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SPECIFIC VOLUME AND VISCOSITY OF METHANOL-WATER MIXTURES UNDER HIGH PRESSURE

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New experimental data on the specific volume and the viscosity of methanol-water mixtures are presented as functions of temperature, pressure and composition.

The specific volume has been measured by means of an improved "high pressure burette" apparatus within an error of 0.05 percent, covering temperatures from 10 to 75°C and pressures up to 2000 bar. The viscosity has been obtained by a falling-cylinder viscometer with the uncertainty of less than two percent, covering the same temperature range and pressures up to 700 bar.

The specific volume of this system is found to decrease monotonously with increasing pressure. The experimental results agree well with several literature values. The numerical data at each temperature and composition are correlated satisfactorily as a function of pressure by the Tait equation. The isothermal compressibilities and the excess volumes are also determined from the experimental data. It is found that a definite minimum appears on the isothermal compressibility versus composition isobars at temperatures lower than 25°C. The excess volumes are always negative and increase with increasing pressure or lowering temperature.

The viscosity of pure methanol and its water mixtures is found to increase almost linearly with increasing pressure, whereas that of water decreases with pressure at 10°C and 25°C within the present experimental conditions. The viscosity isotherms can be represented by a quadratic equation of pressure within the experimental errors. As for the composition dependence of the viscosity, a distinct maximum appears near 0.3 mole fraction of methanol on all isobars at each temperature. The maximum shifts slightly to higher methanol fraction with increasing temperature or pressure.

Introduction

It is well known that alcohol molecules in aqueous solutions give strong influence on the water structure [1,2] and that alcohol-water systems show consequently some anomalies in various physical properties.

Recently, the reliable experimental data of these systems on various physical properties are required for both theoretical works and engineering calculations. Although a number of measurements at atmospheric pressure have been reported, a few are available under high pressure.

This paper provides extensive and accurate data on PVT relations and viscosity for methanol-water binary mixtures as functions of temperature, pressure and composition. Numerical data have

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1) F. Franks and D. J. G. Ives, *Quart. Rev.*, 20, 1 (1966)

2) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, 36, 3382, 3401 (1962)

been determined at temperatures ranging from 10°C to 75°C, and pressures up to 2000 bar for the specific volume, and to 700 bar for the viscosity, employing a modified piezometer and a falling-cylinder viscometer. Empirical correlation formulas have also been presented for both properties using the present results.

Experimentals

PVT measurements

The schematic diagram of the experimental apparatus is shown in Fig. 1. The sample liquid of known weight is introduced into a high pressure vessel D and upper part of burette G. The pressure is transmitted through mercury filled in C and G from an oil pump A. The volume change of the test liquid is detected from the displacement of a small iron float on the surface of the mercury column by means of a differential transformer. The high pressure vessel D consists of coaxial double cylinders as shown in Fig. 2. The inner cylinder is a thin-walled sample cell, to the outer wall of which somewhat lower pressure is applied separately from the oil pump in order to minimize the deformation of the cell.[3]

The vessel D and burette G are immersed in a liquid thermostat controlled within ±0.01°C.

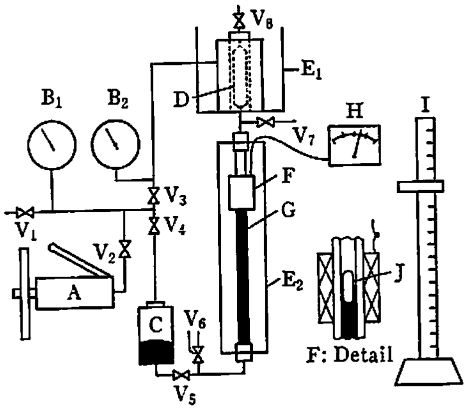

Fig. 1 Schematic diagram for PVT measurement
A Oil pump
B$_{1,2}$ Bourdon gauge
C Mercury reservoir
D High pressure vessel
E$_{1,2}$ Thermostat
F Differential transformer
G High pressure burette
H Ammeter
I Cathetometer
J Iron float

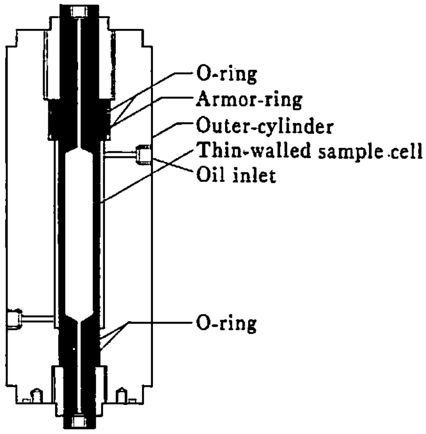

Fig. 2 Diagram of high pressure vessel

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[3] B. Le Neindre and B. Vodar (Ed.), "Experimental Thermodynamics", vol. II, p. 421, Butterworths, London (1975)

The pressure is measured by Bourdon gauges calibrated against a pressure balance. The uncertainty in pressure measurements is estimated to be less than 0.1 percent.

