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Transport Properties of Nonelectrolyte Liquid Mixtures—IV. Viscosity Coefficients for Benzene, Perdeuterobenzene, Hexafluorobenzene, and an Equimolar Mixture of Benzene + Hexafluorobenzene from 25 to 100°C at Pressures up to the Freezing Pressure

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Viscosity coefficient measurements made with an estimated accuracy of ±2% using a self-centering falling body viscometer are reported for benzene, perdeuterobenzene, hexafluorobenzene and an equimolar mixture of benzene + hexafluorobenzene at 25, 50, 75 and 100°C at pressures up to the freezing pressure. The data for each liquid at different temperatures and pressures are correlated very satisfactorily by a graphical method based on plots of $9.118 \times 10^7 \eta V^{2/3}/(MRT)^{1/2}$ versus $\log V$, and are reproduced to within the experimental uncertainty by a free-volume form of equation. Application of the empirical Grunberg and Nissan equation to the mixture viscosity coefficient data shows that the characteristic constant G is practically temperature- and pressure-independent for this system.

KEY WORDS: High pressure; viscosity; benzene; perdeuterobenzene; hexafluorobenzene; Grunberg and Nissan equation.

1. INTRODUCTION

As part of an investigation into the effects of changes in temperature and pressure on the transport properties of liquids and liquid mixtures, viscosity coefficient measurements have been made [1, 2] for certain n-alkanes and binary n-alkane mixtures, using a self-centering falling body viscometer at 25, 50, 75, and 100°C and at pressures up to the freezing pressure or 500

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MPa. The present paper extends the study to aromatic compounds with measurements of viscosity for benzene, perdeuterobenzene, hexafluorobenzene and an equimolar mixture of benzene + hexafluorobenzene from 25 to 100°C at pressures up to the freezing pressure. An outline of the experimental method is given in Section 2 and the results are given in Section 4. For the correlation of the data for a given liquid at different temperatures and pressures, a graphical method derived [3] from consideration of the hard-sphere viscosity results and based on plots of η', where $\eta' = 9.118 \times 10^7 \eta V^{2/3}/(MRT)^{1/2}$, versus log V, is shown in Section 6 to be very satisfactory. In Section 7, a previously proposed [3] free–volume form of equation is applied to the results and shown to reproduce the data generally to better than 2%. The purely empirical equation of Grunberg and Nissan [4] is applied to the mixture viscosity coefficient data in Section 8. It is found that the constant G is practically temperature- and pressure-independent for this system.

2. EXPERIMENTAL

The high pressure falling body viscometer has been fully described elsewhere [2, 5]. It consists basically of a nonmagnetic stainless steel tube of uniform circular cross-section mounted vertically. A self-centering hemispherically nosed sinker, with a small piece of ferrite embedded in it, falls through the liquid in the tube. The change in inductance caused by the sinker as it passes at its terminal velocity through two pairs of coils wound on the outside of the tube is used to start, and to stop, a timer and thus give an accurate fall time for the sinker. The fall time is related to the viscosity coefficient 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, t is the fall time, ρ_L and ρ_s' are the densities of liquid and sinker at pressure P and temperature T, T is the experimental temperature, T_0 is a reference temperature (taken as 25°C), P_0 is atmospheric pressure, α is the linear coefficient of thermal expansion, β is the compressibility coefficient, and A is the viscometer constant.

Values of A were calculated [2] from Eq. (1) from measurements on Shell Vitrea No. 21 oil, Shell Tellus 11 oil, benzene, hexafluorobenzene, n-octane, and n-dodecane at atmospheric pressure and at different temperatures. A was found to increase by 9% over this range of viscosities. The calibration curve is given by

$$A = 8.730\left[1 - \left\{\frac{0.02405}{t(1 - \rho_L/\rho_s')}\right\}^{0.5284}\right] \tag{2}$$

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

Viscosity coefficients for the system under study can be calculated directly from measured fall times using Eq.(1) with the calibration constant given by Eq.(2). However, when the viscosity coefficient at atmospheric pressure is accurately known from some other measurement, it is advantageous to express the ratio of the viscosity coefficient at pressure P to that at atmospheric pressure in terms of the corresponding ratio of measured fall times, ratio of density terms, ratio of A values, and ratio of pressure correction

