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

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A two-coil self-centering falling-body viscometer has been used to measure viscosity coefficients for acetonitrile and three binary mixtures of toluene + acetonitrile at 25, 50, 75, and 100°C and pressures up to 500 MPa. The results for acetonitrile can be interpreted by an approach based on hard-sphere theory, with a roughness factor of 1.46. The binary-mixture data are well represented by the Grunberg and Nissan equation with a mixing parameter which is pressure and temperature dependent but composition independent.

KEY WORDS: acetonitrile; Grunberg and Nissan equation; high pressure; toluene; viscometer; viscosity.

1. INTRODUCTION

Previous studies [1–4] of the effects of increased pressure and temperature on the viscosity coefficients of liquids and liquid mixtures have been restricted to hydrocarbons. In this paper, we extend the investigation to molecular liquids with large permanent dipole moments and their mixtures with aromatic hydrocarbons, with viscosity-coefficient measurements for acetonitrile and three binary mixtures with toluene. The experimental method is outlined in Section 2, and the measured viscosity coefficients are tabulated in Section 4. It is shown in the following section that the data for these systems are satisfactorily correlated by a graphical method involving the volume dependence of the viscosity coefficients in reduced form.

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The results for acetonitrile can be represented satisfactorily by equations developed on the basis of hard-sphere theory [5]. For the binary mixtures, the Grunberg and Nissan equation [6] 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 principle of the method is that the sinker, with a small piece of ferrite embedded in it, passes through two coils and the resulting change in inductance is used to start and stop a timer. Details of the operation have been described in outline previously [4].

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 298.15 K), 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 sinker/tube combination was calibrated [4] 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 $\pm 0.5\%$. The viscosity-coefficient range was from 0.23 to 16 mPa s. 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}. For lower viscosities, improved agreement with experimental results at 75 and 100°C for hexane, acetonitrile, and a mixture of toluene + *n*-hexane with 0.25 mol fraction of toluene using suspended-level viscometers was obtained using the equation

$$A = 20.155 + 0.454t \tag{3}$$

where t is the actual fall time.

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) or (3). The results are estimated to be accurate to better than ±4%. Atmospheric-pressure viscosities were determined using suspended level viscometers.

3. MATERIALS

The toluene and acetonitrile were purchased from Aldrich Chemical Co. Ltd., Gillingham, U.K., with stated minimum purities of 99.9 mol%. The measured densities at 298.15 K for toluene and acetonitrile were 862.0 and 776.7 $\mathrm{kg\,m^{-3}}$, compared with literature values of 862.2 $\mathrm{kg\,m^{-3}}$ [7] and 776.6 $\mathrm{kg\,m^{-3}}$ [8].

4. RESULTS

Measurements of the sinker fall time have been made for acetonitrile and for three binary mixtures with toluene, with the mole fraction of toluene equal to 0.25, 0.50, and 0.75. Care was taken to avoid composition changes on making up the mixtures by weight. 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 [9]. The densities have an estimated accuracy of ±0.2%.

The experimental viscosity coefficients for acetonitrile in equilibrium with vapor have an estimated accuracy of ±0.5% at 25°C, decreasing to ±1% at 75°C. Over the temperature range of the experiments the viscosity of acetonitrile can be represented by an Arrhenius equation

$$\eta = A \exp(E/T) \tag{4}$$

with $A = 17.80\ \mu\mathrm{Pa\cdot s}$ and $E = 880.6$ K. The equation reproduces the data with a maximum deviation of 0.05%.

