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

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The specific volume and the viscosity of enthanol-water mixtures at 25° (298.15K) and 50°C (323.15K) have been measured under pressures up to 3200 and 800 bar (10^5Pa), respectively. The measurements were performed by a modified Adams piezometer and a falling-cylinder viscometer. The maximum uncertainties are estimated to be 0.05% for the specific volume and 2% for the viscosity.

The specific volume of the pure components and their mixtures is found to decrease monotonously with increasing pressure. The results obtained are compared with several sets of literature values. The numerical data at each temperature and composition are correlated satisfactorily as a function of pressure by both polynomial and the Tait equations. It is also found that a definite minimum appears on the isothermal compressibility *versus* composition isobars, arising from the complex interactions between hydrogen-bonded water and alcohol molecules.

The viscosity of pure ethanol and mixtures is found to increase almost linearly with increasing pressure, whereas that of water is nearly independent of pressure in these experimental conditions. The viscosity isotherms can be formulated by a quadratic equation of pressure within the experimental error. As for the composition dependence of the viscosity, a distinct maximum appears near 0.3 mole fraction of ethanol on all isobars at both experimental temperatures.

Introduction

The physico-chemical properties of aqueous solutions of alcohols are of interest in many fields of science. The solutions often show some anomalies in various physical properties such as partial molar volume, compressibility, velocity of sound, sound absorption, viscosity and so on, which have been yet inadequately understood. Such properties of mixtures in a wide region of temperature and pressure are important both in chemical engineering designs and in theoretical investigations of excess thermodynamic properties. However there have been only a few measurements on these properties, especially under high pressure.

The present investigation was undertaken to provide extensive and accurate P-V-T and viscosity data under high pressure for ethanol-water mixtures. Numerical data have been determined at 25° and 50°C under pressures up to 3200 bar for specific volume and 800 bar for viscosity, employing a modified Adams piezometer and a falling-cylinder viscometer. Empirical correlation formulas have also been presented for both properties from the experimental results.

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Experimentals

P-V-T measurements

The specific volume of the ethanol-water mixtures has been measured by a modified Adams piezometer[1] similar to that used by Newitt *et al.*[2] The piezometer is made of Pyrex glass. The schematic diagram is given in Fig. 1 and the typical dimensions are summarized in Table 1. The volumes of the piezometer and the capillary stem were determined by weighing them filled with distilled water or mercury. The piezometer was set in a high pressure vessel equipped with a pair of optical windows which enable us to observe and control precisely the mercury level in the capillary stem. The high pressure vessel was immersed in a thermostat bath controlled within ±0.01°C. The pressure was measured by Heise Bourdon gauges calibrated against a pressure balance. The uncertainty in pressure measurements is estimated to be less than 0.1%.

The mercury trapped in the piezometer was washed with ethanol and weighed after drying.

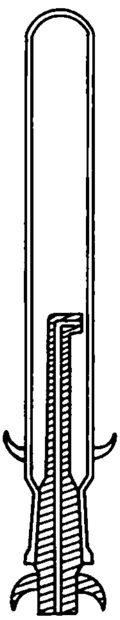

Fig. 1 Schematic diagram of modified Adams piezometer

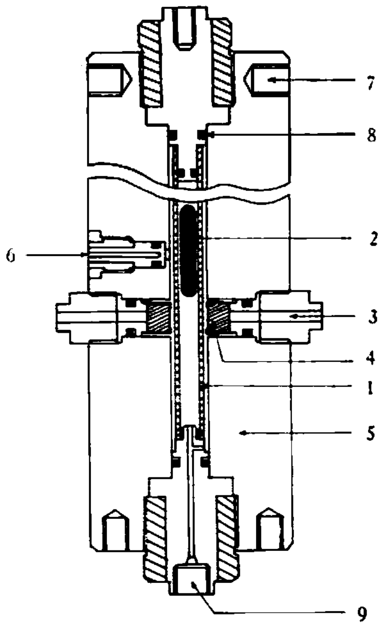

Fig. 2 Schematic diagram of falling-cylinder viscometer
1. Pyrex glass tube
2. Falling cylinder
3. Laser beam
4. Optical window
5. High pressure vessel
6. Thermister
7. Pivot
8. O-ring
9. Sample inlet

1) L. H. Adams, *J. Amer. Chem. Soc.*, 53, 3769 (1931)
2) D. M. Newitt and K. E. Weale, *J. Chem. Soc.*, 3092 (1951)

Table 1 Dimensions of Instruments used

Piezometer	at 25°C
Length	16.7 cm
Outer diameter	1.6 cm
Inner diameter	1.4 cm
Total volume	18.2215 cm^3
Volume of capillary	0.03616 cm^3
Viscometer	at 29°C
Glass tube	
Length	15.5 cm
Outer diameter	1.0869 cm
Inner diameter	0.8042 cm
Plummet	
Length	3.570 cm
Diameter	0.7607 cm
Weight	3.5278 g
Volume	1.5199 cm^3
Density	2.321 g·cm^{-3}