Table I. Viscosity Coefficient and Density of Benzene

Temperature (°C)	Pressure (MPa)	Density (kg · m^{-3})	Viscosity coefficient (mPa · s)
25.23	0.1	873.37	0.601
	23.9	891.5	0.736
	51.8	909.1	0.911
	68.4	918.4	1.031
50.16	0.1	846.6	0.4358
	16.5	861.5	0.5019
	65.5	896.1	0.718
	99.3	914.6	0.893
	148.8	937.6	1.200
	189.9	954.7	1.513
75.14	0.1	819.2	0.3334
	32.0	851.1	0.4350
	73.8	881.9	0.574
	101.3	898.0	0.675
	151.5	922.3	0.892
	200.0	941.9	1.146
	249.4	959.6	1.465
	298.6	976.1	1.831
100.02	0.1	791.3	0.2646
	29.0	826.7	0.3391
	75.6	864.6	0.4625
	103.2	881.1	0.541
	153.1	905.3	0.697
	201.8	924.9	0.880
	251.1	942.8	1.099
	300.6	960.0	1.362
	349.6	977.0	1.661
	402.2	995.8	2.003

terms, by application of Eq.(1) at these pressures. This method reduces systematic errors and leads to an estimated accuracy of ±2% in the viscosity coefficients at elevated pressures. Viscosity coefficients at saturated vapor pressure were measured in sealed suspended-level viscometers specially designed [6] for measurements at temperatures up to 20° above the normal boiling point. They have an estimated accuracy of ±0.5%.

3. MATERIALS

"UltraR" benzene, having a stated purity of not less than 99.5% by GLC was purchased from Hopkin and Williams Ltd., Chadwell Heath, Essex, England. The density at 25.00°C was 873.61 kg · m^{-3}, in good agreement

Table II. Viscosity Coefficient and Density of Perdeuterobenzene

Temperature (°C)	Pressure (MPa)	Density (kg · m^{-3})	Viscosity coefficient (mPa · s)
25.18	0.1	943.2	0.642
	21.0	961.9	0.768
	38.9	976.0	0.886
	49.4	983.6	0.956
50.21	0.1	914.1	0.4629
	27.0	940.5	0.578
	47.2	956.4	0.669
	97.4	987.5	0.935
	148.1	1012.8	1.292
	172.9	1024.2	1.460
75.12	0.1	884.3	0.3533
	37.0	922.1	0.4732
	72.1	949.9	0.595
	103.8	970.5	0.721
	154.9	997.9	0.957
	201.0	1018.5	1.210
	250.2	1037.6	1.538
	299.2	1054.8	1.933
100.07	0.1	854.0	0.2793
	28.8	890.6	0.3563
	74.0	931.2	0.4768
	103.2	951.0	0.565
	151.7	977.8	0.727
	201.3	1000.3	0.922
	249.9	1019.7	1.145
	300.0	1038.2	1.412
	351.0	1056.4	1.745
	400.8	1074.0	2.123

with literature values of 873.65 kg · m^{-3} [7] and 873.62 kg · m^{-3} [8]. Hexafluorobenzene and perdeuterobenzene were supplied by Fluorochem Ltd., Glossop, England. The hexafluorobenzene had a minimum stated purity of 99% and the perdeuterobenzene had 99.6% isotopic enrichment. Their densities were 1606.4 and 943.4 kg · m^{-3}, respectively at 25.00°C. The perdeuterobenzene was used as received, and the other liquids were fractionally distilled before use.

4. RESULTS

Measurements of the fall times for the sinker were made at pressures up to the freezing pressure in benzene, perdeuterobenzene, and hexafluoroben-

Table III. Viscosity Coefficient and Density of Hexafluorobenzene

Temperature (°C)	Pressure (MPa)	Density (kg · m^{-3})	Viscosity coefficient (mPa · s)
25.06	0.1	1606.3	0.873
	26.3	1650.3	1.183
	42.2	1671.8	1.390
	45.7	1676.2	1.433
	60.8	1694.1	1.660
50.16	0.1	1548.6	0.604
	19.2	1588.9	0.755
	47.7	1635.2	0.998
	75.8	1671.1	1.280
	103.4	1700.8	1.602
	117.1	1714.2	1.781
75.08	0.1	1489.0	0.4441
	34.9	1569.4	0.655
	70.1	1624.9	0.892
	102.3	1663.5	1.140
	125.8	1687.1	1.354
	154.3	1712.3	1.633
	164.0	1720.2	1.747
	200.4	1747.9	2.201
100.03	0.1	1428.2	0.3421
	25.5	1501.2	0.4683
	70.1	1584.8	0.696
	101.1	1625.7	0.872
	150.9	1676.9	1.212
	195.9	1714.5	1.586
	251.6	1755.4	2.165
	303.5	1790.8	2.841