Values for the viscosity of acetonitrile have been reported by a number of authors [10–16]. A comparison between the values given in the literature and the present results as represented by Eq. (4) is shown in Fig. 1. There is considerable scatter in the literature values. The results given by Friend and Hargreave [12] appear to be systematically low by about 5%, and those of Mato and Hernandez [13] and Ritzoulis et al. [11] show a significantly different temperature dependence from each other and from our results. The value given by Reid et al. [16] at 25°C is higher by 2.6% than our measured viscosity. Agreement with the present results within the estimated combined uncertainties is shown by the

Table I. Viscosity Coefficient and Density of Acetonitrile

Temperature (°C)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity coefficient (mPa · s)
25.10	0.1	776.6	0.3410
	50.8	812.4	0.461
	73.2	825.2	0.506
	118.7	847.7	0.589
	150.9	861.5	0.654
	201.4	880.8	0.766
	260.7	900.4	0.868
	326.7	919.5	1.062
49.98	0.1	749.6	0.2715
	23.0	770.0	0.314
	49.2	789.5	0.356
	75.5	806.0	0.402
	101.2	820.2	0.439
	151.7	844.2	0.539
	200.5	863.8	0.613
	280.6	891.0	0.779
	399.6	924.0	0.988
	511.7	950.0	1.227
75.01	0.1	721.3	0.2232
	24.0	745.5	0.258
	49.4	766.3	0.292
	75.4	784.3	0.329
	99.8	799.0	0.374
	150.6	825.0	0.436
	202.2	846.8	0.524
	300.3	881.8	0.661
	402.7	911.3	0.826
	512.4	938.0	1.028
100.03	0.1	693.8	0.1885
	24.5	724.3	0.214
	50.2	748.8	0.245
	75.2	768.3	0.275
	99.2	784.3	0.304
	150.2	812.7	0.364
	201.4	836.1	0.429
	299.7	872.4	0.559
	398.5	902.0	0.691
	502.4	928.3	0.834

Table II. Viscosity Coefficients for Toluene (1) + Acetonitrile (2) with $x_2 = 0.750$

Temperature (°C)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity coefficient ($mPa \cdot s$)
24.95	0.1	812.0	0.3935
	23.9	830.3	0.469
	51.0	848.0	0.573
	78.0	863.4	0.645
	102.4	875.7	0.737
	150.8	897.1	0.912
	201.4	916.2	1.069
	302.9	948.2	1.510
	414.2	976.8	2.115
49.90	0.1	786.2	0.3080
	25.0	808.0	0.371
	50.3	826.4	0.443
	77.0	843.1	0.514
	100.3	856.1	0.573
	151.2	880.5	0.681
	198.3	899.7	0.817
	301.4	934.6	1.126
	401.9	962.3	1.500
	505.1	986.7	1.925
75.03	0.1	759.2	0.2491
	27.6	786.7	0.299
	49.9	804.7	0.347
	74.9	822.0	0.401
	101.4	837.9	0.455
	149.5	862.5	0.544
	200.2	884.1	0.661
	300.3	919.1	0.884
	400.9	947.7	1.171
	509.8	973.9	1.508
100.00	0.1	732.9	0.2076
	24.4	761.7	0.246
	50.1	785.5	0.282
	75.4	804.7	0.323
	103.2	822.8	0.361
	149.9	848.4	0.445
	200.3	871.3	0.530
	309.4	911.3	0.697
	411.4	941.2	0.890
	520.7	968.3	1.175

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

Temperature (°C)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity coefficient ($mPa \cdot s$)
25.02	0.1	835.5	0.4526
	26.1	854.1	0.596
	50.2	869.2	0.694
	75.0	882.9	0.785
	101.4	896.1	0.904
	150.6	917.7	1.149
	201.1	936.9	1.423
	304.3	969.9	2.133
	401.0	995.6	3.089
	510.7	1020.7	4.593
49.94	0.1	810.9	0.3497
	25.3	832.0	0.433
	49.9	849.3	0.508
	77.4	866.0	0.605
	99.2	877.8	0.636
	150.1	901.6	0.802
	201.7	922.1	1.037
	297.9	953.9	1.460
	392.3	979.6	2.039
	440.2	991.3	2.356
	497.1	1004.1	2.795
75.08	0.1	784.8	0.2798
	24.0	807.3	0.339
	49.2	826.9	0.401
	75.9	844.6	0.469
	100.7	859.0	0.528
	149.5	883.2	0.663
	200.3	904.5	0.813
	299.8	938.8	1.151
	405.9	968.6	1.537
	516.5	994.7	2.061
99.95	0.1	760.0	0.2312
	26.5	789.4	0.297
	48.1	808.5	0.324
	74.8	828.4	0.379
	100.1	844.6	0.426
	152.1	872.5	0.543
	200.6	894.2	0.649
	300.8	930.6	0.894
	401.4	960.2	1.217
	515.5	988.4	1.637

