Shear Viscosity of Methanol and Methanol + Water Mixtures Under Pressure

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Shear viscosities have been measured for methanol up to 400 MPa at 298, 313, and 323 K and for methanol–water mixtures (a) at 0.1 MPa and 278 K and (b) up to 300 MPa at 298 K. Where a comparison is possible the results are in good agreement with literature data. The data for the mixtures are discussed in terms of hydrogen bonding in methanol and water and by the use of excess viscosities.

1. INTRODUCTION

The transport properties of methanol–water mixtures are of particular interest because both pure components have extensive hydrogen-bonded networks and both have labile protons which can be freely exchanged between them [1]. Easteal and Woolf [2] have recently measured volume ratios (V_p/V_0) of methanol–water mixtures for pressures up to 280 MPa at several temperatures and used them to obtain thermodynamic and excess thermodynamic properties of the mixtures [3]. Although Kubota and co-workers [4] had made p–V–T measurements for similar mixtures up to 200 MPa, their shear viscosity measurements extended to only 60 MPa. Here shear viscosities are reported for (a) methanol up to 400 MPa at 298.15, 313.15, and 323.15 K and methanol–water mixtures (b) up to 310 MPa at 298.15 K and (c) at 0.1 MPa and 278.15 K.

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2. EXPERIMENTAL

2.1. Atmospheric-Pressure Measurements

The methanol was Merck "pro analysi" grade which had been distilled over magnesium. Kinematic viscosities were measured with a flared capillary viscometer which had been calibrated using n-hexane, toluene, benzene, cyclohexane, and ethanol. Shear viscosities were evaluated from the kinematic viscosities using literature [2] densities.

2.2. High-Pressure Measurements

The methanol was Aldrich spectrophotometric grade (gold label) of stated purity 99.9%. This was used for all experiments except those of mol fraction (methanol) 0.65 and 0.80, which were prepared from Rathburn chemicals, HPLC grade. The solutions were made by weight with distilled water.

The measurements were made using a self-centering falling body viscometer which has been described in detail elsewhere [5, 6]. For laminar flow in this instrument the viscosity coefficient, η_p, at pressure p and temperature T, is related to the sinker fall time, t_p, by the equation

$$\eta_p = \frac{t_p(1 - \rho_L/\rho_s)}{A[1 + 2\alpha(T - T_r)][1 - 2\beta(p - p_0)]} \tag{1}$$

where ρ_L and ρ_s are, respectively, the liquid and sinker densities at T and p, α is the linear expansion coefficient and β the linear compressibility of the sinker and tube, T_r is a reference temperature (298.15 K), and the subscript 0 indicates a value at atmospheric pressure. The viscometer constant, A, is determined by calibration with liquids of known viscosity at atmospheric pressure and is independent of temperature and pressure. However, A is found to increase slightly (by about 7%) with increasing Reynolds number, and this effect is described by the relation

$$A = A_r \left\{ 1 + \left[\frac{B}{t(1 - \rho_L/\rho_s)} \right]^N \right\} \tag{2}$$

Table I. Viscometer Constants

A_0 (Pa^{-1})	46.6×10^3
β (Pa^{-1})	2×10^{-12}
α (K^{-1})	1.4×10^{-5}
B (s)	0.03
N	0.5

where A_r, B, and N are instrumental constants given in Table I. To minimize systematic errors the instrument is used to determine the ratio of the viscosity at pressure to that at atmospheric pressure and the same temperature. Thus the working equation becomes

$$\frac{\eta_p}{\eta_0} = \frac{t_p}{t_0} \cdot \frac{(1 - \rho_L/\rho_s)}{(1 - \rho_{L0}/\rho_{s0})} \cdot \frac{\left\{ 1 + \left[\dfrac{B}{t_0(1 - \rho_{L0}/\rho_{s0})} \right]^N \right\}}{\left\{ 1 + \left[\dfrac{B}{t_p(1 - \rho_L/\rho_s)} \right]^N \right\} [1 - 2\beta(p - p_0)]} \tag{3}$$

The accuracy of viscosity ratios so obtained is estimated to be $\pm 2\%$.

