International Journal of Thermophysics, Vol. 8, No. 1, 1987

Volumetric Behavior of Pure Alcohols and Their Water Mixtures Under High Pressure

H. Kubota,[1] Y. Tanaka,[1] and T. Makita[1]

Received April 11, 1986

The specific volumes of C_1–C_4 alcohols and binary mixtures of water with methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol are presented as functions of temperature, pressure, and composition. The measurements were carried out using a modified Adams piezometer and a high-pressure burette method in a temperature range from 283.15 to 348.15 K at pressures up to 350 MPa. The uncertainties in the specific volume obtained are estimated to be less than 0.09 %. The specific volumes of the pure alcohols and their mixtures with water are found to decrease monotonously with increasing pressure. The numerical P–V relations at each temperature and composition are correlated satisfactorily as a function of pressure by the Tait equation. Definite inflections appear on the isobars of isothermal compressibility or partial molar volume versus composition of alcohol + water mixtures.

KEY WORDS: alcohols; aqueous mixtures; butanols; compressibility; ethanol; excess volume; high pressure; methanol; propanols; specific volume; Tait equation; water.

1. INTRODUCTION

As alcohol molecules strongly affect water structure, alcohol + water mixtures show definite anomalies in various physical properties. In order to understand these anomalies phenomenally and theoretically, it is necessary to measure the accurate pressure–volume–temperature relations of pure alcohols and of binary mixtures of alcohol with water in a wide range of temperature and pressure. Although a number of measurements at atmospheric pressure have been reported, systematic studies covering wide conditions are scarce among those under high pressures [1–14].

[1] Department of Chemical Engineering, Kobe University, Kobe 657, Japan.

0195-928X/87/0100-0047$05.00/0

The present investigation was undertaken to provide extensive and accurate *PVTx* data of C_1–C_4 alcohols and of alcohol + water mixtures. The temperature and pressure ranges of this experiment are as follows.

Pure alcohols

Methanol (MeOH)	283–348 K	0.1–208 MPa
Ethanol (EtOH)	298–323 K	0.1–310 MPa
1-Propanol (1-PrOH)	283–348 K	0.1–208 MPa
2-Propanol (2-PrOH)	283–348 K	0.1–191 MPa
1-Butanol (1-BuOH)	283–348 K	0.1–206 MPa
2-Butanol (2-BuOH)	283–348 K	0.1–207 MPa
2-Methyl-1-propanol (isoBuOH)	283–348 K	0.1–207 MPa
2-Methyl-2-propanol (*t*-BuOH)	303–348 K	0.1–96 MPa

Mixtures

MeOH + H_2O	283–348 K	0.1–208 MPa
EtOH + H_2O	298–323 K	0.1–349 MPa
1-PrOH + H_2O	283–348 K	0.1–209 MPa
2-PrOH + H_2O	283–348 K	0.1–191 MPa
t-BuOH + H_2O	298–348 K	0.1–211 MPa

2. EXPERIMENTAL

The specific volumes of pure alcohols and of alcohol + water mixtures are measured by a modified Adams piezometer and a high-pressure burette method. The pressure is measured by Heise Bourdon-tube gauges, which were calibrated against a pressure balance. The uncertainty in the pressure measurements is estimated to be less than 0.10 MPa. The piezometer and burette containing the sample liquids are placed in a liquid bath, thermostatically controlled to within ± 10 mK, whose temperature is determined with standard mercury thermometers calibrated by the National Research Laboratory of Metrology, Japan. The accuracy of the temperature measurements is within ± 50 mK. The details of the apparatus and procedures for the determination of the specific volume were described elsewhere [16, 17].

The best-grade alcohols obtained from Wako Pure Chemical Industries Ltd. were dried by molecular sieve and then purified several times by fractional distillation and degassed by the crystallization in vacuum. The purities of the alcohols are better than 99.9 wt%. The mixtures of alcohol and water were prepared by weighing, using an analytical balance with a sensitivity of ± 0.1 mg. Therefore their composition, the mole fraction of alcohol, should be accurate within 0.01 %.

The final uncertainty of the specific volumes obtained is estimated to be less than 0.09 %.

3. RESULTS AND DISCUSSION

The reliability of the present *PVT* apparatus was confirmed by measuring the specific volume of pure water. At 298.15 and 323.15 K, our data coincided with the literature values of Kell and Whalley [18], Chen et al. [19], and Grindley and Lind [20] within 0.025, 0.007, and 0.03 %, respectively, and at 283.15 and 348.15 K within 0.09 %.

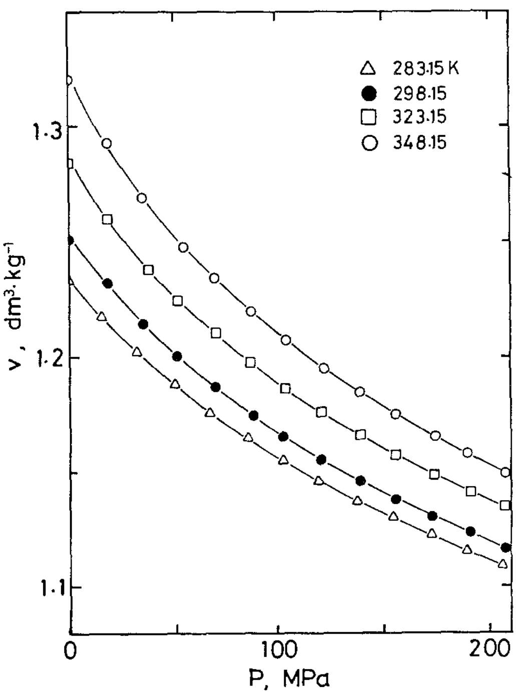

Fig. 1. Pressure dependence of the specific volume for 2-propanol.

3.1. Pure Alcohols

As a typical example for the volumetric behavior of pure alcohols, the pressure dependence of the specific volume of 2-propanol is illustrated in Fig. 1. The specific volume of alcohols decreases monotonously with increasing pressure. The present results are in good agreement with reliable data in the literature [1, 3, 9, 10, 12, 14, 15].

The pressure dependence of the isothermal compression of each alcohol at 323.15 K is shown in Fig. 2, where a remarkable effect of molecular structures is found. At the same temperature and pressure, the isothermal compression of normal alcohols decreases with increasing numbers of carbon atoms. On the one hand, the branched structure introduces a kind of softness which increases the isothermal compression. In butyl