Using the displacement of the iron float, the specific volume of the sample liquid is calculated by the following equation:

$$v=v_0-\frac{1}{W}\{\Delta V_{\mathrm{app}}-(\Delta V_{\mathrm{tub}}+\Delta V_{\mathrm{bur}}+\Delta V_{\mathrm{cell}})\} \qquad (1)$$

where

v_0: specific volume in $\mathrm{cm^3 \cdot g^{-1}}$ of the sample at pressure P_0 bar,
ΔV_{app}: apparent volume change in $\mathrm{cm^3}$ of the sample at P bar,
ΔV_{tub}: volume change in $\mathrm{cm^3}$ of the connecting tube at P bar,
ΔV_{bur}: volume change in $\mathrm{cm^3}$ of the high pressure burette at P bar,
ΔV_{cell}: volume change in $\mathrm{cm^3}$ of the thin-walled sample cell at P bar,
W: total weight in g of the sample.

ΔV_{tub}, ΔV_{bur}, and ΔV_{cell} were calculated employing the elasticity theory. The uncertainty of the present specific volume values is estimated to be less than 0.05 percent.

Viscosity measurements

The viscosity is measured by a falling-cylinder viscometer. The details of the viscometer were described elsewhere[4].

The apparatus consists of a precisely bored Pyrex glass tube equipped coaxially in a high pressure vessel and a glass cylindrical plummet with hemispherical ends. The plummet is provided with four small projecting lugs at each end of the cylindrical part, which acts as a guide to keep plummet concentric when it falls. The falling time of the plummet is determined within ±0.1 ms by an electronic time-interval counter using a He-Ne gas laser beam passed through a pair of optical windows and a phototransister. The temperature of the sample is maintained constant within ±0.05°C by circulating a thermostatic fluid through the jacket around the pressure vessel. The pressure is measured by a Bourdon gauge with the same accuracy as in the case of *PVT* measurements.

The instrument constant and its change with both temperature and pressure are calibrated with the aid of the experimental viscosity values under atmospheric pressure obtained by an Ostwald viscometer and of the reference viscosity of water correlated by the International Association for the Properties of Steam (1974). The uncertainty of the present viscosity values is estimated to be less than 2.0 percent.

Materials

Methanol used was obtained from Wako Pure Chemical Industries Ltd. The reported purity is more than 99.5% in volume. Methanol and water were purified several times by the fractional distillation.

The mixtures of methanol and water were prepared by weighing, using an analytical balance

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[4] Y. Tanaka, T. Yamamoto, Y. Satomi, H. Kubota and T. Makita, *Rev. Phys. Chem. Japan*, **47**, 12 (1977)

with a sensitivity of ±0.1mg. Therefore their composition, mole fraction of methanol, should be substantially accurate within 0.01%.

