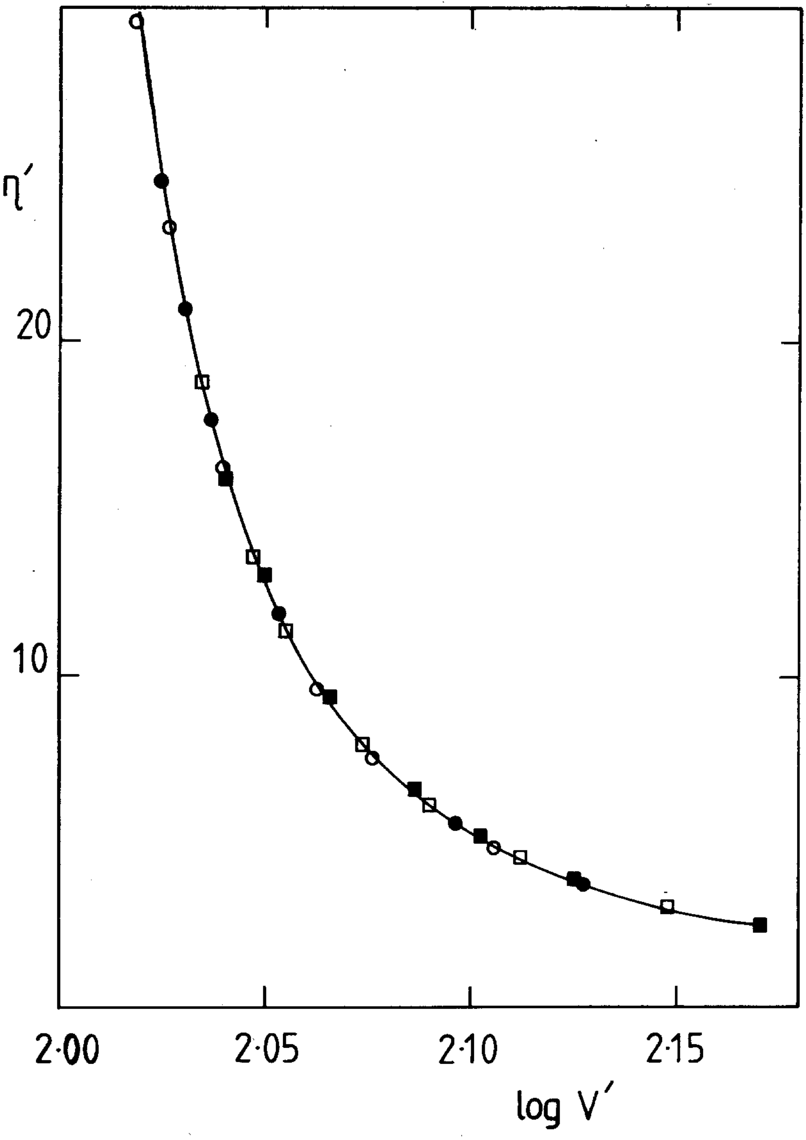


Fig. 8. Correlation of experimental viscosity coefficient data for n-hexane at different temperatures and pressures based on the 373.2 K data. η' is defined by Eq. (11), $V' = V \cdot V_0(T_R)/V_0(T)$. ○, 298.2 K; ●, 323.2 K; □, 348.2 K; ■, 373.2 K.

viscosity data also for large aspherical molecules such as bicyclic hydrocarbons [22], where the molecular shape is not expected to vary much with changes in temperature.