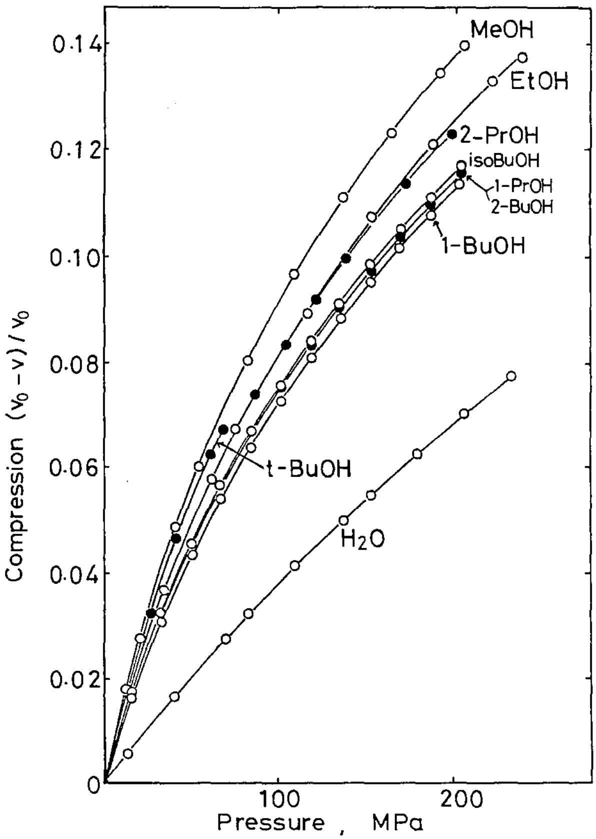

Fig. 2. Pressure dependence of the compression for various alcohols at 323.15 K.

alcohols, the compression increases in the order of 1-BuOH, 2-BuOH, isoBuOH, and *t*-BuOH. The specific volumes of pure alcohols and water are listed in Table AI (Appendix).

At each temperature, the specific volume v is correlated as a function of pressure P by the Tait equation:

$$\frac{v_0 - v}{v_0} = C \ln\left(\frac{B+P}{B+P_0}\right) \tag{1}$$

where v_0 is the specific volume at a reference pressure P_0, and B and C are empirical constants depending on the substance and temperature. This equation is found to reproduce experimental specific volume data of pure alcohols within average and maximum deviations of 0.03 and 0.08%, respectively.[2]

3.2. Alcohol + Water Mixtures

The specific volume data of alcohol + water mixtures are listed in Table AII (Appendix). The only data available for direct comparison with the present work are the ethanol + water mixtures of Yusa et al. [9]. At 298 K and a low concentration of ethanol, their data agree quite well with the present results, but the discrepancies become larger at high ethanol mole fractions.

Equation (1) is also used to represent the present experimental results at each constant temperature and composition. This equation could reproduce the present results within an average deviation of 0.02% and a maximum deviation of 0.07% over the entire experimental conditions.

The isothermal compressibility β_T of alcohol + water mixtures,

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_{T,x} \tag{2}$$

is calculated using Eq. (1). Some of the data are plotted against the mole fraction of alcohol in Fig. 3. The compressibility decreases with increasing pressure and increases with increasing temperature for each mixture. A definite minimum exists near 0.1 mole fraction of each alcohol, but it fades out gradually as the temperature and pressure increase. At constant temperature and pressure, the mole fraction of alcohol, where the minimum isothermal compressibility appears, decreases in the following order:

$$\text{MeOH} > \text{EtOH} > \text{1-PrOH} \simeq \text{2-PrOH} > t\text{-BuOH}$$

[2] The empirical constants of Eq. (1) for pure alcohols and alcohol + water mixtures are available from the authors on request.

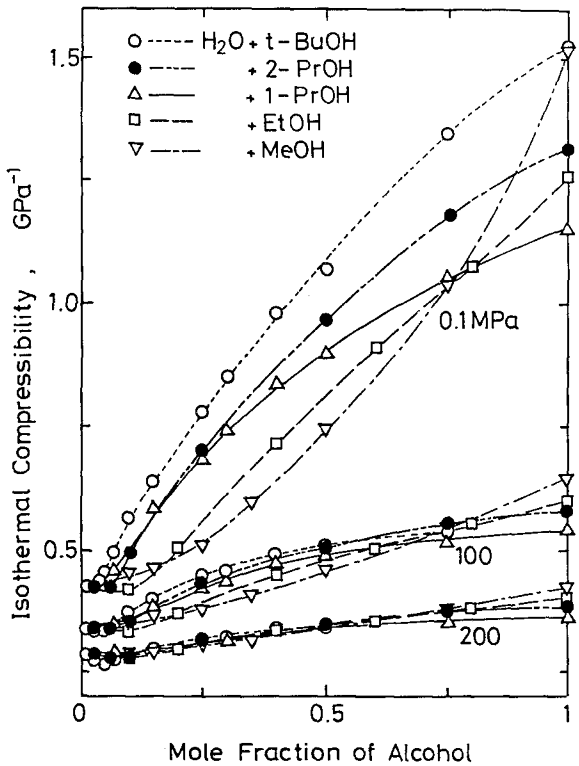

Fig. 3. Composition dependence of the isothermal compressibility for alcohol + water mixtures at 323.15 K.

Excess properties of the real solution express a deviation of the mixture from the ideal solution behavior. The excess volume V^E of alcohol + water mixtures is calculated by the following equation:

$$V^E = V - (x_1 V_1^0 + x_2 V_2^0) \tag{3}$$

where V_1^0 and V_2^0 denote the molar volumes of pure alcohol and water, respectively. As seen in Fig. 4, all the alcohol + water mixtures have negative excess volumes, implying a reduced free volume in the liquid structure. As the pressure increases, the excess volume becomes less negative, and in a sense, the mixture approaches the ideal solution with increasing pressure.

Partial molar quantities, in particular their deviations from values expected for ideal solutions, are of considerable interest in connection with

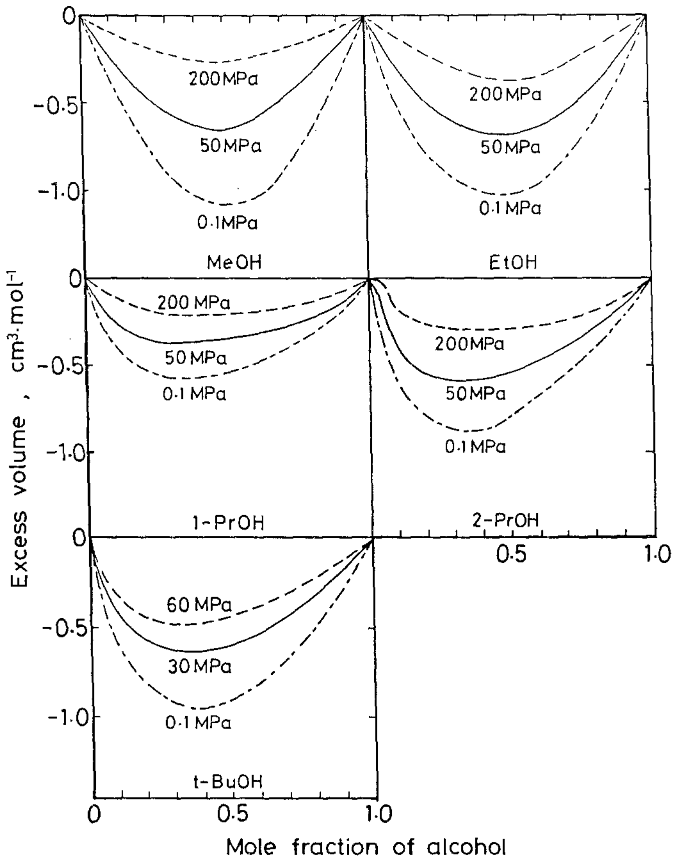

Fig. 4. Excess volume of alcohol + water mixtures at 323.15 K.

the theory of solutions. Partial molar volumes $\bar{V}$ of alcohol and water in each mixture are calculated by the following equations:

$$\bar{V}_1 = [v + w_2(\partial v/\partial w_2)_{T,P}]M_1 \tag{4}$$

$$\bar{V}_2 = [v + (1 - w_2)(\partial v/\partial w_2)_{T,P}]M_2 \tag{5}$$

where w_2 is the mass fraction of water, and M_1 and M_2 are the relative molar masses of alcohol and water, respectively. The partial molar volumes of 2-propanol and water are illustrated in Fig. 5. Each isobar of the alcohol has a minimum at a low alcohol concentration, while that of water has a small maximum at the same concentration. The mole fractions of the extremes are nearly equal to those for the isothermal compressibility. The minimum of alcohol becomes smaller and it shifts slightly to a higher alcohol concentration with increasing pressure.