zene at 25, 50, 75, and 100°C and in an equimolar mixture of benzene + hexafluorobenzene at 50, 75, and 100°C. The derived viscosity coefficients are presented in Tables I–IV, together with values for the density under corresponding conditions, calculated from values of the isothermal secant bulk modulus used to fit experimental density data [9]. The densities have an estimated accuracy of ±0.2%.

5. COMPARISON OF VISCOSITY COEFFICIENT RESULTS WITH LITERATURE VALUES

Viscosity coefficient measurements at elevated pressures and different temperatures have been made for benzene by Bridgman [10], Kuss [11], Collings and McLaughlin [12], Parkhurst and Jonas [13], and Isdale and Spence [5]. Kuss found that the logarithm of viscosity varied linearly with pressure up to his maximum pressure of 196 MPa, a result which differs from that found by all other workers. It is therefore not surprising that his viscosity

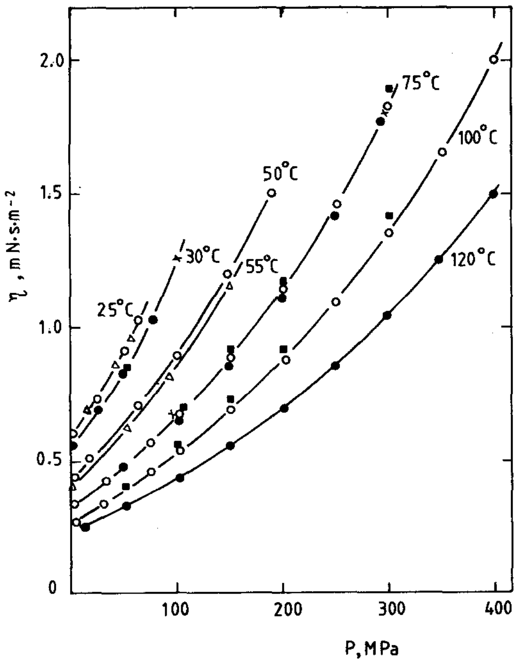

Fig. 1. Comparison of present viscosity coefficient measurements (○) for benzene with literature values (△, ref.[12]; +, ref.[10]; ●, ref.[13]; ■, ref.[5]).

Table IV. Viscosity Coefficient and Density of an Equimolar Mixture of Benzene + Hexafluorobenzene

Temperature (°C)	Pressure (MPa)	Density (kg · m^{-3})	Viscosity coefficient (mPa · s)
50.16	0.1	1233.9	0.4837
	1.3	1236.0	0.4885
	28.9	1279.0	0.640
	52.6	1305.0	0.780
	74.0	1325.0	0.917
75.01	0.1	1190.0	0.3625
	4.9	1200.0	0.3824
	72.4	1293.0	0.677
	105.2	1323.0	0.842
	126.1	1339.0	0.959
	153.7	1357.0	1.132
99.94	0.1	1145.0	0.2836
	42.5	1228.0	0.4261
	50.2	1239.0	0.4522
	100.3	1294.0	0.630
	152.2	1335.0	0.854
	195.7	1364.0	1.083

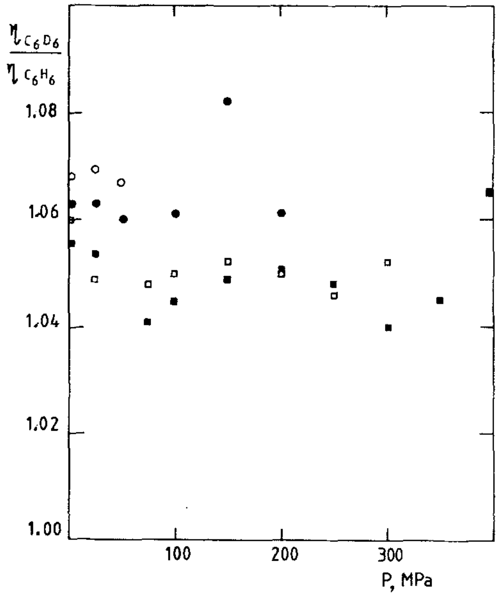

Fig. 2. Pressure dependence of the ratio of the viscosity coefficients of perdeuterobenzene and benzene. ○, 25°C; ●, 50°C; □, 75°C; ■, 100°C.