When this method is applied to the viscosity coefficient data obtained for the system n-hexane plus n-hexadecane, it is found that the results can be correlated very satisfactorily on the basis of a single curve, not only for the pure liquids as illustrated in Fig. 8 for n-hexane, but also for mixtures. A typical plot is shown in Fig. 9 for the mixtures with 0.600 mole fraction of n-hexadecane. The 373 K isotherm was chosen as a reference isotherm for

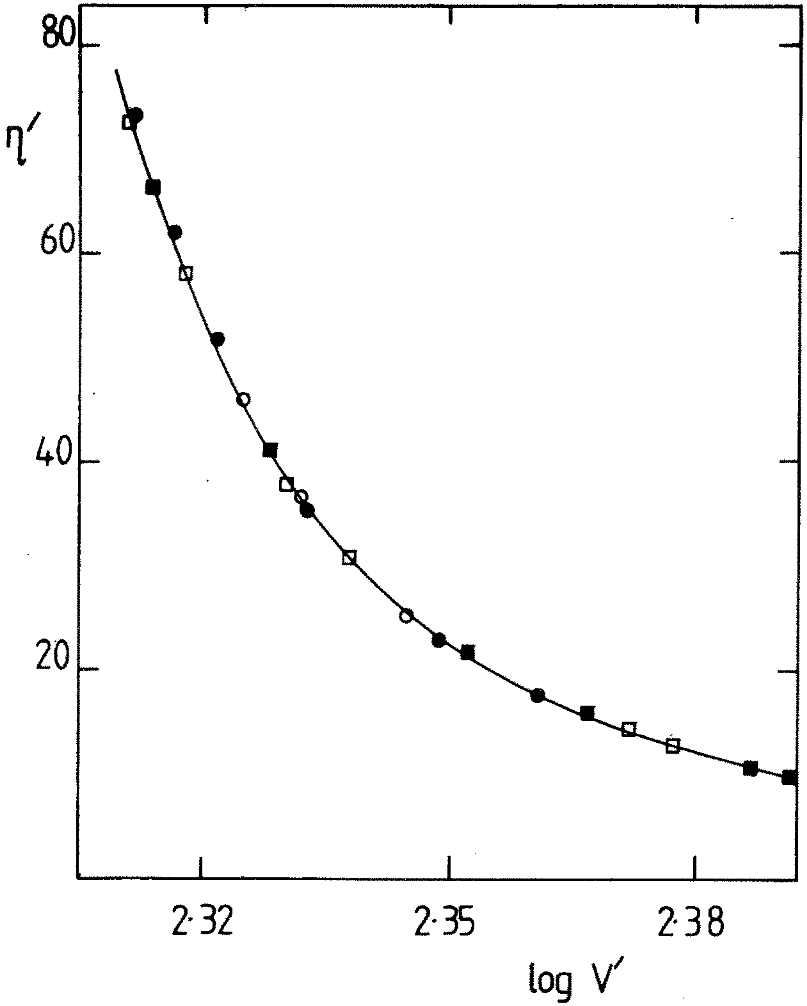


Fig. 9. Correlation of experimental viscosity coefficient data for the n-hexane + n-hexadecane mixture with 0.600 mole fraction n-hexadecane. Definitions and key same as for Fig. 8.

Table VII. Values of $V_0(T)/V_0(T_R)$ for n-Hexane (1) Plus n-Hexadecane (2)

X_2	T (°C)			
	25	50	75	100
0.000	1.027	1.016	1.009	1.000
0.200	1.034	1.021	1.011	1.000
0.400	1.039	1.026	1.012	1.000
0.600	1.040	1.025	1.012	1.000
0.800	1.044	1.029	1.016	1.000
1.000	1.048	1.033	1.015	1.000

each liquid and liquid mixture. The deviation of points from the curve of η' versus log V at this temperature when the other isotherms were superimposed was in all cases less than 5%, and usually considerably less than this. Values derived for $V_0(T)/V_0(T_R)$ for the pure liquids and the mixtures are given in Table VII. The fractional change in V_0 with temperature is about one and a half times as large in the case of n-hexadecane and n-hexadecane rich mixtures than for n-hexane.