Table IV. Viscosity Coefficients for Toluene (1) + Acetonitrile (2) with $x_2 = 0.250$

Temperature (°C)	Pressure (MPa)	Density (kg · m^{-3})	Viscosity coefficient (mPa · s)
25.04	0.1	851.9	0.5085
	51.0	884.2	0.739
	75.5	897.0	0.858
	99.9	908.6	1.011
	150.8	929.6	1.353
	202.1	947.8	1.731
	298.0	976.5	2.538
	400.6	1002.0	3.862
	467.5	1016.6	5.011
49.93	0.1	827.9	0.3879
	48.5	863.6	0.556
	74.7	878.8	0.649
	102.7	893.0	0.751
	149.7	913.6	0.969
	200.4	932.6	1.181
	249.5	948.6	1.465
	308.2	965.5	1.849
	411.8	991.0	2.703
75.08	0.1	802.9	0.3097
	25.2	825.9	0.391
	49.2	843.9	0.466
	75.2	860.5	0.524
	102.3	875.6	0.623
	150.1	898.2	0.751
	200.9	918.4	0.915
	245.9	934.0	1.093
	301.1	950.9	1.338
	406.9	978.7	1.958
100.07	0.1	778.2	0.2537
	25.2	804.9	0.316
	50.1	825.6	0.378
	74.1	842.3	0.436
	99.9	857.8	0.511
	150.6	883.3	0.644
	201.3	904.3	0.744
	300.2	937.5	1.085
	367.7	956.3	1.361
	436.4	973.2	1.646

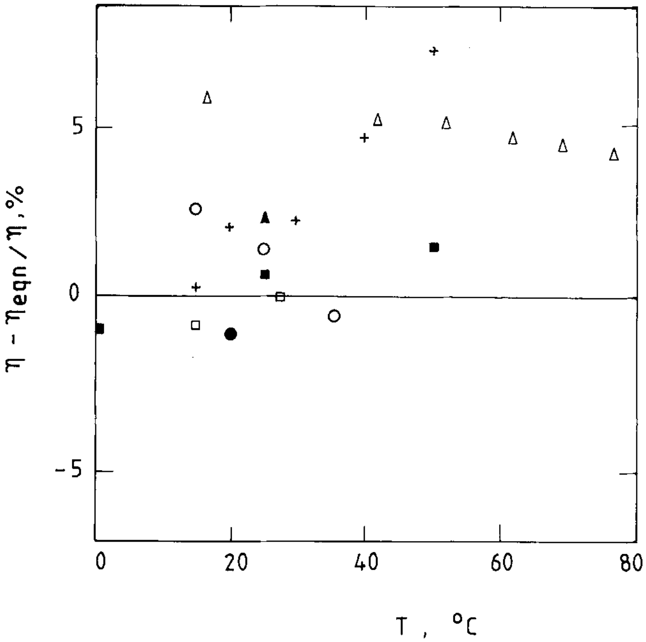

Fig. 1. Comparison between experimental viscosity data from the literature and our experimental results as represented by Eq. (4). ● [10]; ○ [11]; △ [12]; + [13]; □ [14]; ■ [15]; ▲ [16].

measurements reported by Friedel and Rätzsch [10], Timmermans [14], and Walden and Birr [15]. For the acetonitrile + toluene mixtures, the composition dependence of the present results confirms the earlier measurements of Friedel and Rätzsch [10], which were made at 20°C. The values given by Ritzoulis et al. [11] show a completely different composition dependence, as shown in Fig. 2.