Table 1 The Specific Volume of Methanol-Water Mixtures in cm³/g

Temp. °C	X = 0.00		X = 0.25		X = 0.50		X = 0.75		X = 1.00	
	P	v	P	v	P	v	P	v	P	v
10	1.0	1.0003	1.0	1.0594	1.0	1.1214	1.0	1.1861	1.0	1.2486
	174.4	0.9918	33.1	1.0578	14.5	1.1205	8.6	1.1854	21.0	1.2459
	343.7	0.9845	168.9	1.0513	336.8	1.0993	162.0	1.1704	157.5	1.2282
	517.8	0.9774	341.5	1.0436	508.5	1.0899	330.6	1.1559	329.9	1.2094
	690.5	0.9706	514.3	1.0366	681.2	1.0812	501.9	1.1429	502.3	1.1934
	863.6	0.9641	687.7	1.0296	853.2	1.0733	676.7	1.1311	675.0	1.1793
	1035.6	0.9580	859.4	1.0231	1024.9	1.0657	848.0	1.1205	843.2	1.1670
	1208.3	0.9521	1029.7	1.0170	1197.9	1.0585	1020.8	1.1109	1017.3	1.1552
	1380.0	0.9464	1193.8	1.0115	1370.7	1.0517	1193.8	1.1019	1188.0	1.1445
	1549.6	0.9412	1373.8	1.0054	1515.8	1.0464	1367.2	1.0933	1364.5	1.1346
	1738.5	0.9359	1551.0	0.9997	1715.1	1.0392	1711.6	1.0777	1443.4	1.1303
	1898.5	0.9314	1720.6	0.9945	1886.0	1.0334	1883.3	1.0706	1537.5	1.1255
	2070.8	0.9272	1891.9	0.9895	2063.6	1.0276	2055.0	1.0637	1695.7	1.1179
			2065.0	0.9846					1883.3	1.1091
									2056.3	1.1015
25	1.0	1.0030	1.0	1.0683	1.0	1.1340	1.0	1.2037	1.0	1.2708
	138.9	0.9968	134.5	1.0611	135.2	1.1241	135.2	1.1891	137.9	1.2509
	276.8	0.9909	284.6	1.0546	275.6	1.1150	276.9	1.1762	279.0	1.2335
	416.8	0.9850	420.1	1.0486	420.1	1.1063	417.7	1.1648	415.3	1.2189
	551.2	0.9799	553.6	1.0430	557.0	1.0985	554.9	1.1547	553.6	1.2055
	693.2	0.9745	714.7	1.0366	696.0	1.0913	693.6	1.1452	697.4	1.1930
	831.8	0.9694	830.2	1.0321	850.2	1.0837	831.2	1.1364	837.1	1.1821
	966.3	0.9647	970.6	1.0269	975.4	1.0779	967.8	1.1282	963.0	1.1727
	1102.8	0.9601	1108.2	1.0218	1108.2	1.0719	1109.6	1.1205	1103.3	1.1633
	1241.4	0.9555	1248.6	1.0170	1243.0	1.0661	1245.8	1.1132	1240.3	1.1547
	1383.1	0.9511	1384.1	1.0124	1384.1	1.0603	1384.1	1.1064	1381.4	1.1462
	1522.7	0.9467	1520.4	1.0081	1518.3	1.0552	1520.4	1.1000	1532.8	1.1380
	1652.7	0.9426	1660.0	1.0036	1658.0	1.0500	1657.3	1.0940	1658.7	1.1312
	1798.8	0.9386	1798.4	0.9994	1803.9	1.0448	1797.0	1.0880	1799.7	1.1242
	1937.1	0.9347	1942.2	0.9952	1934.6	1.0403	1938.0	1.0822	1949.8	1.1171
	2077.1	0.9309	2073.6	0.9913	2072.9	1.0355	2075.7	1.0769	2069.4	1.1118
50	1.0	1.0121	1.0	1.0862	1.0	1.1606	1.0	1.2367	1.0	1.3111
	138.6	1.0060	137.9	1.0786	128.3	1.1495	138.6	1.2198	131.0	1.2859
	276.3	1.0003	280.4	1.0713	274.2	1.1383	273.5	1.2053	276.3	1.2646
	412.5	0.9948	415.3	1.0647	415.9	1.1286	413.9	1.1921	413.9	1.2476
	554.3	0.9892	566.7	1.0577	555.6	1.1196	550.8	1.1805	548.7	1.2324
	702.9	0.9838	696.7	1.0521	691.9	1.1116	691.2	1.1697	693.9	1.2181
	835.0	0.9790	832.3	1.0464	828.1	1.1041	834.3	1.1595	832.3	1.2058
	974.7	0.9742	970.6	1.0408	972.0	1.0966	974.7	1.1502	967.1	1.1949
	1104.7	0.9698	1106.1	1.0356	1107.5	1.0900	1114.4	1.1418	1106.1	1.1845
	1247.2	0.9653	1242.3	1.0306	1245.1	1.0836	1248.6	1.1340	1245.1	1.1747
	1379.3	0.9612	1384.1	1.0255	1384.1	1.0773	1380.0	1.1268	1384.1	1.1657
	1533.5	0.9564	1518.3	1.0210	1525.9	1.0712	1524.5	1.1195	1519.7	1.1575
	1659.4	0.9527	1656.6	1.0164	1659.4	1.0659	1656.6	1.1131	1656.6	1.1497
	1799.0	0.9486	1799.0	1.0117	1734.0	1.0629	1801.8	1.1064	1794.2	1.1423
	1934.6	0.9448	1938.0	1.0071	1926.3	1.0556	1943.6	1.1002	1938.7	1.1347
	2075.7	0.9408	2078.4	1.0027	2076.0	1.0502	2215.4	1.0890	2075.0	1.1282
75	1.0	1.0258	34.5	1.1057	45.1	1.1842	8.9	1.2699	34.5	1.3487
	174.4	1.0180	169.6	1.0973	167.2	1.1728	163.0	1.2467	164.1	1.3230
	342.7	1.0106	337.1	1.0873	333.7	1.1584	330.9	1.2257	330.9	1.2956
	513.3	1.0034	510.2	1.0780	505.0	1.1453	506.1	1.2068	505.4	1.2726
	688.1	0.9964	709.5	1.0679	667.0	1.1340	676.0	1.1909	676.7	1.2532
	856.3	0.9899	854.9	1.0611	759.4	1.1280	847.7	1.1767	846.0	1.2364
	1029.0	0.9835	1027.0	1.0535	851.1	1.1226	1020.8	1.1638	1004.9	1.2223
	1202.8	0.9774	1196.2	1.0464	1021.4	1.1128	1192.1	1.1522	1191.7	1.2076
	1370.3	0.9715	1370.7	1.0395	1194.8	1.1036	1352.0	1.1420	1365.1	1.1952
	1549.6	0.9657	1544.4	1.0329	1324.8	1.0969	1541.7	1.1311	1538.5	1.1836
	1732.3	0.9601	1717.1	1.0267	1542.7	1.0865	1710.9	1.1219	1706.8	1.1731
	1895.0	0.9555	1890.2	1.0208	1714.7	1.0790	1886.0	1.1131	1847.4	1.1649
	2067.4	0.9502	2061.9	1.0149	1885.4	1.0719	2058.4	1.1048	1920.5	1.1607
					2060.5	1.0651			1990.5	1.1568
									2058.4	1.1530