The specific volume of the sample liquid was calculated by the following equation :

$$v=\frac{V_0(1-k_g)-V_c(1-k_g)-(W_{Hg}/\rho_{Hg})}{V_0\rho_0} \tag{1}$$

where

v : specific volume of the liquid at P bar in cm^3·g^{-1},

V_0 : inner volume of the piezometer at 1bar in cm^3,

V_c : inner volume of the capillary at 1bar in cm^3,

W_{Hg} : weight of mercury trapped in g,

ρ_0 : density of the liquid at 1bar in g·cm^{-3},

ρ_{Hg} : density of mercury at P bar in g·cm^{-3},

k_g : compression of Pyrex glass at P bar.

The values of k_g and ρ_{Hg} were cited from the results of Adams[1] and Grindley *et al.*,[3] respectively. The densities of mixtures under the atmospheric pressure were determined experimentally by a pycnometer and partly cited from the handbook.[4]

Viscosity measurements

The viscosity has been measured by a falling-cylinder viscometer. The viscosity was determined principally based on the Stokes law on a rigid sphere falling in an infinite homogeneous fluid. The details of the theoretical basis are described by Swift *et al.*[5-7]

The schematic diagram of the viscometer employed is given in Fig. 2. The apparatus consists of a precisely bored Pyrex glass tube equipped coaxially in a high pressure vessel and a glass cylind-

3) T. Grindley and J. E. Lind, Jr., *J. Chem. Phys.*, **54**, 3983 (1971)
4) R. H. Perry and C. H. Chilton, "Chemical Engineers' Handbook" (5th ed.) McGraw-Hill Kogakusha, Ltd. (1973)
5) G. W. Swift, J. A. Christy and F. Kurata, *A. I. Ch. E. Journal*, **5**, 98 (1959)
6) J. Lohrenz, G. W. Swift and F. Kurata, *ibid.*, **6**, 547 (1960)
7) J. Lohrenz and F. Kurata, *ibid.*, **8**, 190 (1962)

rical plummet with hemispherical ends. The instrument dimensions are listed in Table 1. A sample liquid was introduced into both sides of the glass tube through a fine flexible pipe made of stainless steel. The plummet is provided with four small projecting lugs at each end of the cylindrical part, which act as a guide to keep the plummet concentric when it falls. The falling time of the plummet was determined within ± 0.1 ms by an electronic time-interval counter with the aids of a He-Ne gas laser beam passed through a pair of optical windows and a phototransister. The viscometer could be rotated on a horizontal axis in order to return the plummet to its starting position. The temperature of the sample was maintained constant within ± 0.05°C by circulating a thermostatic fluid through the jacket around the pressure vessel and measured by a thermister device. The pressure was measured by a Bourdon gauge with the same accuracy as the case of P-V-T measurements. The falling time ranged from 5 to 20 seconds according to the change of the viscosity of samples and was measured about 20 times at each experimental condition. The mean reproducibility of the falling time is within 0.5%. The arithmetic mean values were taken as the final values.

Due to the geometric effect of the plummet and the wall effect of the glass tube, the Stokes law is not valid strictly for a falling-body other than a rigid sphere in an infinite homogeneous fluid. Therefore, the calibration of the present viscometer is required with fluids of known viscosity. The basic equation of the falling-body viscometer is as follows:

$$\eta = K(\rho_b - \rho)t \qquad (2)$$

where

η : viscosity of a liquid at P bar in 10^{-3}Pa·s,

ρ : density of a liquid at P bar in g·cm^{-3},

ρ_b : density of the plummet at P bar in g·cm^{-3},

t : falling time in s.

The instrument constant K and its change with both temperature and pressure were determined based on the experimental viscosity values under the atmospheric pressure obtained by an Ostwald viscometer and the standard viscosity values of water correlated by the International Association for the Properties of Steam.[8] The densities of mixtures were calculated from Eq. (3) obtained in the present work. When the resistance factor[5] is plotted against the Reynolds number in logarithmic coordinates, the calibration curve is found to be a straight line with a slope of about -1. This means that each measurement was carried out in a laminar flow region with lower Reynolds numbers than 0.5 throughout the experimental condition.

Materials

Extra pure ethanol was obtained from Wako Pure Chemical Industries, Ltd. The reported purity is more than 99.5% in volume. Ethanol and water were purified several times by the fractional distillation. The mixtures of ethanol and water were prepared by weighing, using an analytical balance with a sensitivity of ± 0.1mg. Therefore their composition, mole fraction of ethanol, should

8) International Association for the Properties of Steam, "Dynamic Viscosity of Water Substance" The Eighth International Conference on the Properties of Steam, Giens, France (1974)

be substantially accurate within 0.01%.