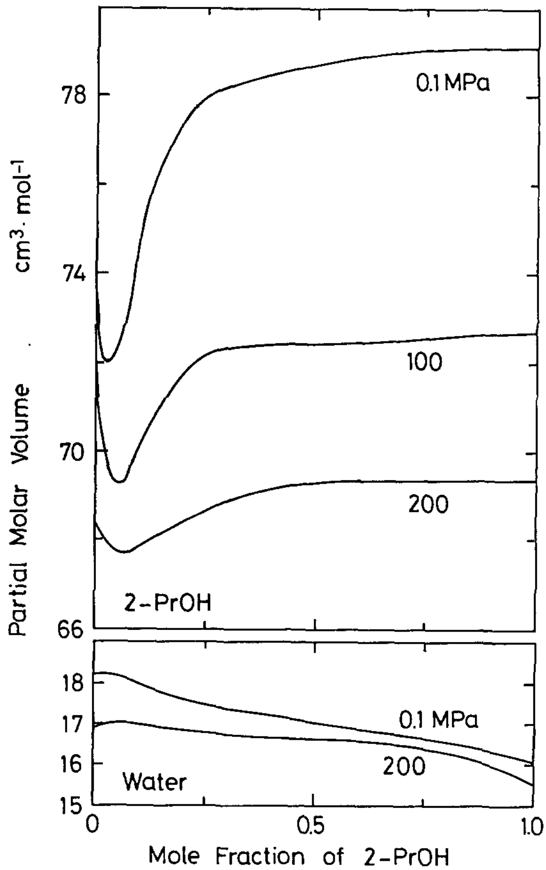

Fig. 5. Partial molar volume of 2-propanol + water mixtures at 323.15 K.

Alcohol molecules in aqueous solutions have a strong influence on the water structure. The anomalous behavior of the composition dependence of the thermodynamic properties would be attributed to complex interaction between the hydrogen-bonded water and the bifunctional nature of alcohol molecules. At low alcohol concentrations, the alcohol molecules form hydrogen bonds with water molecules and the hydrophobic groups of the alcohol accommodate in the cavities of the hydrogen-bonded network. The presence of hydrophobic molecules enhances the degree of hydrogen bonding of pure water around them. In consequence, thermodynamic properties such as isothermal compression and compressibility show a rapid decrease at low alcohol concentrations. As the concentration of alcohol increases, the hydrogen-bonded network is disintegrated and the larger compressibility of alcohols becomes dominant.

APPENDIX

Table AI. Specific Volumes of Pure Alcohols and Water
(P in MPa; v in $dm^3 \cdot kg^{-1}$)

283.15 K		298.15 K		323.15 K		348.15 K	
P	v	P	v	P	v	P	v
			Methanol				
0.1	1.2486	0.1	1.2708	0.1	1.3111	3.5	1.3487
2.1	1.2459	13.8	1.2509	13.1	1.2859	16.4	1.3230
15.8	1.2282	27.9	1.2335	27.6	1.2646	33.1	1.2956
33.0	1.2094	41.5	1.2189	41.4	1.2476	50.5	1.2726
50.2	1.1934	55.4	1.2055	54.9	1.2324	67.7	1.2532
67.5	1.1793	69.7	1.1930	69.4	1.2181	84.6	1.2364
84.3	1.1670	83.7	1.1821	83.2	1.2058	100.5	1.2223
101.7	1.1552	96.3	1.1727	96.7	1.1949	119.2	1.2076
118.8	1.1445	110.3	1.1633	110.6	1.1845	136.5	1.1952
136.5	1.1346	124.0	1.1547	124.5	1.1747	153.9	1.1836
144.3	1.1303	138.1	1.1462	138.4	1.1657	170.7	1.1731
153.8	1.1255	153.3	1.1380	152.0	1.1575	184.7	1.1649
169.6	1.1179	165.9	1.1312	165.7	1.1497	192.1	1.1607
188.3	1.1091	180.0	1.1242	179.4	1.1423	199.1	1.1568
205.6	1.1015	195.0	1.1171	193.9	1.1347	205.8	1.1530
		206.9	1.1118	207.5	1.1282		
			Ethanol				
		0.1	1.2735	0.1	1.3120		
		7.0	1.2649	14.2	1.2913		
		14.0	1.2566	21.1	1.2815		
		20.9	1.2483	28.4	1.2720		
		35.3	1.2331	34.8	1.2636		
		48.5	1.2194	42.1	1.2549		
		62.2	1.2083	48.3	1.2495		
		76.1	1.1975	55.1	1.2430		
		83.2	1.1924	62.5	1.2366		
		89.9	1.1882	69.4	1.2295		
		103.9	1.1786	76.3	1.2239		
		117.6	1.1699	103.9	1.2035		
		131.4	1.1619	117.6	1.1950		
		141.8	1.1558	131.6	1.1868		
		162.1	1.1452	155.2	1.1711		
		176.3	1.1394	189.7	1.1534		
		176.3	1.1396	207.0	1.1433		
		193.2	1.1321	224.2	1.1378		
		210.7	1.1253	241.4	1.1324		
		210.7	1.1244	258.7	1.1225		
		227.6	1.1171	275.9	1.1183		
		241.4	1.1126	293.1	1.1091		
		265.6	1.1024	310.4	1.1053		