At a given pressure and temperature, the viscosity increases with 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, in contrast to the situation with regard to toluene + *n*-hexane mixtures [4], the ratios for a given pressure and temperature are now strongly composition dependent. This is illustrated in Fig. 3 for data at 75°C. The ratio increases on going from acetonitrile to toluene. In all cases the viscosity ratio shows little change with temperature at lower pressures, but it decreases more markedly with increases in temperature on going to larger pressures.

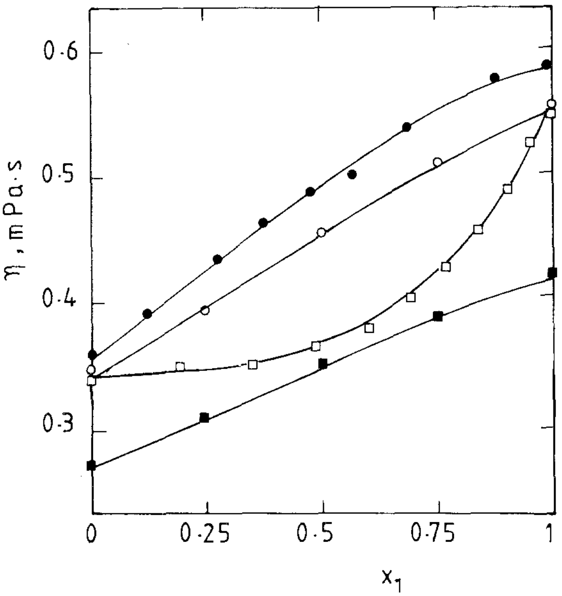

Fig. 2. Experimental viscosity coefficients for acetonitrile + toluene mixtures at 0.1 MPa. Present results: ○, 25°C; ■, 50°C. Literature values: ●, 20°C [10]; □, 25°C [11].

5. CORRELATION OF VISCOSITY COEFFICIENT DATA

Experimental viscosity-coefficient data for liquids and liquid mixtures can be correlated very satisfactorily [17] by a method suggested by consideration of exact hard-sphere theory. In this approach, a quantity η^* is introduced, defined by

$$\eta^* = (\eta/\eta_0)(V/V_0)^{2/3} \qquad (5)$$

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

$$\eta^* = 6.035 \times 10^8 \eta V^{2/3}/(\mathrm{MRT})^{1/2} \qquad (6)$$

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

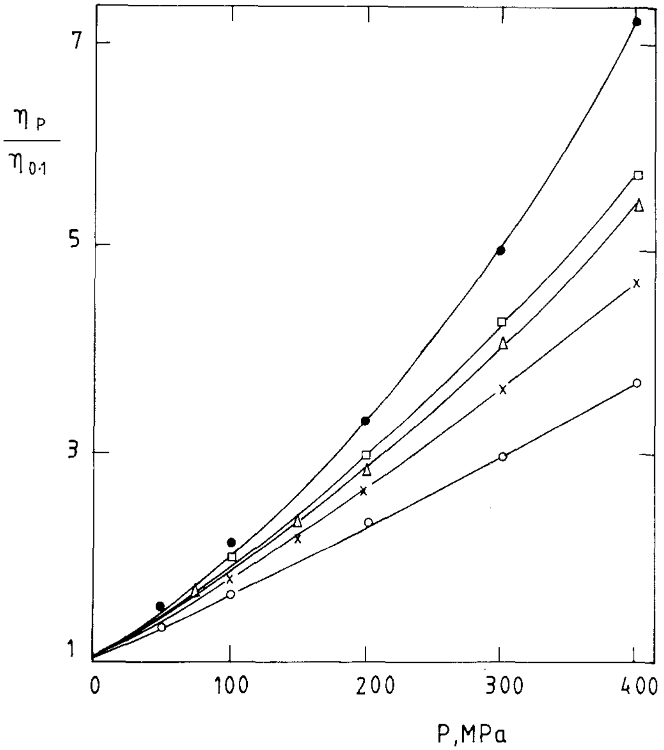

Fig. 3. Experimental viscosity coefficients for acetonitrile + toluene mixtures at different pressures relative to the 0.1 MPa values at 75°C. Mole fraction of toluene: ○, 0.0; ×, 0.25; △, 0.50; □, 0.75; ●, 1.0.