Uncertainty of experimental results

The numerical data of the specific volume and the viscosity obtained contain a definite uncertainty resulting from several sources of experimental errors. The main sources and their portions in the final values are estimated as follows:

(Specific volume measurement)

Error source	*Uncertainty contributing to v*
Temperature	±0.001%
Pressure	±0.01%
Composition of mixture	±0.01%
Piezometer volume	±0.01%

(Viscosity Measurement)

Error source	*Uncertainty contributing to η*
Temperature	±0.1%
Pressure	±0.01%
Composition of mixture	±0.02%
Falling time	±0.5%
Density	±0.01%
Instrument constant, K	±1.0%

Taking into account the above estimations, the uncertainties probable in the present measurements may be less than 0.05% for the specific volume data and 2.0% for the viscosity data. This fact has been verified satisfactorily by the comparison with the reliable data of pure components by other authors, as partly described below.

Results and Discussions

***P-V-T* data**

Table 2 lists the measured P-V-T relations for ethanol-water mixtures at 25° and 50°C under pressures up to 3200 bar. X is the mole fraction of ethanol in the mixtures. The results are also plotted in Figs. 3 and 4 together with the previously published data for pure water and mixtures for comparison. The specific volume decreases monotonously with increasing pressure throughout the experimental conditions at each composition of mixtures. At 25°C, the present results agree quite well with the values given by Kell *et al.*[9] and Grindley *et al.*[3] for pure water up to 3000 bar and those of Moesveld[10] for mixtures up to 1500 bar. However, some discrepancies between the present work and the recent report of Yusa *et al.*[11]* are found to be up

9) G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc. London*, **A258**, 565 (1965)
10) A. L. Moesveld, *Z. Phys. Chem.*, **105**, 450 (1923)
11) M. Yusa, G. P. Mathur and R. A. Stager, *J. Chem. Eng. Data*, **22**, 32 (1977)
* This report was published recently after the completion of experimental part of this study.