coefficients differ by up to 16% with the results given in Table I. His values are not included in Fig. 1, which compares the present measurements with literature values. The agreement is very satisfactory. The only significant differences occur at 100°C, where the viscosity coefficients of Isdale and Spence [5] lie up to 6.3% above the present results. This difference is probably due to the fact that Isdale and Spence did not measure the density of benzene as a function of pressure but calculated values at the experimental pressures from the results of Bridgman [14]. At 75°C, the viscosity coefficients reported here lie below the results of Isdale and Spence by up to 3%, and above the values given by Parkhurst and Jonas [13] by up to 3.4%, within the combined estimated experimental uncertainties. Agreement is also very good with the measured viscosities of Jobling and Lawrence [15] and the more extensive data of Harlow [16].

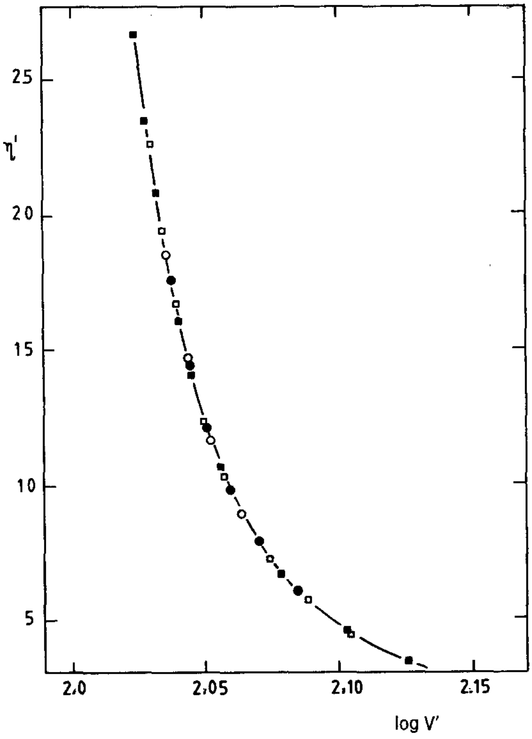

Fig. 3. Correlation of experimental viscosity coefficient data for hexafluorobenzene at different temperatures and pressures, based on the 25°C isotherm. η' is defined in the text; $V' = V \cdot V_0(T_R)/V_0(T)$. ○, 25°C; ●, 50°C; □, 75°C; ■, 100°C.

6. CORRELATION OF VISCOSITY COEFFICIENT DATA

The viscosity coefficients of perdeuterobenzene are consistently higher than those of benzene under the same conditions of temperature and pressure, as shown in Fig. 2. The ratio of 1.055 ± 0.015 shows no significant pressure or temperature dependence. It is greater than a simple square root molecular mass ratio, which would give 1.038. However, allowance must be made for the fact that benzene has a molar volume which is larger than that of perdeuterobenzene by 0.2–0.3% at any given temperature and pressure. A comparison of the viscosity coefficients at the same temperatures and molar volumes results in a lower value for the ratio. At saturated vapor pressures, the ratio is 1.044 at each temperature, in close agreement with the ratio of the square roots of the molecular masses. At lower molar volumes, the ratios range from 1.0 to 1.05. This variation is partly due to the uncertainties in the densities.

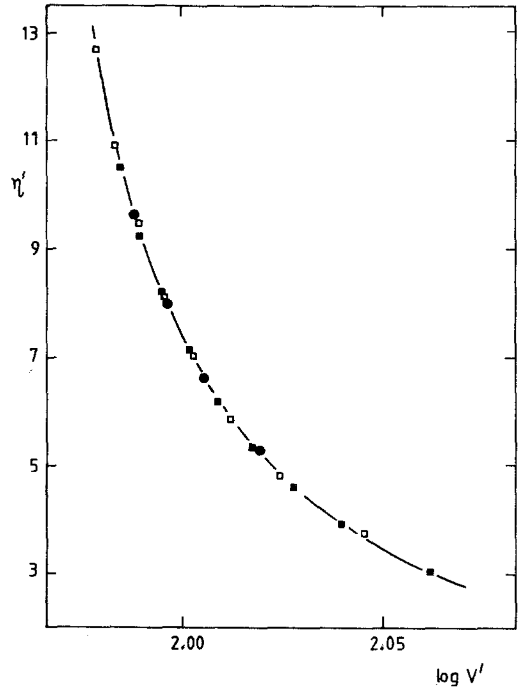

Fig. 4. Correlation of experimental viscosity coefficient data for the equimolar mixture of benzene + hexafluorobenzene at different temperatures and pressures, based on the 100°C isotherm. Definitions and key as for Fig. 3.