Temperatures were measured to ± 0.01 K and were maintained constant to ± 0.03 K; fluctuations in pressure were usually less than 0.4 MPa. For the system studied here accurate values of the shear viscosity at atmospheric pressure are available in the literature [7]. These values were obtained from conventional capillary viscometers and they have been used to provide the reference values at atmospheric pressure in this work.

The use of Eq. (3) requires the density of the liquid. The secant bulk modulus equation coefficients given by Easteal and Woolf [2] enable extrapolation of their data for about 50 MPa (from 280 MPa) without the densities so obtained introducing significant error into η_p/η_0. However, for pure methanol where the measurements exceed 400 MPa, it is necessary at pressures above 300 MPa to use the specific volumes tabulated by Bridgman [8]. Gibson [9] has pointed out that those data contain a systematic (but unspecified) error. Here allowance has been made for that error by the following procedure.

(a)   Values of V_p/V_0 from Bridgman [8] [subscript B in Eq. (4)] and Easteal and Woolf [2] (subscript E) were compared from 150 to 280 MPa using the ratio

$$Q = (V_p/V_0)_E/(V_p/V_0)_B \tag{4}$$

$[(V_p/V_0)_B$ at 298.15 K was interpolated from Bridgman's values at 293, 303, 313, and 323 K].

(b)   The Q were expressed

$$Q = a_0 + a_1 p \tag{5}$$

with the following coefficients

T (K)	a_0	$-10^5 a_1$ (MPa^{-1})
298.15	0.9940	1.935
313.15	0.9914	0
323.15	0.9951	2.054

Table II. Viscosity Coefficients and Flow Times for Methanol

T (K)	p (MPa)	ρ (kg·m^{-3})	t (s)	η (10^{-3} Pa·s)
298.18	0.1	786.63	29.58	0.544
	26.4	809.4	32.95	0.605
	50.3	826.7	36.70	0.673
	95.6	853.2	42.96	0.787
	150.6	878.8	50.49	0.924
	192.6	895.4	55.86	1.021
	284.8	927.1	68.74	1.254
	400.3	959.8	84.40	1.536
298.14	0.1	786.63	30.62	0.544
	28.8	811.4	34.78	0.617
	50.6	826.9	37.81	0.670
	106.8	859.0	45.09	0.797
	154.1	880.3	52.47	0.927
	203.3	899.4	59.30	1.047
	321.3	937.9	75.65	1.332
313.17	0.1	772.32	24.54	0.450
	24.7	795.4	27.59	0.505
	54.0	817.6	31.19	0.571
	99.7	844.9	35.64	0.651
	149.0	868.1	40.84	0.745
	193.4	885.5	46.38	0.845
	302.1	920.3	58.48	1.064
	398.8	946.2	68.86	1.251
323.12	0.1	762.77	21.59	0.396
	23.6	786.0	23.84	0.437
	52.4	808.7	26.82	0.491
	57.6	812.4	28.05	0.513
	109.6	842.9	33.30	0.610
	186.7	876.8	40.64	0.741
	198.8	881.5	41.48	0.756
	300.8	916.9	51.42	0.936
	366.4	936.2	57.95	1.053
	472.8	965.2	69.56	1.262
323.15	0.1	762.77	20.89	0.396
	19.3	782.2	23.36	0.443
	48.6	806.0	26.48	0.501
	88.6	831.6	30.62	0.579
	144.0	859.2	35.69	0.674
	198.6	881.4	40.18	0.757
	294.3	914.8	49.73	0.936
	417.1	950.3	61.57	1.156
323.07	0.1	762.8	20.80	0.396
	203.8	883.3	40.75	0.771
	302.6	917.6	50.11	0.947