Table 2 The Specific Volume of Ethanol-Water Mixtures

25°C		50°C	
P(bar)	v(cm³/g)	P(bar)	v(cm³/g)
X=0.00			
1.0	1.00293	1.0	1.01210
91.7	0.99881	147.8	1.00621
172.7	0.99515	226.6	1.00285
250.1	0.99193	310.5	0.99988
441.9	0.98442	341.2	0.99877
502.0	0.98177	417.1	0.99623
675.3	0.97543	418.2	0.99500
763.8	0.97258	488.9	0.99335
899.9	0.96770	515.8	0.99215
1037.2	0.96281	564.4	0.98943
1314.2	0.95343	623.1	0.98791
1417.9	0.95008	631.8	0.98750
1762.7	0.93978	668.0	0.98579
2107.4	0.93151	692.2	0.98469
2452.2	0.92178	723.7	0.98404
2796.9	0.91390	832.4	0.98049
3148.6	0.90665	934.3	0.97695
		1039.7	0.97328
		1140.9	0.97010
		1242.1	0.96604
		1244.7	0.96604
		1345.5	0.96369
		1348.3	0.96369
		1555.8	0.95715
		1724.8	0.95257
		1762.7	0.95073
		1900.6	0.94720
		2107.4	0.94184
		2245.3	0.93741
		2452.2	0.93321
		2586.6	0.92950
		2965.9	0.92211
		3138.2	0.91853
X=0.10			
1.0	1.03812	1.0	1.05713
63.9	1.03513	207.3	1.04829
145.7	1.03185	286.4	1.04507
223.5	1.02866	347.8	1.04200
288.1	1.02609	422.3	1.03915
345.4	1.02393	483.0	1.03664
414.0	1.02167	554.4	1.03366
480.6	1.01882	622.8	1.03065
555.1	1.01619	690.5	1.02802
625.2	1.01347	948.1	1.02052
690.5	1.01092	1073.2	1.01675
695.7	1.01110	1084.7	1.01598
723.4	1.01014	1210.5	1.01262
831.7	1.00693	1762.7	0.99488
903.8	1.00483	1897.1	0.99032
1043.8	0.99990	2107.4	0.98619
1073.2	0.99883	2448.7	0.97725
1177.3	0.99524	2798.5	0.96835
1318.0	0.99166	3138.2	0.95751
2073.0	0.96923		
2245.3	0.96614		
2421.2	0.96069		
2590.1	0.95702		
2796.9	0.95178		
2934.8	0.94871		
X=0.20			
1.0	1.07120	1.0	1.09616
84.0	1.06685	277.7	1.08192
201.1	1.06128	344.0	1.07900
291.2	1.05717	413.0	1.07471
339.9	1.05546	494.7	1.07120
421.3	1.05153	561.3	1.06844
485.4	1.04879	626.9	1.06491
728.4	1.03935	695.4	1.06274
762.8	1.03786	831.0	1.05697
905.5	1.03250	971.0	1.05043
1042.4	1.02772	1073.2	1.04701
1173.2	1.02225	1086.1	1.04657
1175.9	1.02306	1207.6	1.04209
1316.9	1.01797	1216.4	1.04214
1417.9	1.01504	1329.4	1.03787
1762.7	1.00495	1380.0	1.03492
1900.6	1.00103	1552.4	1.02964
2073.0	0.99560	1762.7	1.02417
2245.3	0.99194	1897.1	1.01849
2468.9	0.98669	2241.9	1.00962
2796.9	0.97768	2586.6	0.99837
2934.8	0.97440	3138.2	0.98535
3141.7	0.96974		
X=0.40			
1.0	1.13649	1.0	1.16660
90.3	1.12981	149.5	1.15560
146.4	1.12631	281.9	1.14651
281.9	1.11744	354.3	1.14113
360.6	1.11278	415.3	1.13708
486.8	1.10546	484.0	1.13219
554.1	1.10114	556.1	1.12755
622.8	1.09737	624.5	1.12264
694.7	1.09333	698.5	1.11836
767.0	1.09108	799.5	1.11195
901.7	1.08418	923.9	1.10532
1039.0	1.07878	1001.5	1.10148
1073.2	1.07669	1211.9	1.09286
1177.3	1.07289	1317.6	1.08873
1211.1	1.07124	1380.0	1.08566
1316.9	1.06731	1762.7	1.07444
1762.7	1.05060	1897.1	1.06623
2107.4	1.03945	2069.5	1.06457
2436.2	1.02893	2586.6	1.04286
2796.9	1.01900	2759.0	1.03590
3145.1	1.00994	2931.4	1.03225
3486.4	1.00209	3103.8	1.02644
X=0.60			
1.0	1.18937	1.0	1.22263
75.7	1.18262	143.0	1.21062
146.4	1.17593	212.8	1.20436
205.9	1.17107	278.4	1.19924
288.8	1.16453	350.6	1.19298
380.6	1.15782	415.7	1.18818
486.1	1.14986	486.4	1.18280
624.5	1.14072	554.1	1.17634
700.5	1.13658	628.3	1.17079
902.4	1.12567	829.3	1.15728
1037.2	1.11827	968.2	1.14709
1073.2	1.11651	1110.4	1.13813
1181.4	1.11178	1247.2	1.13121
1314.9	1.10564	1320.7	1.12741
1417.9	1.10045	1380.0	1.12228
1762.7	1.08713	1552.4	1.11543
1931.6	1.07992	1897.1	1.09961
2107.4	1.07573	2069.5	1.09238
2590.1	1.05954	2241.9	1.08648
2796.9	1.05212	2414.3	1.08144
2934.8	1.04668	2586.6	1.07440
3141.7	1.04173	2759.0	1.07027
		2931.4	1.06175
		3103.8	1.05931
X=0.80			
1.0	1.23352	1.0	1.27115
75.0	1.22518	210.7	1.24579
153.0	1.21645	279.5	1.23797
213.9	1.21105	348.5	1.23114
274.6	1.20477	416.8	1.22417
416.8	1.19205	487.5	1.21721
479.5	1.18675	557.2	1.21196
518.2	1.18407	626.9	1.20465
600.3	1.17811	699.5	1.19984
762.5	1.16755	793.6	1.19274
906.9	1.15864	921.8	1.18502
1037.2	1.15069	968.2	1.17942
1073.2	1.14846	1062.5	1.17379
1178.0	1.14274	1107.6	1.17272
1313.8	1.13548	1236.4	1.16505
1417.9	1.13025	1337.3	1.15908
1621.3	1.12114	1724.8	1.13888
1897.1	1.10804	1897.1	1.13109
2241.9	1.09553	2241.3	1.11583
2452.2	1.08841	2414.3	1.10959
2655.6	1.08158	2586.6	1.10275
2796.9	1.07754	2759.0	1.09635
2934.8	1.07325	2931.4	1.09006
3141.7	1.06674	3103.8	1.08704
3486.4	1.05685		
X=1.00			
1.0	1.27353	1.0	1.31203
70.1	1.26493	141.9	1.29134
139.5	1.25663	211.1	1.28152
208.7	1.24831	283.6	1.27198
352.6	1.23314	347.8	1.26363
485.1	1.21938	421.3	1.25493
621.7	1.20831	483.3	1.24948
761.1	1.19750	551.0	1.24297
832.0	1.19235	625.2	1.23656
899.3	1.18818	694.3	1.22947
1038.6	1.17857	762.5	1.22392
1176.2	1.16985	1039.0	1.20354
1313.8	1.16192	1175.9	1.19502
1417.9	1.15578	1315.6	1.18682
1621.3	1.14523	1552.4	1.17106
1762.7	1.13943	1897.1	1.15339
1762.7	1.13961	2069.5	1.14330
1931.6	1.13212	2241.9	1.13775
2107.4	1.12534	2414.3	1.13239
2107.4	1.12438	2586.6	1.12248
2276.4	1.11709	2759.0	1.11828
2414.3	1.11258	2931.4	1.10914
2655.6	1.10236	3103.8	1.10530