9. FREE-VOLUME FORM OF EQUATION

The above results demonstrate that there is a definite relationship between the viscosity coefficient and the molar volume, specifically the volume relative to some characteristic volume, which on the basis of the hard-sphere models is the volume of close packing. In the case of smooth hard spheres, the relationship can be expressed by [22],

$$\ln \eta' = A + \frac{B V_0}{V - V_0} \tag{12}$$

where A is -0.762 and B is 1.335.

For pseudospherical molecules and relatively rigid ring hydrocarbons, Dymond and Brawn have shown [22] that viscosity coefficient data can be fitted within the estimated experimental uncertainty by Eq. (12), with A and B considered as adjustable parameters to take account of the effects of nonspherical molecular shape and of translational-rotational coupling. For the liquids studied, A was found to be temperature independent and equal to -1.0. B was also found to be temperature independent.

The effectiveness of this equation in fitting viscosity coefficient data for mixtures was tested using the present results. It was found that the best fit to the experimental data arose in all cases when A was equal to -1.0. Values of V_0 were found to vary linearly with mole fraction over the whole composition range at each temperature, and B also varied with composition and temperature. Derived values for A, B, and V_0 are summarized in Table VIII, and B and V_0 are plotted against mole fraction in Figs. 10 and 11. Using these values, viscosity coefficients are fitted to within 3% for 210 out of 224 experimental points, and between 3 and 4% for 8 points, with the remaining 6 points fitted to between 4 and 6%. Isdale et al. [11] found that for the n-hexane plus cyclohexane system, the viscosity coefficient data can be satisfactorily fitted when B values are represented by the equation

$$B = x_1 B_1 + x_2 B_2 + a x_1 x_2 (B_2 - B_1) \tag{13}$$

with $a = 0.2$.

When this relationship is applied to the n-hexane plus n-hexadecane results, the numerical factor a had to be increased to 0.6 to give reasonably close agreement with the optimized B values, as shown in Table VIII. However, a better representation was obtained by a quadratic equation in

Table VIII. Values of A, B, V_0 in Eq. (12) for the n-Hexane Plus n-Hexadecane System

x_{HD}	Temperature (K)	V_0	A	B	B (Eq. 13, $a = 0.6$)	B (Eq. 14)
0.000	298.29	73.0	−1.00	2.064	2.064	2.070
	323.15	72.0	−1.00	2.084	2.084	2.087
	348.38	71.0	−1.00	2.115	2.115	2.112
	373.36	70.0	−1.00	2.144	2.144	2.145
0.200	298.22	98.2	−1.00	2.153	2.150	2.142
	323.19	96.2	−1.00	2.197	2.197	2.193
	348.07	94.2	−1.00	2.239	2.254	2.240
	373.12	92.2	−1.00	2.321	2.313	2.316
0.400	298.12	123.4	−1.00	2.207	2.223	2.207
	323.33	120.4	−1.00	2.287	2.292	2.283
	348.29	117.4	−1.00	2.341	2.370	2.352
	373.24	114.4	−1.00	2.447	2.455	2.458
0.600	298.15	148.6	−1.00	2.258	2.281	2.264
	323.13	144.6	−1.00	2.356	2.369	2.359
	348.31	140.6	−1.00	2.458	2.463	2.447
	373.18	136.6	−1.00	2.583	2.570	2.572
0.800	298.09	173.8	−1.00	2.311	2.326	2.313
	323.21	168.8	−1.00	2.413	2.427	2.419
	348.09	163.8	−1.00	2.525	2.534	2.525
	373.17	158.8	−1.00	2.651	2.653	2.657
1.000	298.08	199.0	−1.00	2.356	2.356	2.353
	323.09	193.0	−1.00	2.467	2.467	2.463
	348.11	187.0	−1.00	2.583	2.583	2.586
	373.24	181.0	−1.00	2.716	2.716	2.714

mole fraction,

$$B = m + nx_2 - px_2^2 \qquad (14)$$

with values of m, n, and p for each isotherm given in Table IX. The B values calculated from this equation are compared with those derived from the best fit to the experimental data in Table VIII. The fit to the experimental viscosity coefficients given by these B values is only marginally inferior.

