Transport Properties of Nonelectrolyte Liquid Mixtures. VIII. Viscosity Coefficients for Toluene and for Three Mixtures of Toluene + Hexane from 25 to 100°C at Pressures up to 500 MPa

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Viscosity coefficients measured using a two-coil self-centering falling-body viscometer are reported for toluene and three binary mixtures of toluene + *n*-hexane at 25, 50, 75, and 100°C at pressures up to 500 MPa. The data for a given composition at different temperatures and pressures are correlated very satisfactorily by a plot of reduced viscosity η^* versus $\log V'$, where $V' = V \cdot V_0(T_R)/V_0(T)$ and V_0 represents a characteristic volume. The binary mixture data are well represented by the Grunberg and Nissan equation with a mixing parameter which is pressure dependent but composition and temperature independent.

1. INTRODUCTION

In our study of the effects of increased pressure and temperature on the viscosity coefficients of hydrocarbons and their mixtures, we have previously made measurements for *n*-alkanes and binary mixtures [1, 2] at temperatures up to 100°C and pressures up to 500 MPa. More recently [3], values have been reported for a branched alkane and binary mixtures with *n*-alkanes over the same range of conditions. This paper extends the investigation to aromatic hydrocarbons and their mixtures with normal alkanes with viscosity coefficient measurements for toluene and three

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binary mixtures with n-hexane. The method of measurement is outlined in Section 2, and the measured viscosity coefficients are given in Section 4. It is shown in the following section that a previously described graphical correlation method applies satisfactorily to the data for the present systems also. The results for the single-component systems can be represented by a theoretically based equation [4]. For the binary mixtures, the Grunberg and Nissan equation [5] is applied, and the pressure and temperature dependence of the mixing parameter is determined.

2. EXPERIMENTAL

Viscosity coefficients are determined from measurements of the fall time of a self-centering hemispherically nosed sinker down a vertical cylindrical tube. The change in inductance as the sinker, with a small piece of ferrite embedded in it, passes through two coils is used to start and stop the timer. This high-pressure two-coil falling-body viscometer is illustrated in Fig. 1. Its operation has been described in outline previously [3]. The use of collapsible transparent ptfe tubing for pressure transmission makes it possible to see air bubbles during the filling process and to remove them.

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

$$\eta_P = \frac{t(1 - \rho_L/\rho_S)}{A[1 + 2\alpha(T - T_0)][1 - 0.666\beta(P - P_0)]} \tag{1}$$

where η_P is the viscosity coefficient at pressure P, and ρ_L, and ρ_S are the densities of liquid and sinker at pressure P and temperature T. T_0 is the reference temperature (taken as 25°C), P_0 is atmospheric pressure, α is the linear coefficient of thermal expansion, β is the bulk compressibility coefficient, and A is the viscometer constant.

The new sinker/tube combination was calibrated using n-octane, isooctane, n-hexadecane, and Shell Vitrea No. 21 oil at temperatures from 25 to 100°C at atmospheric pressure, for which viscosity coefficients were measured in suspended-level viscometers with an estimated accuracy of 0.5%. The viscosity coefficient range was from 0.23 to 16 mPa·s. A was calculated from Eq. (1), and found to vary with the buoyancy-corrected fall time, increasing at the lowest fall times by up to 20% as the flow past the sinker becomes nonlaminar. The calibration curve was represented by the equation