Results and Discussion

Specific volume

A part of experimental results is given in Table 1*, where P, v and X denote pressure in bar, specific volume in cm³/g and mole fraction of methanol in the mixtures, respectively. Specific volume values at 10°C and 75°C are also plotted in Figs. 3 and 4, together with the literature values for pure water. The specific volume decreases monotonously with increasing pressure throughout the experimental conditions at each composition. At the experimental temperatures except 75°C, the present results of pure water is found to agree quite well with the values given by Chen et al.5), Kell et al.6) and Grindley et al.7) The discrepancy between the present results and literature values at 75°C is within 0.09%. For the mixtures, there exist reliable data only at 25°C and 1000 bar by Gibson8) and 25°C and 1013 bar by Moriyoshi et al.9) As for the compression, literature values differ from the present results by less than 1.46% and 0.91%, respectively.

For each temperature and composition, the specific volume data are correlated as a function of pressure by the Tait equation :

$$\frac{v_0-v}{v_0}=C\log\frac{B+P}{B+P_0} \tag{2}$$

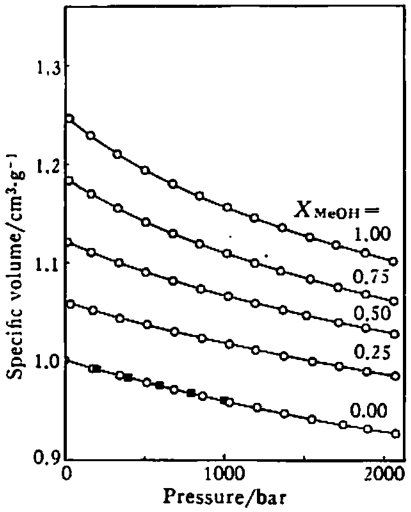

Fig. 3 Pressure dependence of the specific volume of Methanol-Water mixtures at 10°C
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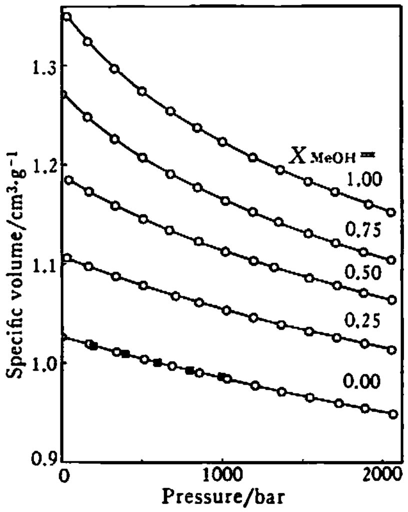

Fig. 4 Pressure dependence of the specific volume of Methanol-Water mixtures at 75°C
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* Data of X=0.15, 0.30, 0.35 at 10°C and 75°C, and of X=0.10, 0.15, 0.35 at 25°C and 50°C are available on request.

5) C. Chen, R.A. Fine and F. J. Millero, *J. Am. Chem. Soc.*, **57**, 1551 (1935)

6) G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc.*, **A258**, 565 (1965)

7) T. Grindley and J. E. Lind, Jr., *J. Chem. Phys.*, **54**, 3933 (1971)

8) R. E. Gibson, *J. Am. Chem. Soc.*, **57**, 1551 (1935)

9) T. Moriyoshi, Y. Morishita and H. Inubushi, *J. Chem. Thermodynamics*, **9**, 577 (1977)