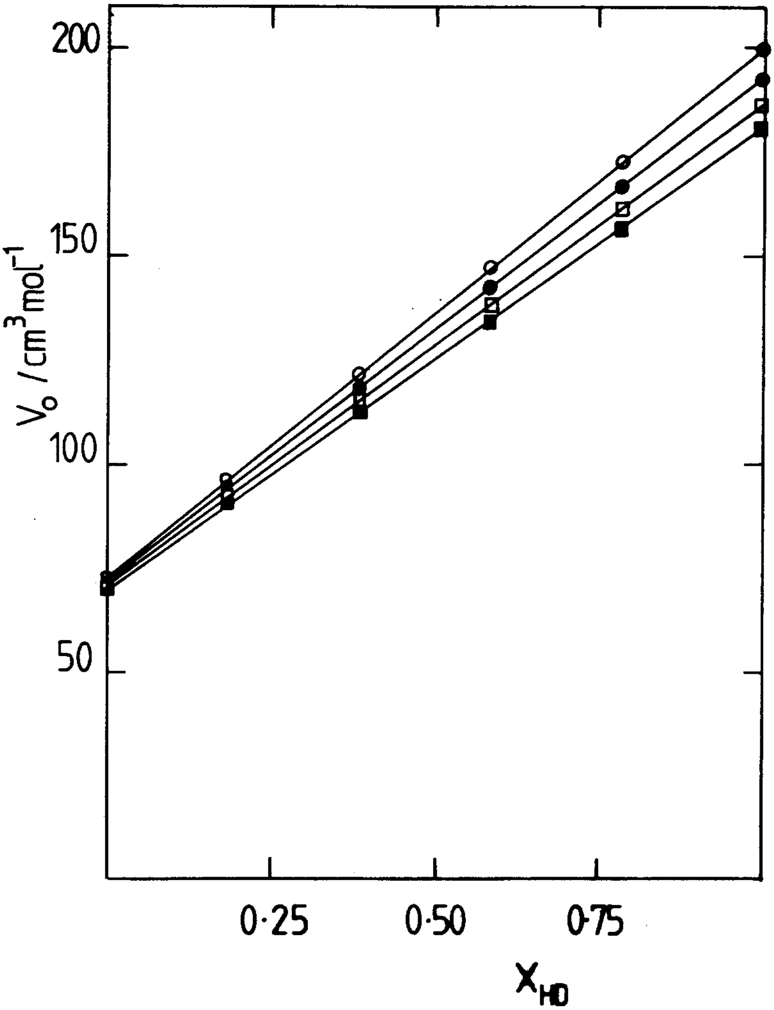


Fig. 10. Dependence of V_0 on mole fraction and temperature. ○, 298.2 K; ●, 323.2 K; □, 348.2 K; ■, 373.2 K.