$$A = 19.05[1 + (2.20/t(1 - \rho_L/\rho_S))^2] \tag{2}$$

where t is in seconds and A has units of mPa^{-1}. Equation (2) was fitted to 19 data points with a maximum deviation of 1.65%.
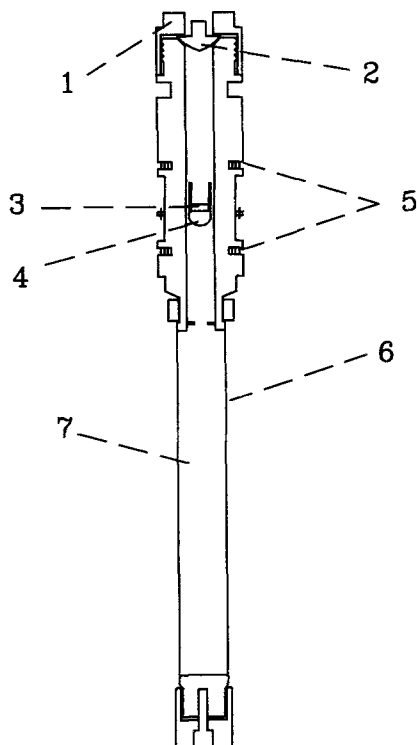
Fig. 1. The high-pressure viscometer: 1, end cap; 2, plug; 3, inductive core; 4, sinker; 5, detection coils; 6, PTFE tube; 7, liquid sample.

Viscosity coefficients at elevated pressure were calculated directly from Eq. (1) using values of A determined from the measured fall times by applying Eq. (2). The results are estimated to be accurate to better than $\pm 4\%$.

3. MATERIALS

The toluene and n-hexane were purchased from Aldrich Chemical Co. Ltd., Gillingham, U.K., with stated minimum purities of 99.9 and 99 mol%, respectively. The measured density at 298.15 K for toluene was $862.0 \, \text{kg} \cdot \text{m}^{-3}$, compared with literature values of $862.2 \, \text{kg} \cdot \text{m}^{-3}$ [6, 7]. For n-hexane at 298.15 K, the measured density was $655.0 \, \text{kg} \cdot \text{m}^{-3}$, in good agreement with the reported values of $655.1 \, \text{kg} \cdot \text{m}^{-3}$ [8, 9].

4. RESULTS

Measurements of the sinker fall time have been made for toluene and for three binary mixtures with n-hexane, with the mole fraction of toluene equal to 0.25, 0.50, and 0.75. The mixtures were made up by weight in bottles in which the final vapor space was small, to avoid composition changes in the liquid. The calculated viscosity coefficients are given in Tables I to IV, together with values for the density under the same conditions. These were calculated from equations for the isothermal secant bulk modulus which were used to fit experimental density measurements [10]. The densities have an estimated accuracy of $\pm 0.2\%$. Experimental viscosity coefficient measurements have previously been made for toluene by Bridgman [11] at 30 and 75°C and 1000 and 4000 kg·cm^{-2} and by Kashiwagi and Makita [12] at 25, 30, 50, and 75°C and pressures up to 110 MPa. Agreement with these data is generally well within the estimated combined uncertainties, but at 75°C the present values are higher than the results of Bridgman by 6%. The agreement with recent absolute measurements using a vibrating-wire viscometer [13] at 30 and 50°C and pressures up to 80 MPa is better than 1.5%. Viscosity coefficients have been measured for toluene-d$_8$ by Wilbur and Jonas [14]. At the common temperature of 50°C, these values are on average about 8% higher than the present data on toluene, as expected from the ratio of the square root of the molecular masses. For the toluene + n-hexane mixtures, measurements have been reported by Ghai and Dullien [15] at 25°C and atmospheric pressure. Agreement with the present values is within 0.25%. The variation of viscosity coefficient with pressure for toluene, n-hexane, and the mixtures is shown in Fig. 2. At a given pressure, the viscosity increases with the concentration of toluene in the mixture. When the results are considered relative to the viscosities at a pressure of 0.1 MPa, it is found that, for the different mixtures, the ratios for a given pressure and temperature are practically identical. The values are slightly higher than those for toluene or for n-hexane. In all cases the viscosity ratio shows little change with temperature at pressures below 200 MPa. At a higher constant pressure, it decreases on going to larger temperatures, the difference becoming as much as 20% at 400 MPa from 25 to 100°C.