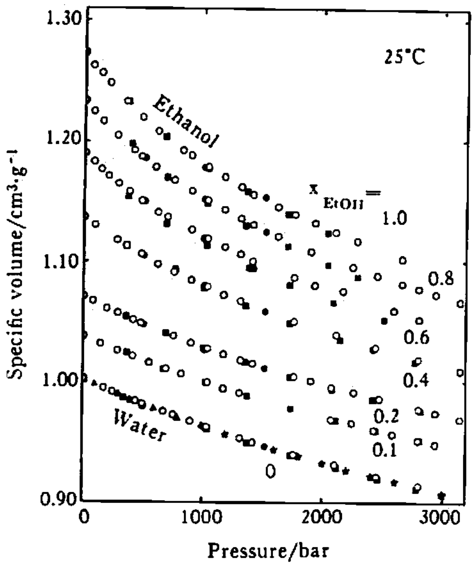

Fig. 3 Pressure dependence of the specific volume of ethanol-water mixtures at 25°C
○: This work, ★: 3), ▲: 9), ●: 10), ■: 11)

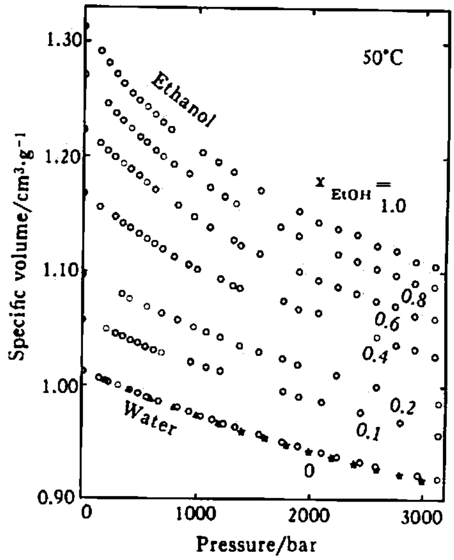

Fig. 4 Pressure dependence of the specific volume of ethanol-water mixtures at 50°C
○: This work, ★: 3), ▲: 9)

Table 3 Coefficients of the Specific Volume Isotherms (P in bar)

$$v = A_1 + A_2P + A_3P^2 + A_4P^3 + A_5P^4$$

Temp. (°C)	X	A_1	$A_2 \times 10^4$	$A_3 \times 10^8$	$A_4 \times 10^{12}$	$A_5 \times 10^{16}$	Ave. Dev. (%)	Max. Dev. (%)
	0	1.002799	−0.443342	0.626552	− 0.87462	0.87226	0.023	0.084
	0.10	1.038026	−0.436395	0.89158	− 2.45667	3.2501	0.022	0.079
	0.20	1.071118	−0.497623	0.856201	− 0.95734		0.024	0.071
25	0.40	1.136553	−0.744170	2.320940	− 6.04088	6.701070	0.025	0.078
	0.60	1.189331	−0.943990	3.227030	− 7.910364	7.73871	0.035	0.114
	0.80	1.232849	−1.103108	3.781940	− 9.09383	9.11887	0.043	0.124
	1.00	1.273663	−1.303024	4.767938	−11.55815	11.0980	0.028	0.085
	0	1.012369	−0.4252248	0.547835	− 0.85752	1.26276	0.031	0.071
	0.10	1.057173	−0.460342	0.836348	− 1.20089		0.051	0.143
	0.20	1.096419	−0.558459	1.121898	− 2.10525	1.91894	0.038	0.099
50	0.40	1.167762	0.853410	2.400286	− 3.64926		0.092	0.279
	0.60	1.223160	−0.903382	1.101615	2.52140	−7.12415	0.052	0.203
	0.80	1.271486	−1.343278	5.624636	−16.81337	20.78308	0.039	0.110
	1.00	1.311687	−1.571652	6.942738	−20.77829	25.21906	0.069	0.224

to 0.9% at high ethanol mole fractions and high pressures. As for 50°C, the present results for pure water are in good agreement with the values of Kell *et al.*[9] and Grindley *et al.*[3] However, there exists no data on mixtures available in literature for direct comparison with the present work.