Table AI. *(Continued)*

283.15 K		298.15 K		323.15 K		348.15 K	
P	*v*	*P*	*v*	*P*	*v*	*P*	*v*
			1-Propanol				
0.1	1.2331	0.1	1.2511	0.1	1.2838	0.1	1.3201
15.6	1.2172	17.5	1.2319	17.9	1.2596	17.8	1.2924
32.4	1.2021	34.9	1.2146	37.5	1.2382	35.3	1.2689
50.0	1.1883	51.8	1.2009	52.5	1.2244	55.3	1.2476
67.5	1.1761	69.4	1.1872	69.4	1.2106	69.7	1.2342
84.8	1.1653	87.9	1.1749	86.8	1.1979	87.2	1.2195
102.0	1.1554	102.7	1.1654	104.2	1.1865	104.2	1.2070
119.5	1.1462	120.4	1.1555	120.8	1.1765	121.6	1.1953
137.0	1.1376	138.5	1.1462	139.0	1.1663	138.7	1.1848
154.0	1.1299	154.7	1.1382	155.6	1.1576	155.9	1.1751
171.5	1.1224	172.5	1.1303	174.0	1.1489	173.3	1.1658
188.9	1.1153	189.9	1.1232	190.9	1.1412	188.7	1.1582
206.0	1.1087	206.9	1.1164	206.6	1.1348	207.6	1.1497
			2-Propanol				
0.1	1.2611	0.1	1.2790	0.1	1.3163	0.1	1.3612
18.7	1.2406	18.8	1.2552	18.3	1.2888	17.8	1.3264
35.3	1.2242	35.5	1.2373	34.9	1.2675	34.9	1.3002
52.9	1.2094	52.6	1.2217	52.9	1.2485	52.6	1.2780
69.6	1.1969	70.2	1.2076	70.0	1.2329	70.0	1.2598
87.5	1.1850	87.0	1.1956	86.9	1.2193	87.5	1.2438
104.9	1.1744	103.7	1.1847	104.6	1.2066	104.2	1.2304
121.4	1.1653	122.0	1.1739	121.6	1.1955	121.2	1.2179
138.3	1.1565	138.9	1.1645	138.9	1.1850	138.0	1.2069
156.1	1.1478	155.7	1.1559	156.1	1.1755	155.7	1.1961
174.1	1.1397	173.4	1.1476	173.9	1.1665	173.5	1.1862
			1-Butanol				
0.1	1.2249	0.1	1.2415	0.1	1.2719	0.1	1.3054
16.2	1.2098	15.5	1.2249	16.2	1.2509	16.4	1.2805
33.1	1.1955	33.0	1.2087	33.4	1.2326	33.3	1.2596
50.4	1.1829	50.4	1.1948	51.4	1.2165	50.6	1.2415
67.4	1.1716	67.7	1.1826	67.8	1.2032	67.9	1.2259
84.8	1.1611	84.7	1.1719	85.0	1.1908	84.9	1.2121
101.6	1.1518	101.9	1.1618	102.4	1.1795	102.1	1.2000
119.1	1.1429	117.2	1.1536	119.6	1.1691	119.5	1.1881
136.6	1.1346	135.9	1.1442	136.6	1.1597	136.1	1.1779
153.7	1.1271	153.5	1.1361	154.0	1.1508	154.2	1.1680
171.1	1.1199	170.9	1.1286	171.3	1.1426	171.6	1.1589
188.7	1.1131	188.9	1.1211	188.8	1.1347	188.9	1.1505
205.8	1.1067	205.9	1.1145	204.7	1.1273	206.1	1.1426

Table AI. *(Continued)*

283.15 K		298.15 K		323.15 K		348.15 K	
P	*v*	*P*	*v*	*P*	*v*	*P*	*v*
			2-Butanol				
0.1	1.2284	0.1	1.2463	0.1	1.2816	0.1	1.3204
16.2	1.2111	15.8	1.2280	15.4	1.2601	15.8	1.2937
33.0	1.1965	33.3	1.2113	32.9	1.2405	32.7	1.2703
50.5	1.1835	50.4	1.1972	50.9	1.2239	50.2	1.2507
67.5	1.1719	67.7	1.1846	67.5	1.2097	67.5	1.2340
85.2	1.1614	84.9	1.1734	84.8	1.1969	84.7	1.2196
101.1	1.1525	102.1	1.1632	102.1	1.1854	101.6	1.2067
119.6	1.1430	119.5	1.1538	119.5	1.1750	118.7	1.1951
136.8	1.1347	136.2	1.1451	136.9	1.1653	138.3	1.1829
154.1	1.1270	154.0	1.1368	154.1	1.1565	153.5	1.1745
171.1	1.1198	171.6	1.1290	171.1	1.1484	170.8	1.1654
188.9	1.1129	188.9	1.1218	188.5	1.1406	188.3	1.1568
206.0	1.1065	206.5	1.1150	206.2	1.1332	205.8	1.1488
			2-Methyl-1-propanol				
0.1	1.2360	0.1	1.2534	0.1	1.2857	0.1	1.3204
15.8	1.2192	15.9	1.2347	16.1	1.2633	16.5	1.2937
33.2	1.2037	33.0	1.2178	33.0	1.2439	32.9	1.2706
50.6	1.1902	50.5	1.2031	50.2	1.2274	50.3	1.2513
67.8	1.1784	67.8	1.1903	67.1	1.2131	67.7	1.2346
84.9	1.1677	85.1	1.1789	84.9	1.1999	83.9	1.2210
101.8	1.1581	102.4	1.1684	102.3	1.1882	101.9	1.2076
118.9	1.1490	119.5	1.1589	119.4	1.1778	119.5	1.1956
136.6	1.1404	136.5	1.1502	135.6	1.1685	136.5	1.1851
154.1	1.1328	153.9	1.1419	153.6	1.1592	154.0	1.1752
171.4	1.1254	171.6	1.1341	171.2	1.1507	171.3	1.1662
188.9	1.1184	188.5	1.1270	188.7	1.1427	188.6	1.1577
206.1	1.1118	206.5	1.1199	205.9	1.1354	205.9	1.1498

Table AI. *(Continued)*

283.15 K		298.15 K		323.15 K		348.15 K	
P	*v*	*P*	*v*	*P*	*v*	*P*	*v*
				2-Methyl-2-propanol			
				0.1	1.3261	0.1	1.3762
				6.7	1.3137	20.1	1.3315
				13.2	1.3023	30.3	1.3144
				18.1	1.2942	40.4	1.2995
				20.2	1.2916	50.7	1.2862
				27.1	1.2818	61.1	1.2740
				33.9	1.2731	71.4	1.2631
				40.8	1.2648	81.6	1.2529
				46.0	1.2588	88.9	1.2464
				51.6	1.2528	95.7	1.2403
				54.0	1.2507		
				61.4	1.2433		
				68.4	1.2368		
				Water			
0.1	1.0003	0.1	1.0030	0.1	1.0121	0.1	1.0258
17.4	0.9918	13.9	0.9968	13.9	1.0060	17.4	1.0180
34.4	0.9845	27.7	0.9909	27.6	1.0003	34.3	1.0106
51.8	0.9774	41.7	0.9850	41.3	0.9948	51.3	1.0034
69.1	0.9706	55.1	0.9799	55.4	0.9892	68.8	0.9964
86.4	0.9641	69.3	0.9745	70.3	0.9838	85.6	0.9899
103.6	0.9580	83.2	0.9694	83.5	0.9790	102.9	0.9835
120.8	0.9521	96.6	0.9647	97.5	0.9742	120.3	0.9774
138.0	0.9464	110.3	0.9601	110.5	0.9698	137.0	0.9715
155.0	0.9412	124.1	0.9555	124.7	0.9653	155.0	0.9657
173.9	0.9359	138.3	0.9511	137.9	0.9612	173.2	0.9601
189.9	0.9314	152.3	0.9467	153.4	0.9564	189.5	0.9555
207.1	0.9272	165.3	0.9426	165.9	0.9527	206.7	0.9502
		179.9	0.9386	179.9	0.9486		
		193.7	0.9347	193.5	0.9448		
		207.7	0.9309	207.6	0.9408		
		221.5	0.9273	221.5	0.9370		
		235.9	0.9236	234.7	0.9334		
		249.3	0.9203	248.6	0.9298		
		263.2	0.9169	263.1	0.9260		
		277.3	0.9136	275.7	0.9226		
				290.0	0.9190		
				303.2	0.9151		