5. CORRELATION OF VISCOSITY COEFFICIENT DATA

It has previously been shown [16] that experimental viscosity coefficient data for liquids and liquid mixtures can be correlated very satisfac-

Table I. Viscosity Coefficient and Density of Toluene

Temperature (°C)	Pressure (MPa)	Density (kg·m⁻³)	Viscosity coefficient (mPa·s)
25.08	0.1	862.1	0.5516
	25.5	880.2	0.673
	50.6	895.6	0.784
	76.3	909.5	0.934
	101.3	921.6	1.065
	146.8	941.0	1.382
	200.5	960.7	1.789
	299.1	990.9	3.032
	400.7	1016.6	4.910
	502.2	1038.5	8.026
49.99	0.1	838.8	0.4211
	25.9	860.8	0.517
	50.2	877.9	0.610
	75.8	893.3	0.702
	101.1	906.6	0.836
	150.2	928.7	1.093
	195.8	946.5	1.289
	294.8	977.0	1.977
	394.9	1002.3	3.039
	487.7	1022.2	4.390
75.09	0.1	814.7	0.3336
	27.2	839.7	0.411
	50.1	856.9	0.477
	74.0	872.4	0.572
	101.9	888.0	0.654
	152.6	912.1	0.840
	202.5	932.0	1.061
	298.9	963.4	1.579
	398.1	989.9	2.299
	501.2	1013.3	3.610
100.12	0.1	790.0	0.2730
	25.1	817.4	0.344
	49.8	838.6	0.416
	73.3	855.3	0.477
	101.8	872.6	0.560
	149.5	896.6	0.691
	200.7	918.0	0.909
	307.8	953.6	1.361
	412.0	981.1	1.971
	518.8	1004.8	2.725

Table II. Viscosity Coefficients for Toluene (1) + n-Hexane
(2) with $x_2 = 0.250$

Temperature (°C)	Pressure (MPa)	Density (kg·m^{-3})	Viscosity coefficient (mPa·s)
25.13	0.1	802.0	0.4404
	25.1	822.7	0.608
	50.3	839.1	0.741
	74.9	852.9	0.838
	100.0	865.6	0.972
	149.8	887.1	1.237
	198.4	905.1	1.636
	300.1	936.2	2.703
	396.5	960.4	4.359
	499.4	982.6	6.428
50.12	0.1	778.6	0.3446
	25.2	803.0	0.471
	51.0	822.2	0.567
	74.7	837.0	0.655
	100.2	850.8	0.773
	150.8	873.9	0.992
	199.9	892.6	1.267
	300.4	923.6	1.985
	400.2	948.4	2.930
	499.1	969.3	4.166
75.20	0.1	754.6	0.2765
	25.2	781.1	0.363
	47.0	799.1	0.449
	75.6	818.6	0.546
	103.9	834.9	0.631
	150.5	857.3	0.792
	199.7	877.1	1.006
	299.5	909.6	1.462
	391.6	934.0	2.072
	499.7	958.1	2.855
100.20	0.1	729.6	0.2302
	26.9	762.5	0.295
	51.7	785.0	0.365
	74.6	801.8	0.446
	98.9	817.1	0.502
	149.0	842.9	0.661
	202.6	865.3	0.839
	299.6	897.6	1.222
	400.1	924.4	1.699
	505.5	947.9	2.250

Table III. Viscosity Coefficients for Toluene $(1) + n$-Hexane
(2) with $x_2 = 0.500$

Temperature (°C)	Pressure (MPa)	Density $(kg \cdot m^{-3})$	Viscosity coefficient $(mPa \cdot s)$
25.08	0.1	748.5	0.3708
	24.2	768.8	0.504
	49.9	786.2	0.610
	75.0	800.7	0.712
	99.7	813.2	0.841
	151.8	835.8	1.109
	200.7	853.7	1.416
	299.9	883.7	2.280
	399.8	908.3	3.544
	503.2	930.0	5.286
50.09	0.1	725.8	0.2943
	25.9	750.7	0.391
	50.0	769.2	0.487
	75.3	785.3	0.571
	100.7	799.2	0.665
	150.9	822.1	0.868
	200.8	840.9	1.079
	300.5	871.3	1.685
	400.2	895.7	2.507
	495.7	915.6	3.396
75.17	0.1	701.7	0.2394
	25.4	722.8	0.299
	49.9	749.8	0.394
	75.2	767.3	0.473
	101.2	782.5	0.537
	151.5	806.9	0.716
	201.2	826.7	0.895
	301.8	858.9	1.350
	401.4	884.4	1.910
	508.9	907.5	2.649
100.08	0.1	676.1	0.2020
	24.9	708.3	0.250
	50.0	732.6	0.318
	75.5	751.9	0.374
	100.4	767.5	0.447
	150.7	793.3	0.600
	200.4	813.9	0.736
	300.8	846.9	1.096
	400.8	873.0	1.508
	510.3	896.9	2.082