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Table 4 Coefficients of the Tait Equation

Temp. (°C)	X	B (bar)	C (−)	Ave. Dev. (%)	Max. Dev. (%)
	0.00	2754	0.2911	0.04	0.07
	0.10	3124	0.2989	0.04	0.10
	0.20	2288	0.2511	0.05	0.10
25	0.40	1552	0.2308	0.04	0.18
	0.60	1157	0.2179	0.07	0.19
	0.80	989	0.2179	0.03	0.08
	1.00	778	0.2065	0.06	0.18
	0.00	3321	0.3241	0.04	0.08
	0.10	2952	0.2887	0.03	0.11
	0.20	2404	0.2792	0.04	0.15
50	0.40	1551	0.2504	0.09	0.11
	0.60	1410	0.2686	0.07	0.19
	0.80	921	0.2282	0.05	0.14
	1.00	790	0.2278	0.08	0.17

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

$$v=A_1+A_2P+A_3P^2+A_4P^3+A_5P^4 \tag{3}$$

and the Tait equation :

$$\frac{v_0-v}{v_0}=C\log\left(\frac{B+P}{B+1}\right) \tag{4}$$

where v_0 is the specific volume at the atmospheric pressure and P the pressure in bar. The empirical coefficients were determined by the least squares method as given in Tables 3 and 4 together with the average and the maximum deviations of the experimental data from the formulas. Although the polynomial equation gives a better fit to the data in general, the isothermal compressibility

$$\beta_T=-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{5}$$

is calculated by the Tait equation because the polynomial equation sometimes gives unexpected behaviors by the differentiation. The functional dependences of the isothermal compressibility on composition are shown in Figs. 5 and 6 at 25° and 50°C, respectively. It is found that a definite minimum exists near x=0.1 on the lower pressure isobars than 2000 bar. As well known in the case of pure water, the isothermal compressibility has a minimum near 50°C on the isobars lower than 2000 bar. This anomaly could be seen in the range of low ethanol composition, and disappears with increasing composition near x=0.2, where the isothermal compressibility is independent of temperature under each pressure. Furthermore, it seems that another inflection might occur at higher mole fraction of ethanol near x=0.7 on the low pressure isobars. (Concerning this second inflection, more detailed experimental results will be reported in the near future.) Yusa *et al.*[11] have found the similar

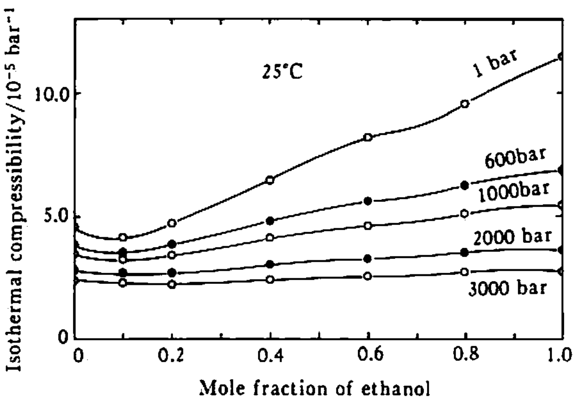

Fig. 5 Composition dependence of the isothermal compressibility of ethanol-water mixtures at 25°C under high pressure

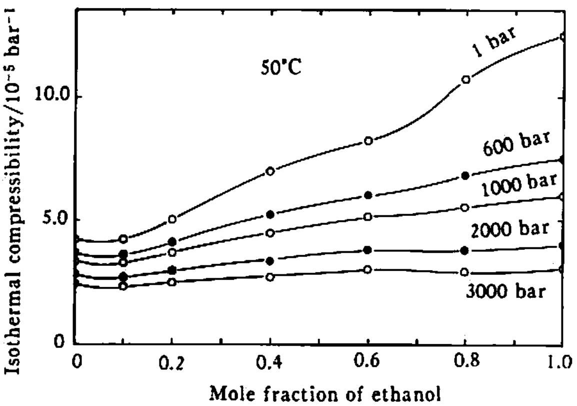

Fig. 6 Composition dependence of the isothermal compressibility of ethanol-water mixtures at 50°C under high pressure

phenomenon in his isothermal compression *versus* composition isobars. These anomaly would be attributed to complex interactions between the hydrogen-bonded water and the bifunctional nature of alcohol molecules.[12,13)]

Viscosity

The viscosity of ethanol-water mixtures has been measured at 25° and 50°C up to 800 bar. The raw data are tabulated in Table 5. Values of the viscosity obtained at the atmospheric pressure are compared as a function of composition to other data available in literature[14-22)] in Fig. 7. The vis-

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Table 5 The Viscosity of Ethanol-Water Mixtures (10^{-3}Pa·s=cP)

X	0.00		0.20		0.30		0.40	
Temp. (°C) / P (bar)	25	50	25	50	25	50	25	50
1	0.8911	0.5468	2.335	1.080	2.314	1.108	2.148	1.072
98	0.8895	0.5486	2.400	1.134	2.407	1.155	2.249	1.146
196	0.8882	0.5504	2.461	1.136	2.481	1.168	2.352	1.166
294	0.8872	0.5522	2.506	1.175	2.559	1.211	2.439	1.214
392	0.8866	0.5541	2.567	1.185	2.638	1.249	2.527	1.264
490	0.8864	0.5561	2.602	1.200	2.703	1.275	2.611	1.298
589	0.8866	0.5583	2.666	1.232	2.777	1.341	2.702	1.333
686	0.8872		2.702		2.845		2.779	
785	0.8881		2.771		2.939		2.884	