Table III. Viscosity Coefficients and Flow Times for
Methanol–Water Mixtures at 298.15 K

x (CH$_3$OH(	p(MPa)	ρ (kg·m^{-3})	t (s)	η (10^{-3} Pa·s)
0.0922	0.1	971.90	72.72	1.282
	30.5	984.3	73.31	1.290
	52.0	992.7	73.58	1.294
	108.0	1013.1	74.67	1.309
	162.9	1031.3	75.92	1.328
	240.6	1054.7	78.85	1.376
	342.5	1081.6	83.71	1.456
0.2474	0.1	936.60	87.30	1.577
	32.4	950.2	93.00	1.678
	53.8	958.6	95.16	1.715
	106.4	977.7	100.10	1.800
	153.6	993.3	103.40	1.856
	220.3	1013.1	110.50	1.980
	268.3	1026.2	116.40	2.083
	327.9	1041.2	123.00	2.197
0.3642	0.1	911.00	84.40	1.524
	25.7	923.0	90.20	1.627
	53.3	934.9	94.67	1.706
	104.8	954.8	102.56	1.844
	145.3	968.9	107.68	1.933
	208.6	988.8	117.97	2.114
	269.1	1006.0	127.48	2.281
	312.0	1017.5	134.44	2.403
0.5017	0.1	881.15	71.62	1.314
	20.3	892.5	76.92	1.410
	43.4	904.3	81.32	1.489
	97.2	928.0	91.47	1.671
	141.4	944.7	99.39	1.813
	199.7	964.2	110.15	2.006
	269.9	985.2	123.32	2.242
	342.2	1005.3	137.72	2.499
0.6519	0.1	850.00	57.68	1.061
	25.2	866.1	62.43	1.147
	52.8	881.5	67.64	1.241
	99.0	903.4	76.24	1.396
	151.8	924.5	85.71	1.567
	214.2	946.1	97.49	1.779
	273.9	964.7	109.08	1.970
	355.3	988.5	125.31	2.279
0.8031	0.1	821.10	44.42	0.827
	20.1	836.3	47.78	0.888
	57.5	859.8	54.43	1.010
	102.1	882.7	61.75	1.144
	160.6	907.4	71.34	1.320
	213.6	926.6	80.18	1.481
	281.5	948.8	91.84	1.694
	352.7	970.8	104.74	1.928

Table IV.   Shear Viscosity of Methanol–Water Mixtures at 278.15 K and 0.1 MPa

x (CH$_3$OH)	η (mPa · s)
0	1.520
0.0494	2.046
0.0969	2.508
0.1990	3.035
0.2755	3.039
0.3920	2.719
0.5821	1.973
0.8125	1.199
1.0	0.737

At pressures above 300 MPa, densities were thus obtained from Bridgman's data corrected by the appropriate value of Q.

Densities ρ_{L0} of methanol at 0.1 MPa were obtained from the data given by Dizechi and Marschell [7]. For the mixtures at 298.15 K the densities were obtained by interpolation of the excess volume data of McGlashan and Williamson [10].
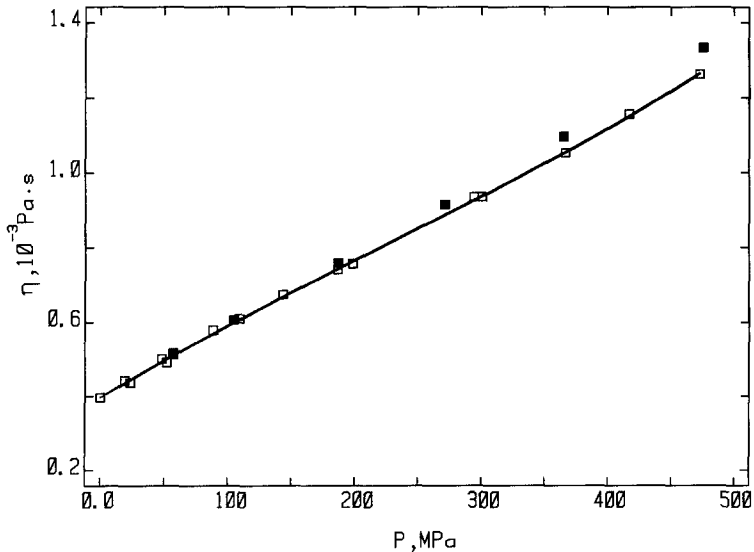
Fig. 1.   Shear viscosity of methanol under pressure at 323 K: ■, Ref. 12; □, this work.