Table IV. Viscosity Coefficients for Toluene $(1) + n$-Hexane (2)
with $x_2 = 0.750$

Temperature (°C)	Pressure (MPa)	Density (kg·m^{-3})	Viscosity coefficient (mPa·s)
25.15	0.1	699.4	0.3227
	24.8	721.0	0.422
	49.4	737.9	0.514
	77.1	754.0	0.619
	100.4	765.8	0.723
	151.3	787.8	0.946
	200.3	805.6	1.214
	301.0	835.5	1.993
	401.4	859.8	3.063
	506.6	881.3	4.329
50.10	0.1	675.8	0.2568
	25.7	702.6	0.338
	50.1	721.7	0.416
	74.9	737.6	0.503
	98.8	750.8	0.550
	149.8	774.0	0.728
	200.0	792.8	0.962
	300.0	822.9	1.466
	400.5	847.1	2.168
	504.5	868.1	3.148
75.05	0.1	651.3	0.2092
	25.4	681.6	0.276
	49.9	703.0	0.339
	75.5	720.9	0.401
	99.5	735.1	0.465
	150.7	760.0	0.609
	201.0	779.7	0.779
	300.1	810.9	1.148
	399.5	835.9	1.669
	508.4	858.8	2.343
100.05	0.1	623.7	0.1765
	26.0	662.7	0.232
	49.4	685.8	0.278
	73.5	704.5	0.334
	101.0	721.9	0.401
	150.3	747.0	0.511
	200.2	767.4	0.672
	303.3	800.7	1.005
	399.6	825.2	1.349
	501.4	847.0	1.810
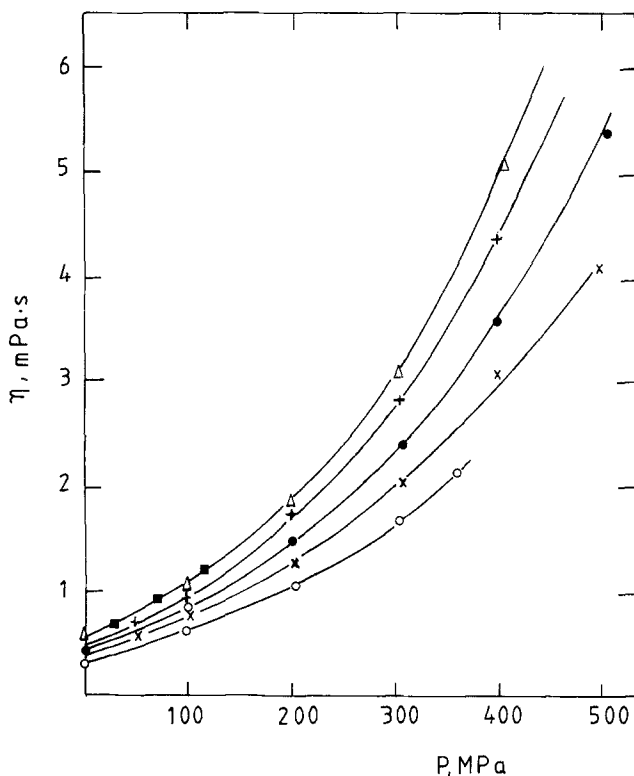
Fig. 2. Experimental viscosity coefficients for toluene + n-hexane mixtures at 25°C. Mol fraction of toluene: $\bigcirc$, 0.0; $\times$, 0.25; $\bullet$, 0.50; +, 0.75; $\triangle$, 1.0; ■, Kashiwagi and Makita [12].