Table 2 Coefficients of the Tait Equation

Temp. °C	Comp. X	B bar	C —	Ave. Dev. %	Max. Dev. %
10	0.00	2366	0.2691	0.02	0.04
	0.15	3172	0.3211	0.01	0.04
	0.25	2738	0.2896	0.01	0.03
	0.30	2471	0.2697	0.01	0.02
	0.35	2347	0.2747	0.00	0.01
	0.50	1564	0.2285	0.02	0.05
	0.75	1164	0.2332	0.02	0.04
	1.00	868	0.2235	0.02	0.03
25	0	2908	0.3069	0.01	0.02
	0.10	3214	0.3233	0.00	0.01
	0.15	3168	0.3196	0.01	0.03
	0.25	2686	0.2904	0.01	0.06
	0.35	2106	0.2606	0.01	0.02
	0.50	1658	0.2470	0.02	0.06
	0.75	1098	0.2290	0.02	0.07
	1.00	815	0.2283	0.02	0.04
50	0.00	3388	0.3406	0.02	0.05
	0.10	2920	0.3055	0.00	0.01
	0.15	2941	0.3037	0.01	0.01
	0.25	2458	0.2888	0.01	0.03
	0.35	1871	0.2583	0.01	0.02
	0.50	1389	0.2398	0.02	0.05
	0.75	963	0.2307	0.02	0.04
	1.00	633	0.2214	0.02	0.05
75	0	3268	0.3467	0.01	0.03
	0.15	2311	0.2805	0.01	0.03
	0.25	1909	0.2639	0.01	0.04
	0.30	1596	0.2450	0.01	0.03
	0.35	1653	0.2640	0.01	0.04
	0.50	1211	0.2419	0.01	0.02
	0.75	749	0.2338	0.01	0.02
	1.00	592	0.2309	0.03	0.05

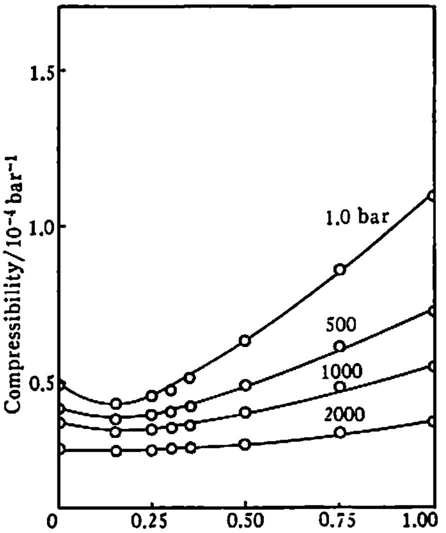

Fig. 5 Composition dependence of the isothermal compressibility at 10°C

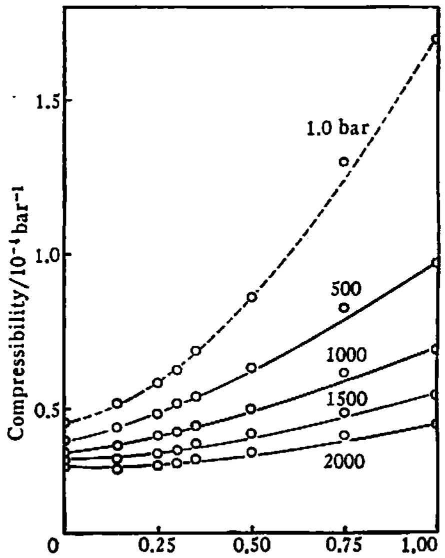

Fig. 6 Composition dependence of the isothermal compressibility at 75°C

where v_0 is the specific volume at a pressure P_0, and B and C are constants. The obtained Tait equations could reproduce experimental data with an average deviation of 0.03%. The coefficients for the Tait equation are listed in Table 2.

The isothermal compressibilities ;

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{3}$$

calculated using the Tait equation, at 10°C and 75°C, are plotted against the mole fraction of methanol in Figs. 5 and 6, respectively. It is found that a definite minimum exists near X=0.15 at 10°C and 25°C, but these minima fade out gradually as the temperature increases. At 75°C these minima disappear completely. This anomaly was also found in the ethanol-water system as reported in previous paper[4].

Excess volumes are also calculated at each experimental temperature by the following equation:

$$V^E = V_{mix} - \{V_{MeOH} \cdot X + V_{water}(1-X)\} \qquad (4)$$

The results of 25°C and 75°C are given in Figs. 7 and 8, respectively. At all the experimental conditions, excess volumes obtained are always negative, and it seems that pressure makes the excess volumes less negative and, in a sense, the mixture approaches the ideal solution with increasing pressure. At 25°C, the present results agree well with the literature values[10].