For the correlation of viscosity coefficient data at different temperatures and pressures, a graphical method based on results given by the hard-sphere model has previously been shown to be very satisfactory, both in the case of pure liquids [3] and liquid mixtures [1, 2]. Plots of η', where $\eta' = 9.118 \times 10^7 \eta V^{2/3}/(MRT)^{1/2}$, versus $\log V$ for a given fluid at different temperatures are found to 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 $V_0(T)/V_0(T_R)$, where V_0 is the close-packed volume in the hard-sphere theory. It was found that the plots were superimposable not only for the range of applicability of this model, but over the whole density range. When this method is applied to the present results, it is found that the data can be correlated on the basis of a single curve for each of the pure liquids and for the liquid mixture. The departure of individual points from the curve is less than 2%, as shown in Fig. 3 for hexafluorobenzene, where the 25°C isotherm was taken as the reference isotherm, and in Fig. 4 for the benzene + hexafluorobenzene mixture, where the 100°C isotherm gave the reference curve. Values obtained for $V_0(T)/V_0(T_R)$ are given in Table V. The temperature dependence is significantly lower than that found [2] for n-alkanes and n-alkane mixtures.

7. FREE-VOLUME FORM OF EQUATION

The equation

$$\ln\eta' = A + \frac{BV_0}{V - V_0} \qquad (3)$$

originally proposed by Dymond and Brawn [3], and shown to give a very satisfactory fit of viscosity coefficient data for pseudospherical molecular liquids and bicyclic rigid ring hydrocarbons with $A = -1.0$, has been found [1, 2] to reproduce experimental data for n-alkanes and n-alkane mixtures

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

	T(°C)			
Liquid	25.0	50.0	75.0	100.0
Benzene	1.000	0.995	0.990	0.985
Perdeuterobenzene	1.000	0.995	0.990	0.985
Hexafluorobenzene	1.000	0.995	0.992	0.989
Benzene + Hexafluorobenzene ($X = 0.5$)		1.010	1.005	1.000

from 25 to 100°C and at pressures up to the freezing pressure or 500 MPa generally to within 5% with the same constant value for A. V_0 for the pure liquids decreased with increase in temperature, as expected on physical grounds, and this temperature dependence was taken as linear. B values for the pure liquids increased smoothly with increase in temperature. For the mixtures, V_0 was obtained from V_0 values for the pure components, assuming a linear dependence on mole fraction, and B was simply related to the values for the pure liquids.

Application of Eq. (3) to the present data on benzene, perdeuterobenzene, hexafluorobenzene, and equimolar mixtures of benzene + hexafluorobenzene leads to a very satisfactory fit with $A = 1.0$ and V_0 and B values given in Table VI. The V_0 values for perdeuterobenzene were taken as the same as those for benzene, and the derived B values are only marginally smaller. Figure 5 shows a comparison of experimental viscosity coefficients with values calculated using Eq. (3) with $A = -1.0$, and B values for perdeuterobenzene taken as identical to those for benzene. Other parameters are taken from Table VI. Experimentally, viscosity coefficients at the highest pressures are up to eight times the atmospheric viscosities, and the fit is generally within ±2% over the whole density range. At 400 MPa, it appears that the calculated viscosities are too high by about 5%.

For the equimolar benzene + hexafluorobenzene mixture, V_0 is given by the average of the V_0 values for benzene and for hexafluorobenzene. It is interesting to note that the values for B differ only slightly from the values

Table VI. Values of V_0 and B in Eq. (3)

Liquid	T (°C)	V_0 ($\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$)	B
Benzene	25.0	58.1	1.654
	50.0	57.2	1.671
	75.0	56.3	1.691
	100.0	55.4	1.717
Perdeuterobenzene	25.0	58.1	1.646
	50.0	57.2	1.667
	75.0	56.3	1.684
	100.0	55.4	1.708
Hexafluorobenzene	25.0	77.7	1.560
	50.0	76.6	1.584
	75.0	75.5	1.616
	100.0	74.4	1.654
Benzene + Hexafluorobenzene	50.0	66.9	1.593
($X = .05$)	75.0	65.9	1.618
	100.0	64.9	1.629