torily by a method suggested by consideration of exact hard sphere theory. In this approach, a quantity η^* is introduced, defined by

$$\eta^* = (\eta/\eta_0)(V/V_0)^{2/3} \tag{3}$$

where V is molar volume, V_0 is the close-packed volume, and η_0 is the low-density hard-sphere viscosity coefficient. An important property of η^* is that it depends only on reduced volume. On substitution for the hard-sphere expressions for η_0 and V_0, η^* is related to experimental quantities by the equation

$$\eta^* = 6.035 \times 10^8 \eta V^{2/3}/(MRT)^{1/2} \tag{4}$$

For a real liquid, on the assumption that corrections for nonspherical molecular shape and molecular roughness are temperature and density

independent, plots of η^* versus $\log V$ for different temperatures will be superimposable laterally on the curve obtained for a given reference temperature, T_R, over the whole density range. The amount by which $\log V$ is adjusted leads to a value for the ratio of the characteristic volumes, V_0, at the two temperatures.

This method has been applied to the present viscosity coefficient measurements for toluene and the three binary mixtures of toluene + n-hexane. It is found that these data also can be very satisfactorily correlated on the basis of a single curve for each system. The 25°C isotherm was taken as the reference in each case. The results are shown in Fig. 3 for toluene. Values derived for $V_0(T)/V_0(T_R)$ for toluene and its mixtures with hexane are given in Table V. The ratios for toluene agree closely with those previously obtained for hexane [2], and there is little difference on going to the mixtures, assuming these behave like a single-component liquid.
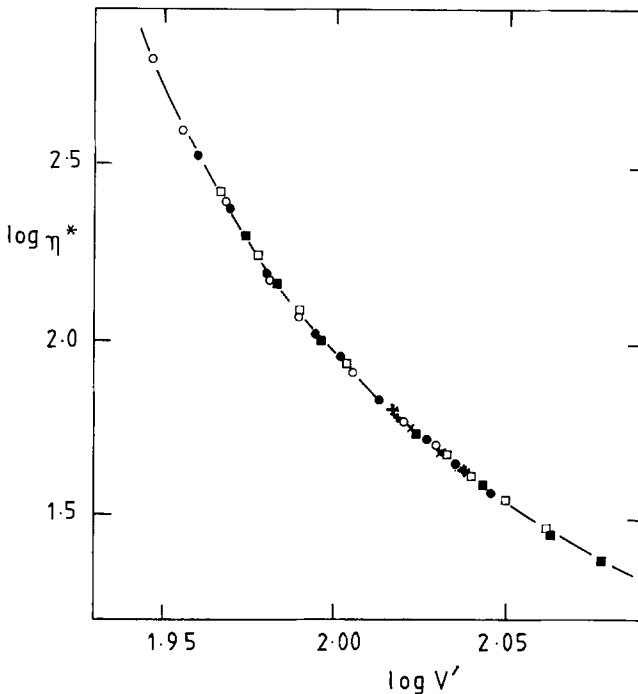

Fig. 3. Correlation of experimental viscosity coefficient data for toluene at different temperatures and pressures, based on the 298 K isotherm. η^* is defined by Eq. (4), $V' = V \cdot V_0(T_R)/V_0(T)$. $\bigcirc$, 25°C; $\bullet$, 50°C; $\square$, 75°C; $\blacksquare$, 100°C; +, Assael et al. [13] at 50°C; $\times$, Kashiwagi and Makita [12] at 50°C.

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

	T (°C)			
Liquid	25	50	75	100
Toluene	1.000	0.986	0.981	0.973
Toluene (1) + n-hexane (2)				
$x_2 = 0.25$	1.000	0.989	0.982	0.973
$x_2 = 0.50$	1.000	0.989	0.979	0.973
$x_2 = 0.75$	1.000	0.991	0.982	0.974
Hexane	1.000	0.989	0.982	0.974

The results for toluene can be expressed quantitatively, by making use of the approach recently described [17] for the simultaneous correlation of the viscosity coefficient, diffusion coefficient, and thermal conductivity coefficient for n-alkanes. Universal curves were developed for η^* (and the corresponding D^* and λ^*), as a function of the reduced volume V_r, equal to V/V_0. Specifically, for the viscosity coefficient

$$\log \eta^* = 0.877 - 3.79208/V_r + 16.4416/V_r^2 - 24.2509/V_r^3$$
$$+ 16.3540/V_r^4 \tag{5}$$