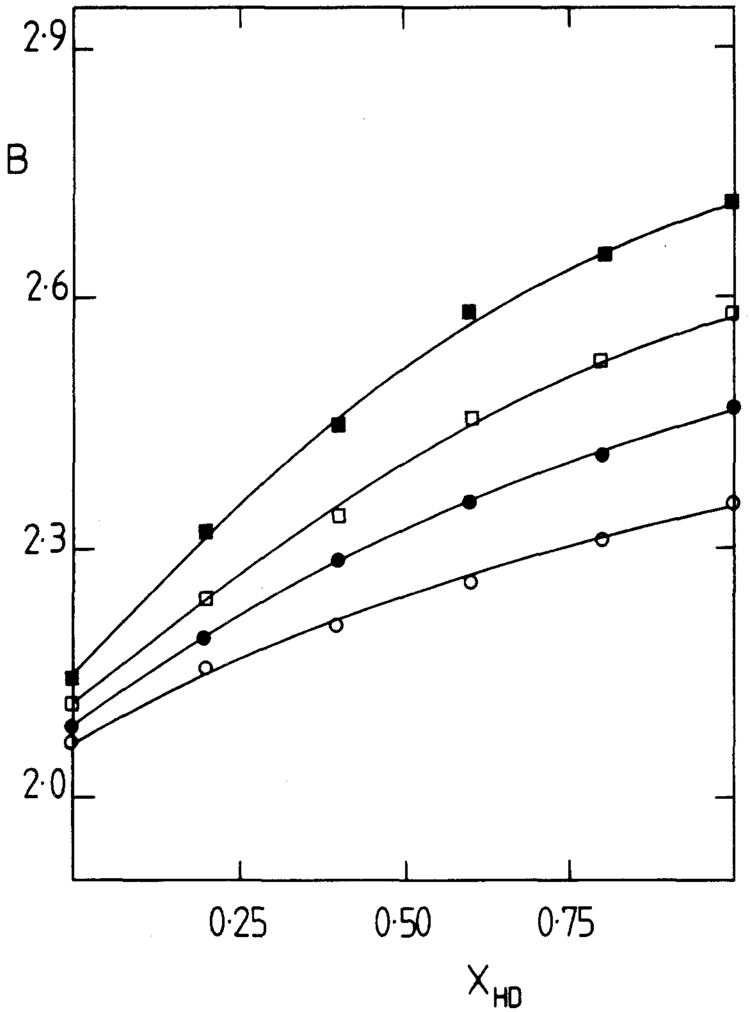


Fig. 11. Dependence of *B* on mole fraction and temperature. Symbols the same as for Fig. 10.

Table IX. Values of *m*, *n*, and *p* in Eq. (14)

T (K)	*m*	*n*	*p*
298.2	2.0697	0.3835	0.1000
323.2	2.0873	0.5666	0.1906
348.2	2.1121	0.6834	0.2098
373.2	2.1451	0.9230	0.3536

Thus for the n-hexane plus n-hexadecane system, Eq. (12) provides a very convenient way of summarizing the experimental data, and will provide a very reliable estimate of the viscosity coefficient under other conditions of composition, temperature, and pressure. The one disadvantage is that the density must be accurately known.

10. THE EMPIRICAL GRUNBERG AND NISSAN EQUATION

The Grunberg and Nissan equation [5], originally proposed in 1949, has been recommended by Irving [6] after a study of more than 25 equations as being the most effective in representing viscosity coefficient data for binary mixtures. This empirical expression may be written

$$\ell n \eta = x_1 \, \ell n \, \eta_1 + x_2 \, \ell n \, \eta_2 + x_1 x_2 G \tag{15}$$

where η is the viscosity coefficient of the mixture, x_i is the mole fraction of component i, and η_i is its viscosity coefficient. G is the Grunberg and Nissan constant, which Irving recommended should be considered as a single disposable parameter.

In Table X, G values are presented for the n-hexane plus n-hexadecane system. These values have a definite composition dependence but, for a

Table X. G Values for the n-Hexane plus n-Hexadecane System at Elevated Pressure

Temperature (K)	Pressure (MPa)	X_{HD}			
		0.2000	0.4000	0.6000	0.8000
298.2	0.1	1.29	1.12	0.95	0.92
323.2	0.1	1.37	1.14	1.00	0.90
	50.0	1.33	1.07	0.92	0.78
	100.0	1.38	1.16	0.99	0.90
348.2	0.1	1.43	1.07	1.05	0.91
	50.0	1.27	1.02	1.04	0.74
	100.0	1.38	1.14	0.99	0.92
	150.0	1.41	1.16	0.96	0.98
	200.0	1.50	1.28	1.02	0.98
	250.0	1.53	1.31	1.08	0.96
373.2	0.1	1.34	1.10	0.98	0.86
	50.0	1.34	1.08	1.00	0.81
	100.0	1.34	1.08	0.95	0.81
	150.0	1.41	1.13	1.02	0.90
	200.0	1.42	1.18	1.03	0.85
	250.0	1.46	1.22	1.08	0.96
	300.0	1.54	1.27	1.17	1.11
	350.0	1.57	1.30	1.17	1.11
	400.0	1.65	1.37	1.25	1.11