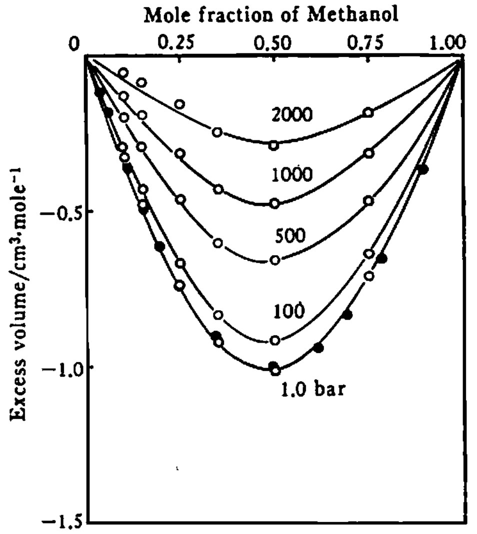

Fig. 7 Composition dependence of the excess volume of Methanol-Water mixtures at 25°C ○ : This work
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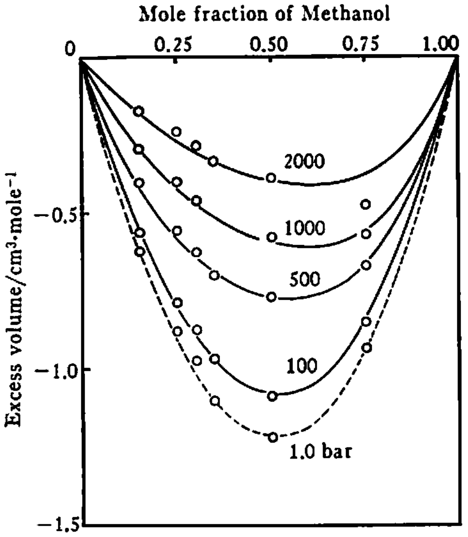

Fig. 8 Composition dependence of the excess volume of Methanol-Water mixtures at 75°C

Viscosity

The experimental results are tabulated in Table 3. The data obtained at atmospheric pressure are plotted as a function of composition in Fig. 9, where other experimental data[11~19] are also plotted for comparison. Each viscosity isotherm has a maximum at a composition near $X=0.30\sim0.35$. Agreement with the available data is satisfactory at 10°C and 25°C. However the discrepancy among them is somewhat notable at 50°C, where the largest deviation between the data of Sabnis et al.[13] and those of Traube[14] is about 11% near the maximum. The present data agree quite well

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[10] M. L. McGlashan and A. G. Williamson, *J. Chem. Eng. Data*, **21**, 196 (1976)

[11] S. Z. Mikhail and W. R. Kimel, *J. Chem. Eng. Data*, **6**, 533 (1961)

[12] T. W. Yergovich, G. W. Swift and F. Kurata, *J. Chem. Eng. Data*, **16**, 222 (1971)

[13] S. W. Sabnis, W. V. Bhagwat and R. B. Kanugo, *J. Indian Chem. Soc.*, **25**, 575 (1948)

[14] J. Traube, *Ber.*, **19**, 871 (1886)

Table 3 The Viscosity of Methanol-Water Mixtures in 10^{-3} Pa·s

Temp. °C	P bar	$X=0.00$	$X=0.15$	$X=0.25$	$X=0.30$	$X=0.35$	$X=0.50$	$X=0.75$	$X=1.0$
10	1.0	1.311*	2.360	2.551	2.500	2.419	1.971	1.272	0.6953
	99.1	1.301	2.364	2.588	2.575	2.491	2.044	1.327	0.7394
	197.2	1.292	2.378	2.637	2.616	2.561	2.095	1.374	0.7841
	295.2	1.284	2.381	2.667	2.656	2.624	2.152	1.426	0.8147
	393.3	1.278	2.399	2.708	2.737	2.694	2.225	1.472	0.8611
	491.4	1.270	2.408	2.733	2.793	2.767	2.275	1.528	0.8834
	589.4	1.268	2.428	2.756	2.848	2.835	2.346	1.581	0.9164
	687.5	1.264	2.448	2.792	2.902	2.906	2.384	1.624	0.9508
25	1.0	0.8911*	1.461	1.581	1.575	1.536	1.325	0.9031	0.5459
	99.1	0.8895	1.464	1.611	1.617	1.620	1.362	0.9770	0.5957
	197.2	0.8882	1.469	1.625	1.631	1.634	1.404	1.012	0.6220
	295.2	0.8872	1.468	1.646	1.637	1.675	1.437	1.048	0.6470
	393.3	0.8866	1.479	1.664	1.654	1.710	1.482	1.087	0.6730
	491.4	0.8864	1.495	1.686	1.698	1.753	1.524	1.124	0.7006
	589.4	0.8866	1.503	1.706	1.723	1.788	1.572	1.169	0.7330
	687.5	0.8872	1.508	1.731	1.745	1.818	1.617	1.197	0.7556
50	1.0	0.5468*	0.7811	0.8375	0.8423	0.8335	0.7551	0.5760	0.3947
	99.1	0.5486	0.8002	0.8497	0.8555	0.8462	0.7780	0.6012	0.4118
	197.2	0.5504	0.8102	0.8621	0.8638	0.8733	0.7875	0.6178	0.4280
	295.2	0.5522	0.8167	0.8682	0.8920	0.8937	0.8238	0.6318	0.4481
	393.3	0.5541	0.8213	0.8754	0.9002	0.9098	0.8389	0.6477	0.4663
	491.4	0.5561	0.8284	0.8870	0.9149	0.9192	0.8561	0.6710	0.4799
	587.4	0.5583	0.8307	0.8951	0.9205	0.9193	0.8682	0.6849	0.5090
	687.5	0.5605	0.8340	0.9095	0.9302	0.9364	0.8892	0.7074	0.5192
75	1.0	0.3783*	—	—	—	—	—	—	—
	99.1	0.3808	0.4958	0.5439	0.5555	0.5507	0.5220	0.4077	0.3130
	197.2	0.3832	0.5023	0.5510	0.5677	0.5640	0.5377	0.4284	0.3288
	295.2	0.3857	0.5154	0.5662	0.5788	0.5762	0.5506	0.4464	0.3421
	393.3	0.3882	0.5235	0.5776	0.5909	0.5901	0.5631	0.4725	0.3581
	491.4	0.3908	0.5341	0.5876	0.6029	0.6024	0.5781	0.4907	0.3728
	589.4	0.3934	0.5412	0.5977	0.6141	0.6141	0.5924	0.5075	0.3879
	687.5	0.3960	0.5454	0.6084	0.6260	0.6270	0.6053	0.5258	0.4036