3. RESULTS AND DISCUSSION

The shear viscosity ratios obtained from Eq. (1) are given with the experimental fall times and liquid densities in Tables II and III; the shear viscosities measured at 278.15 K and 0.1 MPa are given in Table IV. At 298 K the results for methanol agree within the estimated error ($\pm 2\%$) with the measurements of Kubota and co-workers [4] which were made up to 68 MPa. At 313 K there is a similar good agreement with the measurements of Isakova and Oshueva [11] up to their maximum pressure of 25 MPa. The comparison in Fig. 1 over the full pressure range of the measurements at 323 K with those of Harlow [12] shows the latter to diverge with increasing pressure. The errors in the specific volume data
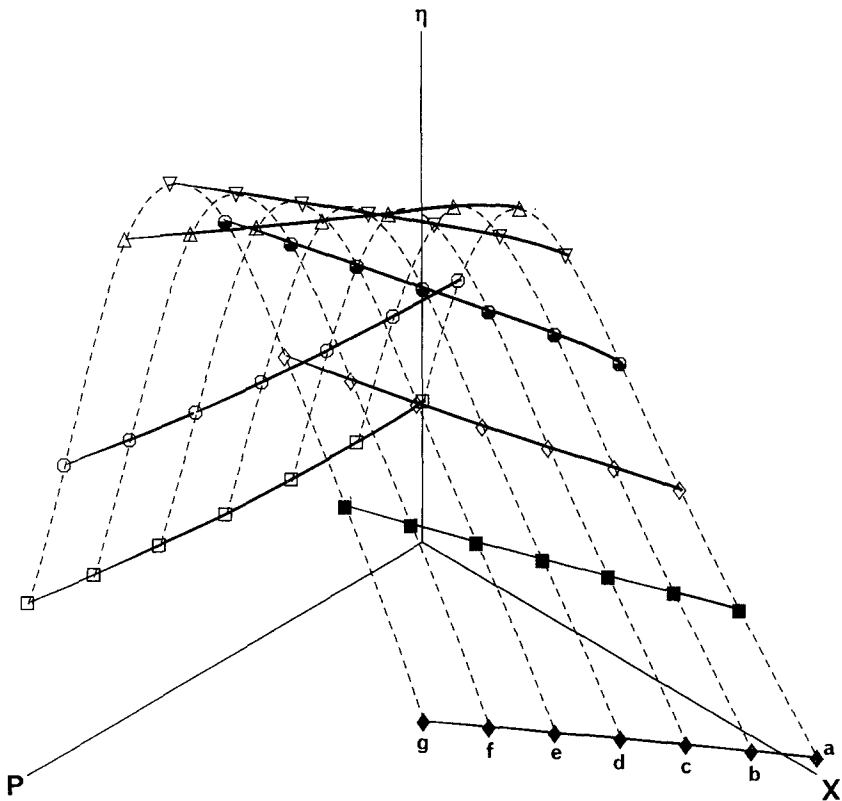
Fig. 2. Shear viscosity of methanol–water mixtures at 298 K on pressure, p, and methanol mol fraction, x. (a) 0.1 MPa; (b) 50 MPa; (c) 100 MPa; (d) 180 MPa; (e) 200 MPa; (f) 250; (g) 300 MPa. □, $x = 0$; ○, $x = 0.0922$; △, $x = 0.2474$; ▽, $x = 0.3612$; ◗, $x = 0.5$; ◇, $x = 0.6$; ■, $x = 0.8$; ◆, $x = 1$.

of Bridgman [8] used by Harlow would probably account for most of the differences observed, although part may be due to the use in his viscometer of a guided falling body.

For the mixtures at 298 K the agreement with the data ($p_{max} = 68$ MPa) of Kubota and co-workers [4] is within their experimental error ($\pm 2\%$).