Table AII. Specific Volume of Alcohol + Water Mixtures (P in MPa; v in $dm^3 \cdot kg^{-1}$)[a]

(A) Methanol + water

283.15 K		298.15 K		323.15 K		348.15 K	
P	v	P	v	P	v	P	v
			$x(MeOH) = 0.15$				
0.1	1.0367	0.1	1.0431	0.1	1.0573	0.8	1.0734
17.2	1.0287	14.3	1.0367	13.1	1.0512	16.7	1.0646
34.6	1.0215	29.1	1.0307	28.1	1.0443	33.8	1.0559
51.7	1.0147	42.9	1.0247	41.7	1.0383	50.9	1.0477
69.0	1.0083	55.7	1.0197	55.6	1.0324	68.2	1.0401
85.8	1.0022	69.5	1.0145	70.0	1.0265	84.6	1.0329
103.2	0.9961	83.5	1.0092	83.2	1.0215	102.9	1.0257
120.4	0.9904	97.4	1.0043	97.3	1.0162	120.0	1.0192
137.6	0.9848	110.6	0.9997	111.5	1.0111	137.3	1.0130
154.9	0.9793	125.3	0.9949	124.9	1.0064	154.5	1.0071
172.4	0.9740	139.0	0.9904	138.6	1.0018	189.3	0.9958
189.5	0.9689	152.3	0.9863	153.8	0.9970	206.4	0.9905
206.8	0.9640	166.2	0.9822	166.7	0.9930		
		180.2	0.9780	179.0	0.9891		
		194.1	0.9740	193.8	0.9848		
		207.7	0.9702	207.6	0.9809		
			$x(MeOH) = 0.25$				
0.1	1.0594	0.1	1.0683	0.1	1.0862	3.5	1.1057
3.3	1.0578	13.5	1.0611	13.8	1.0786	17.0	1.0973
16.9	1.0513	28.5	1.0546	28.0	1.0713	33.7	1.0873
34.2	1.0436	42.0	1.0486	41.5	1.0647	51.0	1.0780
51.4	1.0366	55.4	1.0430	56.7	1.0577	71.0	1.0679
68.8	1.0296	71.5	1.0366	69.7	1.0521	85.5	1.0611
85.9	1.0231	83.0	1.0321	83.2	1.0464	102.7	1.0535
103.0	1.0170	97.1	1.0269	97.1	1.0408	119.6	1.0464
119.4	1.0115	110.8	1.0218	110.6	1.0356	137.1	1.0395
137.4	1.0054	124.9	1.0170	124.2	1.0306	154.4	1.0329
155.1	0.9997	138.4	1.0124	138.4	1.0255	171.7	1.0267
172.1	0.9945	152.0	1.0081	151.8	1.0210	189.0	1.0208
189.2	0.9895	166.0	1.0036	165.7	1.0164	206.2	1.0149
206.5	0.9846	179.8	0.9994	179.9	1.0117		
		194.2	0.9952	193.8	1.0071		
		207.4	0.9913	207.8	1.0027		

[a] Other experimental data available from T. Makita on request are as follows: $MeOH + H_2O$—$x = 0.10$, 0.30, 0.35; $1\text{-}PrOH + H_2O$—$x = 0.15$, 0.30, 0.40; $2\text{-}PrOH + H_2O$—$x = 0.03$, 0.10; $t\text{-}BuOH + H_2O$—$x = 0.01$, 0.02, 0.03, 0.04, 0.07, 0.10, 0.15, 0.30, 0.40, 0.65.

Table AII. *(Continued)*

(A) Methanol + water							
283.15 K		298.15 K		323.15 K		348.15 K	
P	v	P	v	P	v	P	v
			$x(MeOH) = 0.50$				
0.1	1.1214	0.1	1.1340	0.1	1.1606	4.5	1.1842
1.5	1.1205	13.5	1.1241	12.8	1.1495	16.7	1.1728
33.7	1.0993	27.6	1.1150	27.4	1.1383	33.4	1.1584
50.9	1.0899	42.0	1.1063	41.6	1.1286	50.5	1.1453
68.1	1.0812	55.7	1.0985	55.6	1.1196	66.7	1.1340
85.3	1.0733	69.6	1.0913	69.2	1.1116	75.9	1.1280
102.5	1.0657	85.0	1.0837	82.8	1.1041	85.1	1.1226
119.8	1.0585	97.5	1.0779	97.2	1.0966	102.1	1.1128
137.1	1.0517	110.8	1.0719	110.8	1.0900	119.5	1.1036
151.6	1.0464	124.3	1.0661	124.5	1.0836	132.5	1.0969
171.5	1.0392	138.4	1.0603	138.4	1.0773	154.3	1.0865
188.6	1.0334	151.8	1.0552	152.6	1.0712	171.5	1.0790
206.4	1.0276	165.8	1.0500	165.9	1.0659	188.5	1.0719
		180.4	1.0448	173.4	1.0629	206.1	1.0651
		193.5	1.0403	192.6	1.0556		
		207.3	1.0355	207.6	1.0502		
			$x(MeOH) = 0.75$				
0.1	1.1861	0.1	1.2037	0.1	1.2367	0.9	1.2699
0.9	1.1854	13.5	1.1891	13.9	1.2198	16.3	1.2467
16.2	1.1704	27.7	1.1762	27.4	1.2053	33.1	1.2257
33.1	1.1559	41.8	1.1648	41.4	1.1921	50.6	1.2068
50.2	1.1429	55.5	1.1547	55.1	1.1805	67.6	1.1909
67.7	1.1311	69.4	1.1452	69.1	1.1697	84.8	1.1767
84.8	1.1205	83.1	1.1364	83.4	1.1595	102.1	1.1638
102.1	1.1109	96.8	1.1282	97.5	1.1502	119.2	1.1522
119.4	1.1019	111.0	1.1205	111.4	1.1418	135.2	1.1420
136.7	1.0933	124.6	1.1132	124.9	1.1340	154.2	1.1311
171.2	1.0777	138.4	1.1064	138.0	1.1268	171.1	1.1219
188.3	1.0706	152.0	1.1000	152.5	1.1195	188.6	1.1131
205.5	1.0637	165.7	1.0940	165.7	1.1131	205.8	1.1048
		179.7	1.0880	180.2	1.1064		
		193.8	1.0822	194.4	1.1002		
		207.6	1.0769	221.5	1.0890		