* IAPS (1974)

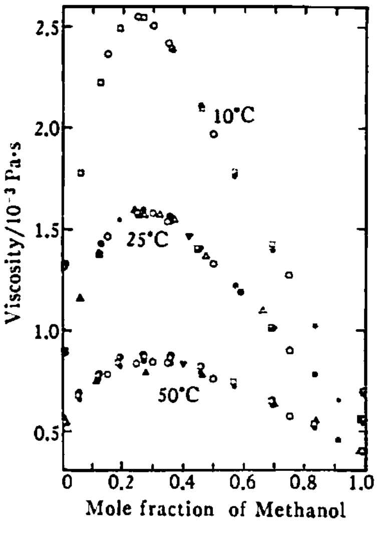

Fig. 9 Composition dependence of the viscosity of Methanol-Water mixtures at 1.0 bar

○ : This work ◗ : 14) ▼ : 18)
● : 11) △ : 15) □ : 19)
★ : 12) ▄ : 16)
▲ : 13) ⊗ : 17)

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with the results of Yergovich et al.12) at 10°C and those of Mikhail et al.11) at 25°C and 50°C obtained by the modified Ostwald viscometer.

The pressure dependences of the viscosity of this mixture at 10°C and 75°C are shown in Fig. 10. So far as we know, there exist no experimental viscosity data for this binary system under high pressure. On the other hand, three sets of experimental data are found in literature20~22) for pure methanol under pressures as shown in Fig. 11. Although the overlap of experimental conditions is limited, the consistence between our data and others is reasonable in view of the distances between the viscosity isotherms and their gradients.

The viscosity isotherms both in Fig. 10 and Table 3 show the following features:

1) The viscosity of mixtures always increases with pressure almost linearly, whereas the pressure coefficient of viscosity, $(\partial\eta/\partial P)_T$ for pure water is slightly negative at 10°C and 25°C within the present pressure range.
2) $(\partial\eta/\partial P)_T$ increases with the mole fraction of methanol at each temperature.
3) $(\partial\eta/\partial P)_T$ decreases with rising temperature for the mixture of a constant composition.

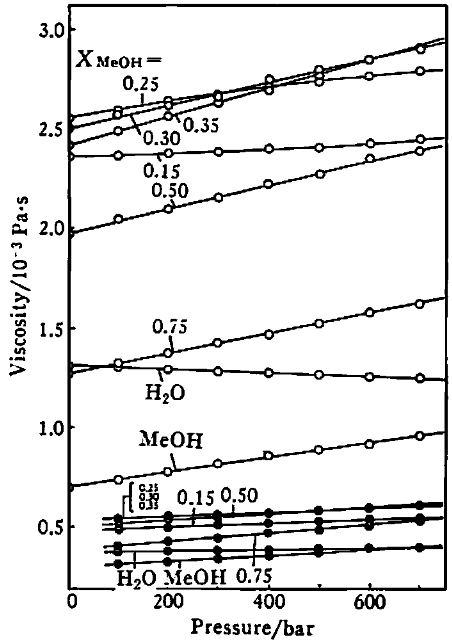

Fig. 10 Pressure dependence of the viscosity of Methanol-Water mixtures at 10°C and 75°C ○ : 10°C
● : 75°C

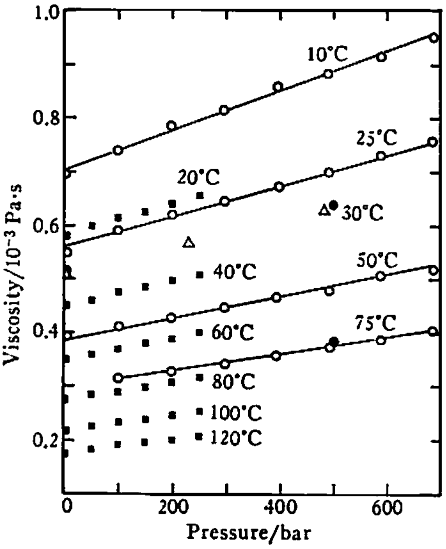

Fig. 11 Pressure dependence of the viscosity of Methanol
○ : This work △ : 21)
● : 20) ■ : 22)