The variation of η for the mixtures with pressure and composition at 298.15 K is shown in Fig. 2 with viscosities for water taken from the literature [13, 14]. The isopleths show that up to about $x = 0.25$ the pressure dependence is similar to that of water, and for $x \geqslant 0.50$ the dependence resembles methanol-like behavior; however, in the intermediate region there is a more complex variation of η with pressure. This varying
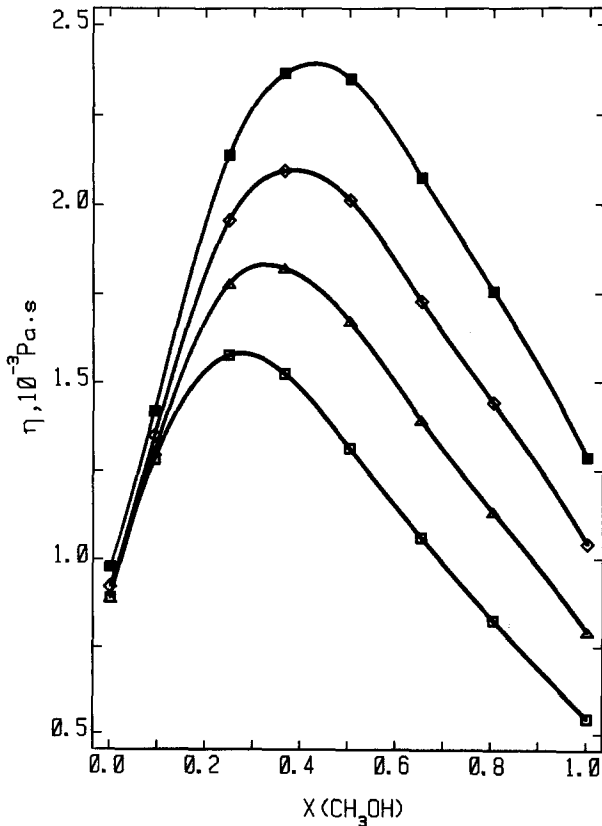
Fig. 3. Dependence of shear viscosity of methanol–water mixtures at 298 K on pressure and methanol mol fraction: □, 0.1 MPa; △, 100 MPa; ◇, 200 MPa; ■, 300 MPa.

behavior is similar to that described by Lumry and co-workers [15] as characteristic of solutions of hydrophilic solutes in water.

The isobars in Fig. 2 indicate a change in the position of the maximum value of η with increasing pressure; Fig. 3 shows that the change is from $x \approx 0.28$ at 0.1 MPa to $x \approx 0.44$ at 300 MPa (Kubota and co-workers [4] observed similar changes for pressures up to their maximum of 68 MPa).

It is useful to remove from the position of the maximum in η versus p the contribution of the pure components by defining the excess viscosity.

$$\eta_E(x, T, p) = \eta(x, T, p) - [\eta_1(x = 1, T, p)$$

$$- \eta_2(x = 0, T, p)]x - \eta_2 \ (x = 0, T, p) \qquad (6)$$
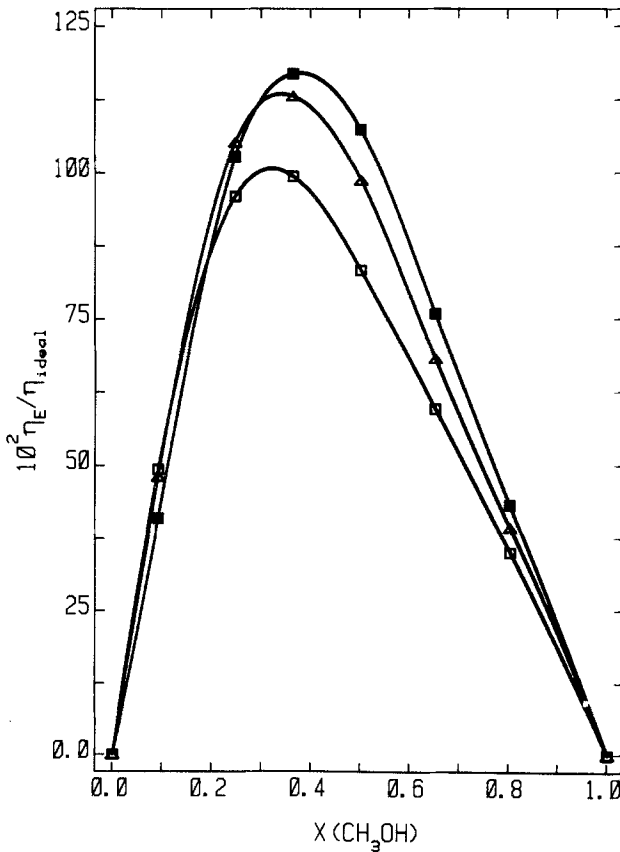
Fig. 4. Excess shear viscosity for methanol–water mixtures under
pressure at 298 K: legend as for Fig. 3.