Table AII. *(Continued)*

(B) Ethanol + water							
298.15 K		323.15 K		298.15 K		323.15 K	
P	v	P	v	P	v	P	v
x(EtOH) = 0.20				x(EtOH) = 0.40			
0.1	1.0712	0.1	1.0962	0.1	1.1365	0.1	1.1666
8.4	1.0669	27.8	1.0819	9.0	1.1298	15.0	1.1556
20.1	1.0613	34.4	1.0790	14.6	1.1263	28.2	1.1465
29.1	1.0572	41.3	1.0747	28.2	1.1174	35.4	1.1411
34.0	1.0555	49.5	1.0712	36.1	1.1128	41.5	1.1371
42.1	1.0515	56.1	1.0684	48.7	1.1055	48.4	1.1322
48.5	1.0488	62.7	1.0649	55.4	1.1011	55.6	1.1276
72.8	1.0394	69.5	1.0627	62.3	1.0974	62.5	1.1226
76.3	1.0379	83.1	1.0570	69.5	1.0933	69.9	1.1184
90.6	1.0325	97.1	1.0504	76.7	1.0911	80.0	1.1120
104.2	1.0277	107.3	1.0470	90.2	1.0842	92.4	1.1053
117.3	1.0223	108.6	1.0466	103.9	1.0788	100.2	1.1015
117.6	1.0231	120.8	1.0421	107.3	1.0767	121.2	1.0929
131.7	1.0180	121.6	1.0421	117.7	1.0729	131.8	1.0887
141.8	1.0150	132.9	1.0379	121.1	1.0712	138.0	1.0857
176.3	1.0050	138.0	1.0349	131.7	1.0673	176.3	1.0744
190.1	1.0010	155.2	1.0296	176.3	1.0506	189.7	1.0662
207.3	0.9956	176.3	1.0242	210.7	1.0395	207.0	1.0646
224.5	0.9919	189.7	1.0185	243.6	1.0289	258.7	1.0429
246.9	0.9867	224.2	1.0096	279.7	1.0190	275.9	1.0359
279.7	0.9777	258.7	0.9984	314.5	1.0099	293.1	1.0323
293.5	0.9744	313.8	0.9854	348.6	1.0021	310.4	1.0264
314.2	0.9697						

Table AII. *(Continued)*

(B) Ethanol + water							
298.15 K		323.15 K		298.15 K		323.15 K	
P	v	P	v	P	v	P	v
x(EtOH) = 0.60				x(EtOH) = 0.80			
0.1	1.1894	0.1	1.2226	0.1	1.2335	0.1	1.2712
7.6	1.1826	14.3	1.2106	7.5	1.2252	21.1	1.2458
14.6	1.1759	21.3	1.2044	15.3	1.2165	28.0	1.2380
20.6	1.1711	27.8	1.1992	21.4	1.2111	34.9	1.2311
28.9	1.1645	35.1	1.1930	27.5	1.2048	41.7	1.2242
38.1	1.1578	41.6	1.1882	41.7	1.1921	48.8	1.2172
48.6	1.1499	48.6	1.1828	48.0	1.1868	55.7	1.2120
62.5	1.1407	55.4	1.1763	51.8	1.1841	62.7	1.2047
70.1	1.1366	62.8	1.1708	60.0	1.1781	70.0	1.1998
90.2	1.1257	82.9	1.1573	76.3	1.1676	79.4	1.1927
103.7	1.1183	96.8	1.1471	90.7	1.1586	92.2	1.1850
107.3	1.1165	111.0	1.1381	103.7	1.1507	96.8	1.1794
118.1	1.1118	124.7	1.1312	107.3	1.1485	106.3	1.1738
131.5	1.1056	132.1	1.1274	117.8	1.1427	110.8	1.1727
141.8	1.1005	138.0	1.1223	131.4	1.1355	123.6	1.1651
176.3	1.0871	155.2	1.1154	141.8	1.1303	133.7	1.1591
193.2	1.0799	189.7	1.0996	162.1	1.1211	172.5	1.1389
210.7	1.0757	207.0	1.0924	189.7	1.1080	189.7	1.1311
259.0	1.0595	224.2	1.0865	224.2	1.0955	224.1	1.1158
279.7	1.0521	241.4	1.0814	245.2	1.0884	241.4	1.1096
293.5	1.0467	258.7	1.0744	265.6	1.0816	258.7	1.1028
314.2	1.0417	275.9	1.0703	279.7	1.0775	275.9	1.0964
		293.1	1.0618	293.5	1.0733	293.1	1.0901
		310.4	1.0593	314.2	1.0667	310.4	1.0870
				348.6	1.0569		

Table AII. *(Continued)*

(C) 1-Propanol + water							
283.15 K		298.15 K		323.15 K		348.15 K	
P	v	P	v	P	v	P	v
			x(1-PrOH) = 0.07				
0.1	1.0281	0.1	1.0350	0.1	1.0513	0.1	1.0703
17.3	1.0210	18.7	1.0270	18.2	1.0430	18.0	1.0610
35.3	1.0140	35.8	1.0200	35.5	1.0354	35.1	1.0526
52.8	1.0076	52.9	1.0135	52.5	1.0284	52.2	1.0449
70.4	1.0015	69.9	1.0076	70.4	1.0212	69.2	1.0376
86.6	0.9963	87.0	1.0016	87.0	1.0150	86.3	1.0306
103.4	0.9908	103.9	0.9960	104.7	1.0086	103.5	1.0241
122.0	0.9850	120.0	0.9908	121.5	1.0028	121.3	1.0177
139.2	0.9800	138.9	0.9850	139.0	0.9972	138.0	1.0119
156.1	0.9751	156.3	0.9800	155.9	0.9920	155.4	1.0062
174.4	0.9701	173.5	0.9751	173.9	0.9866	172.6	1.0007
191.1	0.9656	190.9	0.9704	190.6	0.9819	191.4	0.9948
208.0	0.9613	208.3	0.9658	208.7	0.9770	208.8	0.9898
			x(1-PrOH) = 0.25				
0.1	1.0995	0.1	1.1120	0.1	1.1360	0.1	1.1641
17.5	1.0890	17.7	1.1007	18.7	1.1224	17.5	1.1491
34.9	1.0795	35.1	1.0906	35.6	1.1115	35.1	1.1360
52.2	1.0709	52.9	1.0812	52.2	1.1014	52.3	1.1243
69.4	1.0630	69.7	1.0732	69.4	1.0921	69.4	1.1141
84.2	1.0565	87.0	1.0658	89.0	1.0823	86.8	1.1043
104.2	1.0483	104.2	1.0582	104.9	1.0751	104.0	1.0956
122.0	1.0417	121.5	1.0515	121.3	1.0681	121.3	1.0873
138.9	1.0356	139.0	1.0450	138.2	1.0613	139.9	1.0788
156.2	1.0297	156.3	1.0389	155.2	1.0546	156.8	1.0720
173.5	1.0242	173.5	1.0330	173.0	1.0483	173.2	1.0658
190.1	1.0190	190.1	1.0278	190.9	1.0420	190.2	1.0594
207.3	1.0141	208.0	1.0222	208.3	1.0364	207.1	1.0533