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 acetonitrile and the three binary mixtures of acetonitrile + toluene. These data are very satisfactorilly 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. 4 for acetonitrile. Values derived for $V_0(T)/V_0(T_R)$ for acetonitrile and its mixtures with toluene are given in Table V. It is significant that, whereas for hydrocarbon mixtures so far studied [1–4], the ratios for different compounds agree closely at any given temperature and there is little difference on going to the mixtures, assuming that these behave like a single-component liquid,

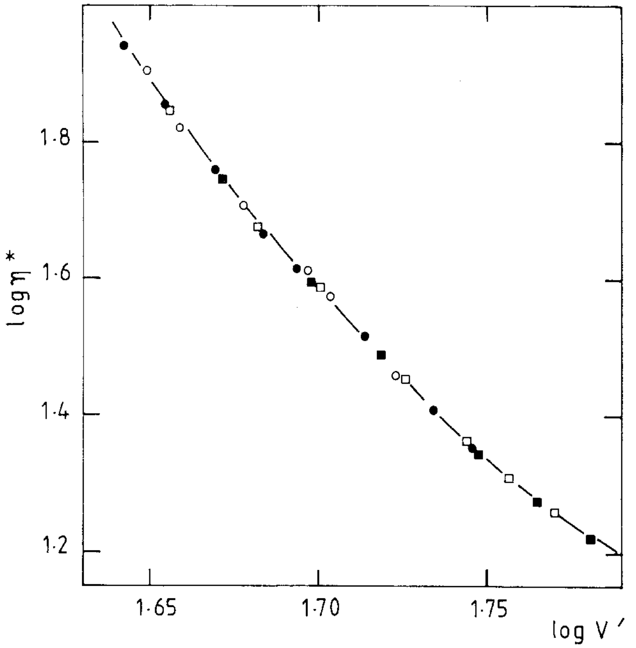

Fig. 4. Correlation of experimental viscosity coefficient data for acetonitrile at different temperatures and pressures, based on the 298 K isotherm. η^* is defined by Eq. (6), $V' = V \cdot V_0(T_R)/V_0(T)$. ○, 25°C; ●, 50°C; □, 75°C; ■, 100°C.

the ratios for acetonitrile and toluene are very different. Ratios for the mixtures fall between the values for the pure compounds and vary fairly smoothly with mole fraction.

The results for acetonitrile can be expressed quantitatively, by making use of the approach recently described [18] for the simultaneous correla-

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

Liquid	T (°C)			
	25	50	75	100
Toluene	1.000	0.986	0.981	0.973
Toluene (1) + acetonitrile (2)				
$x_2 = 0.25$	1.000	0.984	0.976	0.966
$x_2 = 0.50$	1.000	0.982	0.973	0.953
$x_2 = 0.75$	1.000	0.982	0.968	0.947
Acetonitrile	1.000	0.982	0.968	0.942

tion of the viscosity coefficient, diffusion coefficient, and thermal conductivity coefficient for *n*-alkanes. A universal curve was developed for the reduced viscosity coefficient η^* as a function of the reduced volume V_r, equal to V/V_0, and expressed by the equation

$$\log_{10} \eta^* = 0.877 - 3.79208/V_r + 16.4416/V_r^2 - 24.2509/V_r^3 + 16.3540/V_r^4 \tag{7}$$

Viscosity coefficients were then calculated from $R_\eta \cdot \eta$ with the reported values for V_0 and R_η. For acetonitrile, R_η is 1.46, which is significantly larger than unity, indicating an appreciable contribution from translational-rotational coupling. The corresponding values for the characteristic volume V_0 in $cm^3 \cdot mol^{-1}$ are 30.2 at 25°C, 29.6 at 50°C, 29.0 at 75°C, and 28.3 at 100°C. An independent estimate [19] of the core size of acetonitrile, considered as a hard sphere, from diffusion measurements gives a value of 0.409 nm at 25°C, in excellent agreement with the present value of 0.414 nm. When viscosities are calculated as above with the given values for R_η and V_0, only four deviate by more than 5% from the experimental values, with a maximum deviation of 6.2%. Now the estimated experimental accuracy of the viscosity measurements is $\pm 4\%$, and possible errors of $\pm 0.2\%$ 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 very satisfactory.