The η_E shown in Fig. 4 have maxima between $x = 0.29$ (0.1 MPa) and $x = 0.36$ (300 MPa). It is of interest to note that the excess Gibbs energies of the solutions [2] also have maxima varying similarly with pressure at compositions in the range $x = 0.25$ to 0.35. The variation of η_E with temperature at 0.1 MPa is shown in Fig. 5. Values of η for the calculation of η_E were obtained from this work at 278.15 K, from Refs. 4, 16, and 17 at 298.15 K, and from Refs. 4, 7, and 16–19 at 323.15 K. The effect of an isobaric increase in temperature is similar to that of the isothermal increase in pressure shown in Fig. 4: the position of the curve and its maximum is shifted to higher methanol compositions. However, the overall effect of an increase in temperature is to decrease η_E, whereas up to 300 MPa at 298 K, an increase in pressure increases η_E. This implies that the effect of pressure
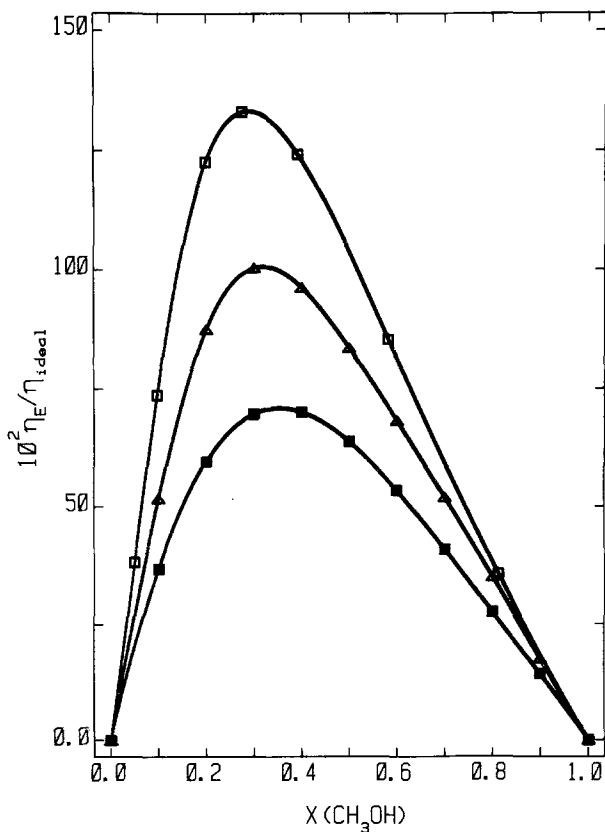

Fig. 5. Temperature dependence of excess shear viscosity for methanol–water mixtures at 0.1 MPa: □, 278.15 K; △, 298.15 K; ■, 323.15 K.

has a proportionately different influence on the two components, and of course, this is evident from the well-known anomalous effect of pressure on the shear viscosity of water for temperatures up to 305 K.

At low methanol concentrations the rapid increase in shear viscosity consequent on the addition of methanol seems to be due to an enhancement of the water network structure, presumably by accommodation of methanol molecules in cavities within the structure accompanied by formation of hydrogen bonds between the methanol and the water molecules. The shift of the maximum in η to higher mol fractions with increasing pressure suggests a pressure-induced promotion of the incorporation of methanol molecules into water cavities, thereby stabilizing the water structure. The decrease in shear viscosity above $x \cong 0.35$ presumably reflects the disintegration of the water structure by the methanol.

ACKNOWLEDGMENTS

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