Table AII. *(Continued)*

(C) 1-Propanol + water

283.15 K		298.15 K		323.15 K		348.15 K	
P	v	P	v	P	v	P	v
			x(1-PrOH) = 0.50				
0.1	1.1621	0.1	1.1774	0.1	1.2076	0.1	1.2418
16.2	1.1492	17.8	1.1622	18.0	1.1893	17.6	1.2206
34.0	1.1366	34.8	1.1499	34.6	1.1750	34.5	1.2036
52.5	1.1249	52.5	1.1378	51.5	1.1624	51.4	1.1885
70.2	1.1147	69.6	1.1276	69.2	1.1506	69.3	1.1753
87.0	1.1062	87.3	1.1178	85.8	1.1405	86.2	1.1634
104.7	1.0978	103.0	1.1097	103.5	1.1310	103.4	1.1527
121.5	1.0904	120.4	1.1016	120.9	1.1217	121.2	1.1423
137.6	1.0835	138.5	1.0937	138.0	1.1133	137.7	1.1332
156.3	1.0764	155.4	1.0867	155.4	1.1060	155.5	1.1249
173.4	1.0700	172.6	1.0801	172.5	1.0985	172.4	1.1170
190.2	1.0641	190.2	1.0736	190.1	1.0916	189.6	1.1097
207.9	1.0579	207.5	1.0676	207.8	1.0848	207.5	1.1024
			x(1-PrOH) = 0.75				
0.1	1.2012	0.1	1.2190	0.1	1.2519	0.1	1.2884
17.9	1.1852	17.3	1.2013	18.4	1.2301	17.7	1.2630
36.3	1.1701	34.9	1.1863	34.9	1.2134	35.3	1.2424
51.8	1.1594	52.0	1.1734	52.2	1.1984	52.2	1.2255
69.2	1.1486	68.9	1.1621	69.4	1.1851	68.7	1.2107
86.3	1.1389	86.3	1.1510	86.3	1.1736	87.0	1.1968
104.2	1.1286	103.5	1.1413	103.4	1.1631	104.2	1.1852
121.5	1.1203	120.9	1.1325	121.1	1.1529	121.5	1.1743
138.7	1.1125	138.7	1.1236	138.2	1.1439	138.3	1.1645
156.1	1.1051	155.2	1.1163	155.4	1.1355	155.9	1.1551
174.0	1.0981	172.8	1.1089	172.8	1.1276	173.3	1.1464
191.4	1.0918	189.7	1.1021	190.1	1.1205	190.6	1.1383
208.5	1.0858	206.9	1.0957	205.2	1.1149	207.6	1.1309

Table AII. *(Continued)*

(D) 2-Propanol + water

283.15 K		298.15 K		323.15 K		348.15 K	
P	v	P	v	P	v	P	v
			x(2-PrOH) = 0.06				
01	1.0256	0.1	1.0306	0.1	1.0459	0.1	1.0653
19.8	1.0176	19.3	1.0224	19.2	1.0378	18.9	1.0560
37.1	1.0113	37.1	1.0156	36.3	1.0307	36.0	1.0479
54.2	1.0052	53.8	1.0094	52.6	1.0242	52.9	1.0405
71.8	0.9992	71.5	1.0033	71.0	1.0174	70.7	1.0334
87.8	0.9940	88.3	0.9976	87.1	1.0116	87.1	1.0268
105.9	0.9884	105.5	0.9921	105.0	1.0054	104.8	1.0202
122.2	0.9833	122.3	0.9868	121.3	1.0001	122.5	1.0139
139.9	0.9781	140.4	0.9815	139.4	0.9945	139.2	1.0084
156.9	0.9732	157.1	0.9766	156.6	0.9892	156.0	1.0029
174.1	0.9685	173.8	0.9717	173.7	0.9844	174.2	0.9974
190.6	0.9640	190.8	0.9669	190.9	0.9796	190.4	0.9924
			x(2-PrOH) = 0.25				
0.1	1.1015	0.1	1.1149	0.1	1.1424	0.1	1.1722
18.9	1.0903	18.4	1.1030	18.4	1.1286	18.7	1.1562
36.2	1.0809	35.6	1.0928	35.3	1.1171	35.1	1.1439
53.0	1.0726	52.6	1.0837	53.1	1.1065	52.5	1.1321
70.0	1.0648	69.4	1.0756	70.4	1.0971	69.7	1.1217
87.7	1.0575	86.6	1.0678	87.1	1.0887	86.6	1.1120
104.2	1.0507	103.7	1.0605	104.6	1.0806	103.5	1.1028
121.5	1.0444	121.4	1.0534	121.8	1.0730	121.4	1.0943
139.0	1.0382	138.7	1.0470	139.3	1.0659	138.1	1.0867
156.0	1.0325	155.5	1.0410	155.6	1.0595	155.1	1.0793
173.0	1.0269	172.7	1.0352	172.7	1.0532	173.2	1.0720
190.4	1.0224	190.5	1.0294	190.1	1.0470	189.7	1.0655

Table AII. *(Continued)*

(D) 2-Propanol + water							
283.15 K		298.15 K		323.15 K		348.15 K	
P	*v*	*P*	*v*	*P*	*v*	*P*	*v*
			x(2-PrOH) = 0.50				
0.1	1.1753	0.1	1.1923	0.1	1.2259	0.1	1.2638
19.0	1.1599	18.3	1.1758	17.5	1.2062	19.0	1.2400
35.3	1.1480	35.2	1.1623	35.3	1.1895	35.7	1.2216
52.8	1.1368	53.1	1.1499	53.3	1.1753	52.6	1.2059
70.4	1.1267	69.9	1.1394	70.3	1.1632	69.2	1.1924
87.1	1.1177	87.1	1.1296	86.4	1.1528	87.0	1.1794
104.5	1.1093	105.1	1.1203	104.6	1.1422	104.4	1.1680
120.9	1.1017	122.1	1.1121	122.2	1.1328	121.8	1.1576
138.8	1.0941	139.4	1.1045	138.3	1.1247	138.9	1.1481
155.4	1.0874	156.3	1.0973	155.8	1.1166	155.5	1.1395
173.7	1.0805	173.8	1.0903	172.6	1.1092	173.2	1.1310
190.3	1.0746	190.9	1.0838	190.1	1.1019	190.3	1.1230
			x(2-PrOH) = 0.75				
0.1	1.2243	0.1	1.2424	0.1	1.2790	0.1	1.3226
18.9	1.2058	18.6	1.2225	17.5	1.2554	17.7	1.2929
35.4	1.1914	35.9	1.2060	35.8	1.2347	35.5	1.2689
52.3	1.1784	52.8	1.1921	53.6	1.2175	52.8	1.2494
69.3	1.1669	70.3	1.1795	70.4	1.2038	70.6	1.2328
86.7	1.1564	87.7	1.1682	88.0	1.1909	87.7	1.2185
103.9	1.1468	104.4	1.1583	104.8	1.1795	104.7	1.2058
121.6	1.1377	121.9	1.1488	121.4	1.1694	122.0	1.1941
138.3	1.1297	138.5	1.1403	139.4	1.1593	138.1	1.1838
155.6	1.1219	156.3	1.1320	157.3	1.1501	155.9	1.1737
		173.7	1.1244	172.5	1.1427	172.9	1.1648
				190.4	1.1345	189.8	1.1563