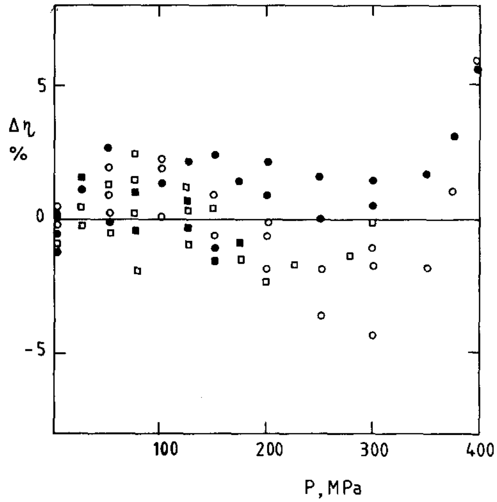

Fig. 5. Comparison of experimental viscosity coefficient data with values calculated using Eq. (3) with V_0 and B given in Table VI, except for C_6D_6, for which B values of C_6H_6 were used. ○, benzene; ●, perdeuterobenzene; □, hexafluorobenzene; ■, equimolar mixture of benzene + hexafluorobenzene. $\Delta\eta = 100(\eta_{\text{calc}} - \eta_{\text{exp}})/\eta_{\text{exp}}$.

derived for hexafluorobenzene and are significantly lower than the values expected on the basis of the equation used [Eq. (6), ref. 2] to represent the B values for n-alkane mixtures in terms of the values of the pure components. Such a difference in behavior is not unexpected since there is evidence [17] for weak enhanced intermolecular interactions in liquid mixtures of benzene + hexafluorobenzene.

8. THE GRUNBERG AND NISSAN EQUATION

The viscosity coefficient data for the benzene + hexafluorobenzene system have been used to determine the pressure and temperature dependence of the parameter G in the Grunberg and Nissan equation [5]:

$$\ln\eta_M = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2G \tag{4}$$

where η_M is the viscosity coefficient of the mixture, and η_i is the viscosity of component i of mole fraction x_i. G is the characteristic constant. The results are shown in Fig. 6. G is small and negative and shows no significant variation with changes in temperature and pressure for this system. Indeed, a constant value of G of -0.28 reproduces the mixture viscosities to within ±1.6%.

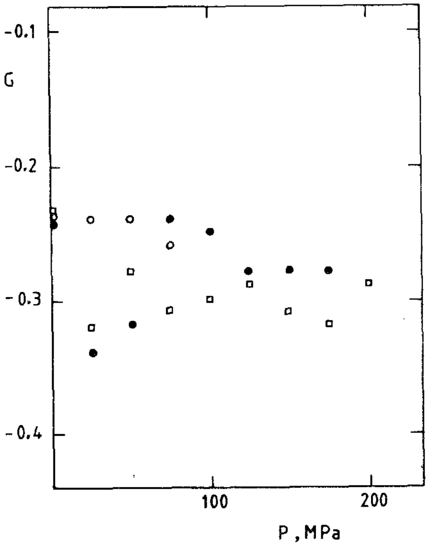

Fig. 6. Pressure and temperature dependence of the Grunberg G for the equimolar benzene + hexafluorobenzene mixture. ○, 50°C; ●, 75°C; □, 100°C.

9. CONCLUSIONS

Viscosity coefficients for benzene, perdeuterobenzene, hexafluorobenzene, and an equimolar mixture of benzene + hexafluorobenzene have been measured with an estimated accuracy of ±2% using a self-centering falling body viscometer at 25, 50, 75, and 100°C and at pressures up to the freezing pressure. Results for a given liquid at different temperatures are correlated very satisfactorily by superimposing plots of η', where $\eta' = 9.118 \times 10^7 \eta V^{2/3}/(MRT)^{1/2}$, versus $\log V$. This method can be used for accurate prediction of viscosity coefficients under other experimental conditions. An alternative prediction method is given by the free-volume form of equation, containing two adjustable parameters which have a smooth temperature dependence. For the benzene + hexafluorobenzene mixture, the Grunberg and Nissan equation with a constant G of -0.28 reproduces the data to within ±1.6%.

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