X	0.60		0.78	0.80	1.00	
Temp. (°C) / P (bar)	25	50	25	50	25	50
1	1.740	0.9408	1.423	0.8101	1.087	0.6885
98	1.848	1.029	1.518	0.8555	1.170	0.7473
196	1.941	1.059	1.614	0.8839	1.246	0.7788
294	2.051	1.113	1.703	0.9397	1.326	0.8379
392	2.137	1.166	1.800	0.9969	1.397	0.8800
490	2.220	1.182	1.875	1.018	1.475	0.9261
589	2.330	1.234	1.966	1.081	1.547	0.9682
686	2.389		2.052		1.613	
785	2.531		2.107		1.694	

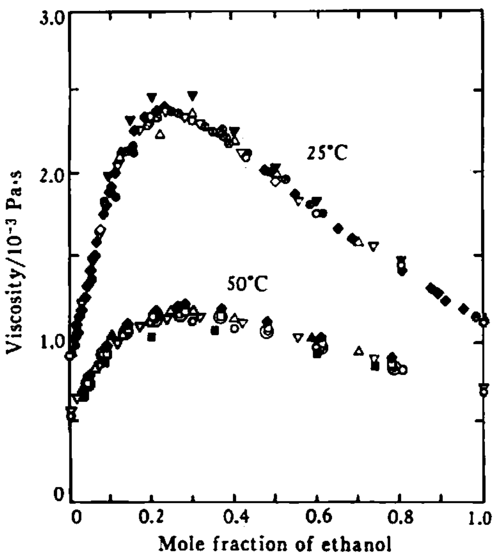

Fig. 7 Composition dependence of the viscosity of ethanol-water mixtures at 25° and 50°C at the atmospheric pressure
○: This work, ▼: 11), ◆: 14), ⊗: 15), △: 16), ▲: 17), ■: 18), ▽: 19), ◇: 20), □: 21), ◎: 22)

cosity data display a maximum at a composition from 0.2 to 0.3 mole fraction of ethanol at each temperature. Agreement of the data among researchers is comparatively good at 25°C, except the

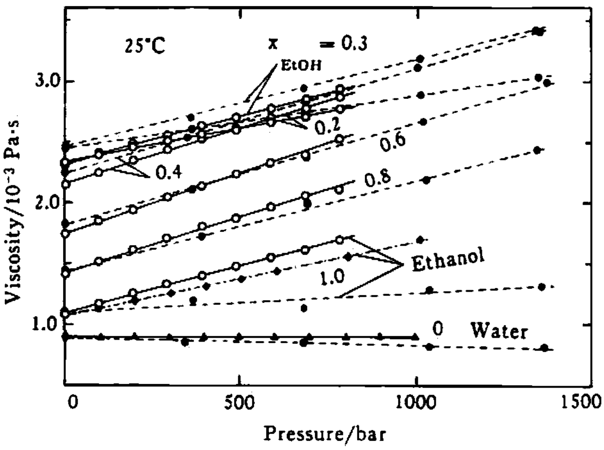

Fig. 8 Pressure dependence of the viscosity of ethanol-water mixtures at 25°C
○: This work, ▲: 8), ●: 11), ◆: 23)

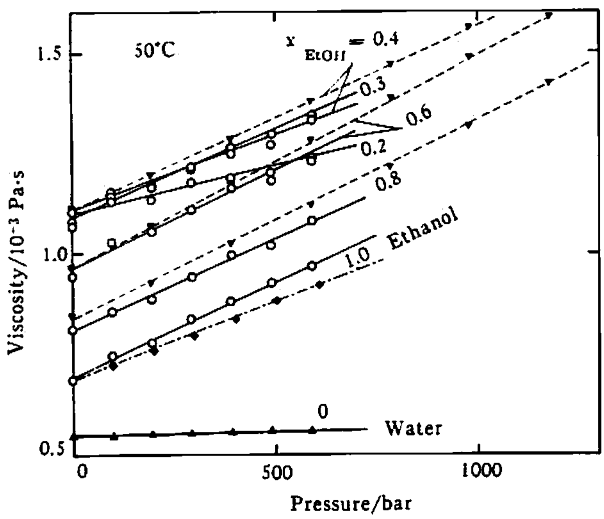

Fig. 9 Pressure dependence of the viscosity of ethanol-water mixtures at 50°C
○: This work, ▲: 8), ▼: 22), ◆: 23)

results reported by Yusa *et al.*,[11] whose data are about 4% higher than others near the maximum. Inconsistency of the data is found to increase at 50°C, where the largest deviation between the data of Sabnis[18] and those of Traube[14] is about 13% near x=0.2.