Table AII. *(Continued)*

(E) 2-Methyl-2-propanol + water					
298.15 K		323.15 K		348.15 K	
P	*v*	*P*	*v*	*P*	*v*
		$x(t\text{-BuOH}) = 0.05$			
01	1.0302	0.1	1.0475	0.1	1.0638
18.7	1.0224	18.0	1.0390	18.4	1.0546
36.5	1.0155	34.9	1.0318	35.3	1.0466
53.4	1.0093	52.9	1.0246	52.9	1.0388
69.7	1.0035	70.4	1.0180	69.7	1.0317
87.1	0.9977	86.5	1.0120	87.0	1.0249
104.8	0.9920	104.6	1.0059	103.7	1.0183
122.8	0.9866	121.3	1.0005	120.9	1.0123
139.1	0.9817	139.0	0.9950	139.2	1.0062
156.6	0.9766	155.4	0.9901	156.1	1.0008
174.4	0.9718	173.7	0.9849	173.3	0.9954
191.3	0.9674	190.7	0.9800	190.7	0.9902
210.1	0.9626	208.2	0.9756	210.9	0.9845
		$x(t\text{-BuOH}) = 0.10$			
0.1	1.0619	0.1	1.0848	0.1	1.1069
18.0	1.0524	17.5	1.0743	17.7	1.0947
35.3	1.0442	34.6	1.0652	34.8	1.0840
52.5	1.0368	51.8	1.0567	52.2	1.0746
69.1	1.0301	69.6	1.0489	69.4	1.0660
86.3	1.0235	86.3	1.0421	85.9	1.0584
104.0	1.0171	104.6	1.0348	104.2	1.0504
121.3	1.0112	120.8	1.0289	120.9	1.0434
138.9	1.0057	138.7	1.0226	139.2	1.0365
155.6	1.0003	155.2	1.0173	155.8	1.0307
173.3	0.9951	173.3	1.0115	174.4	1.0243
190.1	0.9904	189.9	1.0063	190.2	1.0194
208.3	0.9853	208.5	1.0011	208.0	1.0136

Table AII. *(Continued)*

(E) 2-Methyl-2-propanol + water					
298.15 K		323.15 K		348.15 K	
P	v	P	v	P	v
		$x(t\text{-BuOH}) = 0.25$			
0.1	1.1362	0.1	1.1653	0.1	1.1940
18.5	1.1226	18.0	1.1499	17.2	1.1763
35.5	1.1117	35.3	1.1369	34.4	1.1611
52.9	1.1015	52.6	1.1255	52.9	1.1470
69.4	1.0928	69.7	1.1154	69.7	1.1357
86.8	1.0843	85.9	1.1065	86.7	1.1249
104.5	1.0763	104.2	1.0975	104.0	1.1155
121.9	1.0689	119.1	1.0906	123.2	1.1058
138.8	1.0623	139.7	1.0815	139.7	1.0979
155.8	1.0558	156.1	1.0748	155.2	1.0909
173.7	1.0496	173.3	1.0681	173.3	1.0834
190.0	1.0440	189.7	1.0619	189.9	1.0769
209.5	1.0377	209.3	1.0551	109.7	1.0694
		$x(t\text{-BuOH}) = 0.50$			
0.1	1.2096	0.1	1.2448	0.1	1.2774
17.4	1.1923	18.2	1.2231	18.5	1.2507
36.6	1.1758	34.8	1.2061	34.9	1.2313
52.7	1.1642	51.8	1.1912	52.1	1.2139
69.4	1.1535	69.5	1.1781	68.9	1.1991
87.3	1.1425	86.3	1.1668	86.2	1.1858
104.6	1.1333	103.9	1.1563	103.7	1.1735
121.5	1.1248	120.6	1.1468	121.5	1.1624
139.1	1.1167	138.9	1.1373	138.6	1.1525
156.2	1.1092	155.6	1.1293	153.0	1.1450
173.3	1.1023	173.7	1.1214	173.2	1.1347
179.6	1.1005	190.3	1.1144	190.3	1.1269
188.2	1.0971	208.8	1.1070	209.3	1.1186

Table AII. *(Continued)*

(E) 2-Methyl-2-propanol + water					
298.15 K		323.15 K		348.15 K	
P	*v*	*P*	*v*	*P*	*v*
		$x(t\text{-BuOH}) = 0.75$			
0.1	1.2508	0.1	1.2926	0.1	1.3331
4.8	1.2446	8.7	1.2784	6.8	1.3194
8.2	1.2402	17.7	1.2659	9.6	1.3143
11.5	1.2365	20.1	1.2628	18.6	1.2984
16.9	1.2302	24.9	1.2565	25.1	1.2885
27.3	1.2189	34.7	1.2451	34.6	1.2745
34.8	1.2116	36.6	1.2433	51.8	1.2534
41.5	1.2054	51.8	1.2282	68.5	1.2362
51.8	1.1965	68.4	1.2142	86.5	1.2202
58.0	1.1913	85.8	1.2011	104.4	1.2059
69.4	1.1832	102.7	1.1895	121.0	1.1940
76.3	1.1779	120.9	1.1783	123.2	1.1924
85.9	1.1716	208.8	1.1070	138.3	1.1827

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Messrs. M. Morikawa and Y. Doi for their careful experimental efforts in this work.

REFERENCES

1. R. E. Gibson, *J. Am. Chem. Soc.* **57**:1551 (1935).
2. T. Moriyoshi, Y. Morishita, and H. Inubushi, *J. Chem. Thermodyn.* **9**:577 (1977).
3. T. Moriyoshi and H. Inubushi, *J. Chem. Thermodyn.* **9**:587 (1977).
4. J. E. Stutchbury, *Aust. J. Chem.* **9**:536 (1956).
5. S. D. Hamman and F. Smith, *Aust. J. Chem.* **24**:2431 (1971).
6. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **49**:3 (1913).
7. E. H. Amagat, *Ann. Chim. Phys.* **29**:508 (1893).
8. A. L. Moesveld, *Z. Phys. Chem.* **105**:450 (1923).
9. M. Yusa, G. P. Mathur, and R. A. Stage, *J. Chem. Eng. Data* **22**:32 (1977).
10. D. M. Newitt and K. E. Weal, *J. Chem. Soc.* 3092 (1951).
11. M. Nakagawa, Y. Miyamoto, and T. Moriyoshi, *J. Chem. Thermodyn.* **15**:15 (1983).
12. H. Kubota, Y. Tanaka, and T. Makita, *Kagaku Kogaku Ronbunshu* **1**:176 (1975).
13. M. Nakagawa, H. Inubushi, and T. Moriyoshi, *J. Chem. Thermodyn.* **13**:171 (1981).
14. T. Moriyoshi and Y. Uosaki, *J. Soc. Mat. Sci.* **33**:127 (1984).
15. A. J. Easteal and L. A. Woolf, *J. Chem. Thermodyn.* **16**:391 (1984).

16. Y. Tanaka, T. Yamamoto, Y. Satomi, H. Kubota, and T. Makita, *Rev. Phys. Chem. Jpn.* **47**:12 (1977).
17. H. Kubota, S. Tsuda, M. Murata, T. Yamamoto, Y. Tanaka, and T. Makita, *Rev. Phys. Chem. Jpn.* **49**:59 (1980).
18. G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc.* **A258**:565 (1965).
19. C. Chen, R. A. Fine, and F. J. Millero, *J. Am. Chem. Soc.* **57**:1551 (1935).
20. T. Grindley and J.E. Lind, Jr., *J. Chem. Phys.* **54**:3983 (1971).