6. MIXTURE VISCOSITIES

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

The experimental viscosities can be represented by the empirical Grunberg and Nissan equation [6], which can be written in the form

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G \tag{8}$$

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, decreasing from about 0.2 to 0.1 on going from 25 to 100°C, but little composition dependence. At higher pressures, G increases as shown in Fig. 5 for the different mixtures at 50 and 100°C. Very similar results are

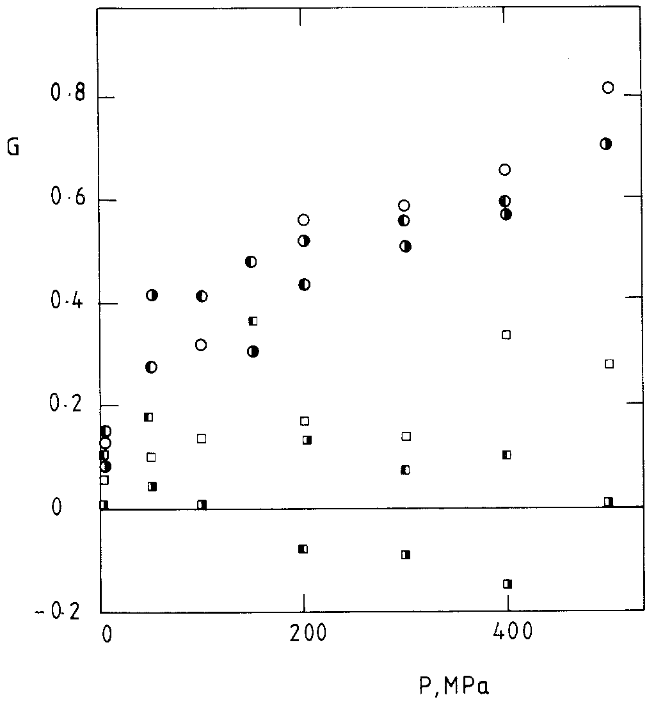

Fig. 5. Grunberg G as a function of pressure for toluene + acetonitrile mixtures. x (toluene) at 50°C—◑, 0.25; ○, 0.50; ◐, 0.75; at 100°C—◨, 0.25; □, 0.50; ◧, 0.75.

obtained for all compositions. Therefore, G can be expressed by the following general composition-independent equation

$$G = a + bP + cP^2 \tag{9}$$

where the pressure is in MPa. The coefficients a, b, and c are temperature dependent. Values derived at the experimental temperatures are given in Table VI.

Table VI. Coefficients in Eq. (9) for G

T (°C)	a	$10^3 b$	$-10^6 c$
25.0	0.17	4.9	10.1
50.0	0.12	2.5	3.3
75.0	0.10	0.7	0.3
100.0	0.06	0.6	1.1

When mixture viscosity coefficients are calculated using Eqs. (8) and (9), with the tabulated values for the coefficients, at rounded pressures of 0.1, 50, 100, 150, 200, 300, and 400 MPa, there is agreement within 6% with the 81 viscosity coefficients obtained from the experimental measurements at these pressures. Only three points differ by more than 5%. Taking into account possible inaccuracies in the experimental viscosities, this is a very satisfactory fit and demonstrates again the usefulness of the Grunberg and Nissan equation.

7. CONCLUSIONS

Viscosity-coefficient measurements are reported for acetonitrile and three binary mixtures with toluene, 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 acetonitrile can be very satisfactorily represented by an equation derived from consideration of hard-sphere theory, with a rougheness factor of 1.46. The mixture coefficients can be reproduced by the Grunberg and Nissan equation with values for the parameter G which are composition independent but both temperature and pressure dependent.

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