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Table 4 Coefficients of Equation (5) for the Viscosity in 10^{-3} Pa·s

Temp. °C	x	B_1	$B_2\times10^4$	$B_3\times10^8$	Ave.Dev. %	Max.Dev. %
10	0.15	2.35982	0.4909	11.222	0.1	0.2
	0.25	2.54964	4.4894	-14.846	0.2	0.3
	0.30	2.50521	5.6206	2.801	0.3	0.7
	0.35	2.41965	6.9770	1.275	0.1	0.2
	0.50	1.97211	6.5852	- 7.250	0.3	0.5
	0.75	1.27307	5.1918	- 0.765	0.2	0.3
	1.00	0.69599	4.5280	-12.557	0.4	0.8
25	0.15	1.46090	0.1983	7.888	0.2	0.4
	0.25	1.58438	2.0574	0.607	0.2	0.4
	0.30	1.57728	3.7294	- 8.592	0.3	0.8
	0.35	1.54936	4.7665	-12.809	0.5	1.6
	0.50	1.32548	3.5879	9.645	0.1	0.3
	0.75	0.91291	5.1208	-14.530	0.6	1.6
	1.00	0.55266	3.4827	- 7.968	0.7	1.6
50	0.15	0.78387	1.4281	-10.483	0.3	0.4
	0.25	0.83942	0.9534	0.488	0.2	0.5
	0.30	0.83905	1.8249	- 7.071	0.4	1.0
	0.35	0.82950	2.5289	-14.873	0.5	0.8
	0.50	0.75363	2.3272	- 5.406	0.5	1.3
	0.75	0.57920	1.8117	0.402	0.5	0.7
	1.00	0.39410	1.7618	1.407	0.5	1.3
75*	0.15	0.48214	1.2488	- 4.518	0.3	0.6
	0.25	0.53042	1.2230	- 1.274	0.2	0.6
	0.30	0.54363	1.2077	- 0.149	0.03	0.1
	0.35	0.53721	1.3690	- 0.953	0.05	0.1
	0.50	0.50848	1.4282	- 0.248	0.1	0.2
	0.75	0.38381	2.3570	- 4.184	0.3	0.8
	1.00	0.29863	1.4747	0.730	0.1	0.3

* For 75°C isotherms, Eq. (5) is valid from 99 to 688 bar.

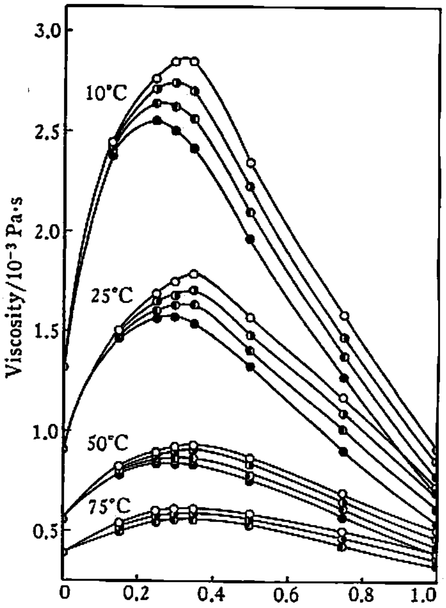

Fig. 12 Composition dependence of the viscosity of Methanol-Water mixtures at various temperatures

○ : 600 bar ◐ : 200 bar
◑ : 400 bar ● : 1.0 bar

The viscosity isotherms can be represented by a quadratic equation of pressure:

$$\eta=B_1+B_2P+B_3P^2 \tag{5}$$

where η is the viscosity in 10^{-3} Pa·s (=cP) and P the pressure in bar. The empirical coefficients for each mixture are listed in Table 4, with the average and the maximum deviations of the experimental data from the equation.

The composition dependence of the viscosity under high pressure is shown in Fig. 12. The viscosity isobars have the following features:

1) The composition dependence of the viscosity is evident at low temperatures, but it diminishes gradually with rising temperature.
2) Each isobar has a maximum near the composition of X=0.30~0.35. The maximum shifts slightly to higher methanol fraction with rising temperature or increasing pressure. The shift is more explicit at low temperatures.

These characteristic behaviors of viscosity for methanol-water mixtures under pressures are quite similar to those of ethanol-water system as reported in our previous paper[4]. The large positive departure in the viscosity-composition isobars from those of regular solutions, in which the additive law is held approximately, shows that the interaction between unlike molecules is seriously strong, as well as the behavior of the excess volume in Figs. 7 and 8. Water and alcohol molecules form various complex "clusters" according to the composition of mixtures, in addition to the "icebergs" of water molecules themselves and the association of alcohols. It is quite interesting that the maximum of viscosity and the minimum of excess volume occur at different compositions of mixtures.

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