mixture of given composition, the effect of a change in temperature at constant pressure on the G values is insignificant. For a particular isotherm, the effect of an increase in pressure on G is first slightly to reduce its value up to 50 MPa, after which its value increases with increase in pressure. These effects can be summarized by the following equation for G:

$$G = 1.66 - 1.7\, x_2 + 0.9\, x_2^2 + 0.001\,(P - 100) \tag{16}$$

where x_2 is the mole fraction of n-hexadecane, and P is in MPa. The final term is included only for pressures above 100 MPa. The Grunberg and Nissan equation with G given by this expression fits the mixtures data from 298 to 373 K up to 400 MPa within 2%. For prediction of viscosity coefficients of mixtures of different composition at other temperatures and pressures, it is first necessary to determine the pure component viscosities at these temperatures from plots of $\ell n\eta$ versus reciprocal temperature along isobars. Equation (15) is expected to give calculated viscosity coefficients accurate to within 4%. The advantage of this approach is that it does not depend on a knowledge of molar volumes.

11. CONCLUSIONS

Accurate experimental viscosity coefficient data are reported for n-hexane, n-hexadecane, and four binary mixtures at 25, 50, 75, and 100°C and from 0.1 MPa up to 500 MPa or the freezing pressure. For n-hexane, the results can be interpreted on the basis of the rough hard-sphere model with a translational-rotational coupling constant of 1.48 at 25°C, but only for pressures up to about 150 MPa. At higher pressures, this model predicts a fluid-solid transition, but n-hexane remains liquid over the whole pressure range covered in this work, up to 500 MPa, and indeed up to much higher pressures. The model can therefore only be considered adequate over a very limited density range. The second point is that there is at present no method for calculating the translational-rotational coupling constant, except from viscosity coefficient data.

However, based on the rough hard-sphere model, a method for correlation of viscosity coefficients that has previously been applied to pseudospherical molecular liquids and rigid ring hydrocarbons is shown to work successfully for n-hexane, n-hexadecane, and their binary mixtures. From a curve of η', defined as $9.118 \times 10^7 \eta V^{2/3}/(MRT)^{1/2}$, versus $\ell n V$ obtained from experimental data on a given mixture at one temperature, it is possible to calculate viscosity coefficients for that mixture at any pressure at any other temperature, with an estimated accuracy of better than 5%, knowing the saturation pressure viscosity coefficient at that temperature. The one disadvantage is that it is necessary to know the molar volume at the pressure and temperature considered. However, this method is very useful in that it satisfactorily correlates data for mixtures of given composition at different temperatures over the whole available pressure range.

A free-volume expression proposed from consideration of the hard-sphere theories is found to be very satisfactory for representing the present viscosity coefficient data, not only for the pure liquids but also for their mixtures. Moreover, the adjustable parameters in this expression have values for the mixtures which are simply related to the values given by the pure liquids. The only disadvantage of this expression is that values are required for the molar volume of the system under the given experimental conditions. However, the expression can be used for calculation of viscosity coefficients of any mixture for any density with an accuracy which is estimated to be better than 3%. This semitheoretical approach is most strongly recommended for the correlation and prediction of viscosity coefficients.

The purely empirical Grunberg and Nissan equation, which contains only one adjustable parameter, reproduces the present data practically to within the estimated experimental uncertainty, provided that the Grunberg G is allowed to vary with pressure and composition. Once this behavior has been determined, accurate prediction of viscosity coefficients of different mixtures under other conditions is possible. The outstanding advantage of this expression is that knowledge of the molar volumes is not required.

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