Viscosity coefficients were then calculated from $R_\eta \cdot \eta$ with the reported values for V_0 and R_η. For toluene, R_η can be taken as equal to unity. The corresponding values for the characteristic volume V_0 in $cm^3 \cdot mol^{-1}$ are 71.5 at 25°C, 70.5 at 50°C, 69.9 at 75°C, and 69.35 at 100°C. Of the 40 experimental points, only 6 deviate by more than 5% from the calculated values. The estimated experimental accuracy of the viscosity measurements is $\pm 4\%$, and further uncertainties arise from the density values since a difference of 0.2% in density will lead to a change in the calculated viscosity of up to 4% at the highest pressures. The agreement can therefore be considered reasonably satisfactory.

6. MIXTURE VISCOSITIES

For this system of toluene + n-hexane, the variation of viscosity coefficient with mole fraction at constant pressure is practically linear, at each temperature.

The experimental visconsities can be represented by the empirical Grunberg and Nissan equation [5], which can be written

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G \tag{6}$$

where η is the mixture viscosity, x_i is the mole fraction of component i, and η_i is its viscosity. G is the Grunberg and Nissan parameter, which in general may be composition, temperature, and pressure dependent.

Values for G derived at 0.1 MPa show a slight variation with temperature, increasing from about -0.35 to -0.15 on going from 25 to 100°C, but little composition dependence. At higher pressures, G increases as shown in Fig. 4 for the equimolar mixture, with closely similar values for the other compositions. As a result, G can be expressed by the following composition- and temperature-independent equation:

$$G = -0.190 + 0.0027P - 0.000005P^2 \tag{7}$$

where the pressure is in MPa.

Of the 81 viscosity coefficients obtained at rounded pressures of 0.1, 50, 100, 150, 200, 300, and 400 MPa from the experimental measurements, only for 8 do the differences between these values and those calculated from Eqs. (6) and (7) exceed 5 %. Allowing for inaccuracies in viscosity for pure components and the mixtures, this is a generally satisfactory fit.
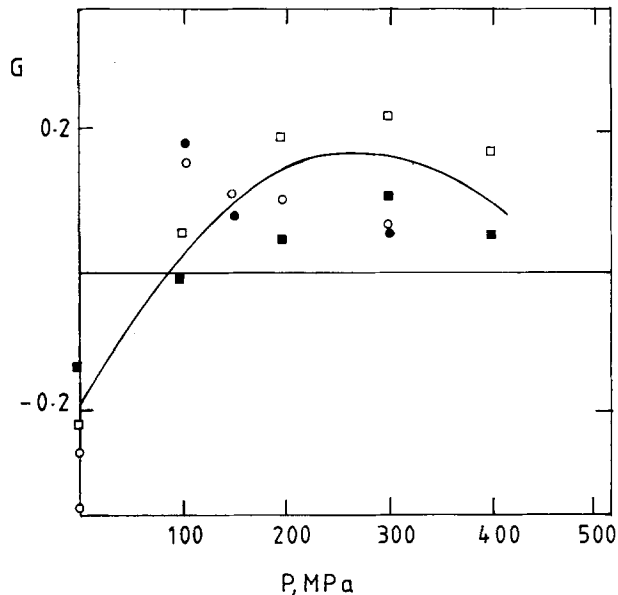

Fig. 4. Grunberg G as a function of pressure for equimolar mixtures of toluene + n-hexane. ○, 25°C; ●, 50°C; □, 75°C; ■, 100°C.

7. CONCLUSIONS

Viscosity coefficient measurements are reported for toluene and three binary mixtures with n-hexane, with mole fractions of 0.25, 0.50, and 0.75. The pressures extend to 500 MPa and the temperatures are 25, 50, 75, and 100°C. The density dependence of the results for toluene can be represented by an equation derived from consideration of smooth hard-sphere theory. The mixture coefficients can be reproduced by the Grunberg and Nissan equation with a pressure-dependent equation for the parameter G.

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