The viscosity data obtained at high pressures are also compared with those in literatures. The pressure effects on the viscosity are shown in Figs. 8 and 9 together with the results of Abaszade *et al.*[22] and Yusa *et al.*[11] for mixtures and those of Golubev *et al.*[23] for pure ethanol. Figs. 8 and 9 include partly interpolated data to the same compositions by a graphical method, because the previous data under pressures available for a direct comparison are limitted. It is found that agreement among the four sets of data is rather good at low pressures, but that the discrepancy increases with increasing pressure. A serious inconsistency is found in the results for pure ethanol. In the results of Yusa *et*

23) I. F. Golubev and V. A. Petrov, Trudy GIAP, No. 2, 5 (1953)

al.,[11] the pressure coefficient of viscosity, $\left(\frac{\partial \eta}{\partial P}\right)_T$ for ethanol is rather small at 25°C, while the data of Golubev *et al.*[23] and the present work give an obvious positive pressure dependences. The viscosity of the mixtures increases almost linearly with pressure, whereas that of water is almost independent of pressure in this pressure range.

The viscosity isotherms in this work can be represented by a quadratic equation of pressure.

$$\eta = B_1 + B_2P + B_3P^2 \tag{6}$$

where η is the viscosity in 10^{-3}Pa·s (=cP) and P the pressure in bar. The coefficients for each mixture are determined by the least squares method and listed in Table 6 with the average and the maximum deviations.

The composition dependence of the viscosity under high pressures is shown in Fig. 10. Each isobar also exhibits a maximum near the composition x=0.3. The maximum shifts slightly to higher ethanol fraction with increasing pressure or temperature.

Conclusion

This paper represents the raw experimental data on the specific volume and the viscosity of ethanol-water mixtures as functions of temperature, pressure and composition. This basic information would be necessary to solve the complicated behavior of aqeous solutions of hydroxy-compounds, which are yet inadequately understood. However, the temperature range is narrow in the present measurements, and more detailed measurements is thought to be needed fully near the composition where the anomaly appears. Furthermore, the relationship between the equilibrium (thermodynamic) properties and the non-equilibrium (transport) properties should be derived, especially as for the appearance of anomalies, as well as in the case of aqueous solutions of other alcohols.

Table 6 Coefficients of the Viscosity Isotherms: $\eta = B_1 + B_2P + B_3P^2$ (P in bar)

Temp. (°C)	x	B_1	$B_2 \times 10^4$	$B_3 \times 10^8$	Ave. Dev. (%)	Max. Dev. (%)
25	0.20	2.34083	5.83501	− 6.0312	0.25	0.41
	0.30	2.32078	8.15612	− 5.317	0.25	0.41
	0.40	2.15289	9.86477	− 8.620	0.24	0.37
	0.60	1.74644	10.0016	− 3.1239	0.45	1.21
	0.78	1.41928	10.3408	−18.7226	0.24	0.53
	1.00	1.08861	8.16548	− 6.331	0.16	0.36
50	0.20	1.08858	3.1009	−13.262	0.74	1.49
	0.30	1.11481	2.64468	18.153	0.60	1.13
	0.40	1.07846	5.21548	−15.191	0.53	1.55
	0.60	0.94929	6.5578	−31.312	0.85	1.79
	0.80	0.80963	4.17241	6.664	0.66	1.36
	1.00	0.690264	5.07855	− 5.885	0.44	1.12

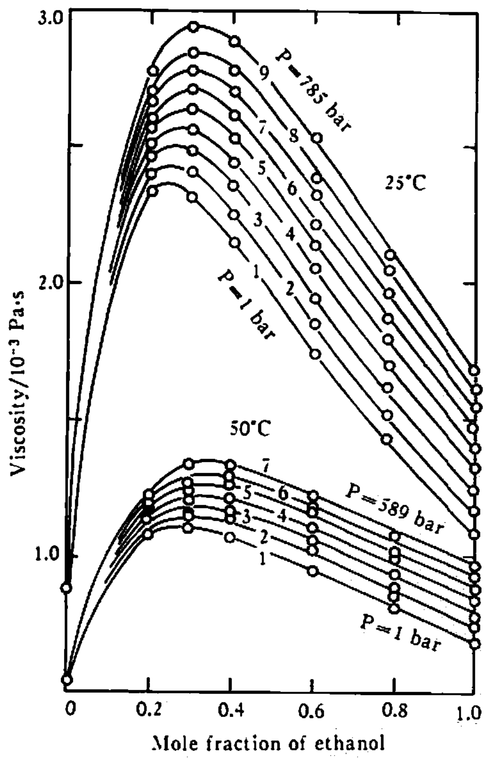

Fig. 10 Composition dependence of the viscosity of ethanol-water mixtures at 25° and 50°C under high pressure
1: 1 bar, 2: 98 bar, 3: 196 bar, 4: 294 bar, 5: 392 bar, 6: 490 bar, 7: 589 bar, 8: 686 bar, 9: 785 bar

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