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Viscosity of (Water + Alcohol) Mixtures Under High Pressure

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New experimental viscosity data are presented for aqueous solutions of methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol (t-butyl alcohol) in the temperature range from 283 to 348 K and pressures up to 120 MPa. The viscosity measurements were performed using a falling-cylinder viscometer on a relative basis with an uncertainty of less than 2%. The viscosity of pure alcohols and aqueous solutions is found to increase almost linearly with increasing pressure, whereas that of water decreases slightly with pressure at temperatures below 298 K. As for the composition dependence of the viscosity, a distinct maximum appears near 0.3–0.4 mole fraction of alcohol on all isobars at each temperature. The viscosity maximum shifts gradually to a higher alcohol concentration with increasing temperature and pressure. The isobars of aqueous 2-propanol and 2-methyl-2-propanol solutions have another shallow minimum near 0.9 mole fraction of alcohol below 323 K. The experimental results were analized empirically by a Tait-type equation and a free-volume theory. It was found that the isothermal viscosity data were satisfactorily correlated by these equations as functions of pressure and composition or of density and composition.

KEY WORDS: alcohols; aqueous alcohol solutions; ethanol; free-volume theory; methanol; 2-methyl-2-propanol; pressure effect; propanol; Tait equation; t-butyl alcohol; viscosity; water.

1. INTRODUCTION

Water is one of the most strongly hydrogen-bonded liquids and has various unusual physicochemical properties compared with normal liquids. Aqueous solutions of nonelectrolytes exhibit some anomalies in the composition dependences of thermodynamic and transport properties. In par-

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ticular, aqueous alcohol solutions are the most interesting systems for investigating complicated molecular interactions between unlike components because alcohols have both hydrophilic hydroxyl groups and hydrophobic alkyl groups in a molecule. Recently, aqueous alcohol solutions are of technical importance in relation to energy sources. Physicochemical studies on aqueous alcohol solutions under atmospheric pressure have been the subject of numerous investigations, however, relatively few works have been reported for the effect of pressure. The present investigation was undertaken to obtain extensive and accurate viscosity data for binary aqueous alcohol solutions under high pressure. Viscosity has been measured on five totally miscible aqueous alcohol solutions of methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), and 2-methyl-2-propanol (t-BuOH) in the temperature range from 283 to 348 K and at pressures up to 120 MPa. Experimental results as functions of pressure, temperature, and composition are discussed.

2. EXPERIMENTAL

2.1. The Viscometer

Viscosity was measured using a falling-cylinder viscometer which has been described in detail previously [1, 2]. The apparatus consists of a precisely bored Pyrex glass tube equipped coaxially in a high-pressure vessel and a blue glass plummet with hemispherical ends. The plummet is provided with four small projecting lugs at each end of the cylindrical part, which act as a guide to keep the falling cylinder concentric when it falls. The falling time of the plummet was determined within ±0.1 ms by a time-interval counter (Takeda Riken TR5820) using a He–Ne gas laser beam which passed through a pair of optical windows to a phototransistor. The high-pressure vessel was water jacketed and maintained isothermally to ±0.05 K by circulating water. Temperature monitoring was done with a thermistor device. The pressure was measured with a strain gauge-type pressure transducer (Toyo Baldwin HT-2000) within ±0.1 MPa. The falling time was measured in about 20 replicates for each experimental condition. The reproducibility of the falling-time measurement is within ±0.5%. The arithmetic mean was used to yield the reported viscosity.

2.2. Viscometer Calibration

The basic equation of the falling-cylinder viscometer is as follows:

$$\eta = K(\rho_b - \rho)t \tag{1}$$

where η is the viscosity, ρ and ρ_b are the densities of the sample liquid and the plummet, t is the falling time, and K is the instrument constant. The instrument constant and its temperature and pressure dependences were calibrated by distilled, deionized water and the viscosity standard liquid JS 5 provided from the National Research Laboratory of Metrology, Japan. The reference viscosity value of water was cited from Watson et al. [3]. The densities of the sample solutions were measured by a high-pressure burrette method [1, 4].

2.3. Materials

Extrapure alcohols were obtained from Wako Pure Chemical Industries, Ltd. The stated minimum purity is more than 99.5 % in volume. Alcohols and water were purified several times by fractional distillation and degassed by crystallization in vacuum. The mixtures were prepared by weighing using an analytical balance (Chyo Balance PT3-1200D) within ±0.005 %.

2.4. Uncertainty of Viscosity Measurements

The viscosity data obtained contain a definite uncertainty resulting from several sources of experimental errors. The main sources of errors and their contributions to the total uncertainty are estimated as follows.

Error source	Uncertainty contribution to η (%)
Temperature	±0.1
Pressure	±0.01
Composition of mixture	±0.02
Falling time	±0.5
Density	±0.1
Instrument constant	±1.0

An analysis of these factors leads to the conclusion that the uncertainty of the present measurements should be less than ±2 %, while the precision is ±0.5 %.

3. EXPERIMENTAL RESULTS

The experimental results are presented in Tables I–V as functions of temperature, pressure, and composition. Although the data for methanol and ethanol systems are obtained from the same experimental results in previous works [1, 2], the numerical values are revised by replacing the

Table I. Viscosity of (Water + Methanol) Mixtures (η in mPa · s)

P (MPa)	x^{a}						
	0.00	0.25	0.30	0.35	0.50	0.75	1.00
283.15 K							
0.1	1.310	2.549	2.498	2.417	1.970	1.271	0.695
9.9	1.299	2.585	2.572	2.488	2.041	1.325	0.738
19.7	1.289	2.632	2.611	2.556	2.091	1.371	0.783
29.5	1.281	2.661	2.650	2.618	2.147	1.423	0.813
39.3	1.274	2.700	2.729	2.686	2.219	1.468	0.859
49.1	1.268	2.725	2.784	2.759	2.268	1.523	0.881
58.9	1.263	2.747	2.839	2.826	2.338	1.576	0.913
68.8	1.260	2.783	2.892	2.896	2.376	1.619	0.948
298.15 K							
0.1	0.891	1.580	1.574	1.535	1.325	0.903	0.546
9.9	0.888	1.610	1.616	1.619	1.361	0.977	0.595
19.7	0.887	1.624	1.630	1.633	1.403	1.011	0.622
29.5	0.886	1.645	1.636	1.674	1.436	1.047	0.647
39.3	0.885	1.663	1.653	1.709	1.481	1.086	0.673
49.1	0.885	1.685	1.697	1.752	1.523	1.123	0.700
58.9	0.885	1.705	1.722	1.787	1.571	1.168	0.733
68.8	0.886	1.730	1.744	1.817	1.616	1.196	0.755
323.15 K							
0.1	0.547	0.837	0.842	0.833	0.755	0.576	0.395
9.9	0.549	0.850	0.856	0.846	0.778	0.601	0.412
19.7	0.551	0.863	0.864	0.874	0.788	0.618	0.428
29.5	0.553	0.869	0.893	0.895	0.825	0.632	0.449
39.3	0.555	0.877	0.901	0.911	0.840	0.649	0.467
49.1	0.557	0.889	0.917	0.921	0.858	0.672	0.481
58.9	0.560	0.897	0.923	0.921	0.870	0.686	0.510
68.8	0.562	0.912	0.933	0.939	0.892	0.709	0.521
348.15 K							
0.1	0.378						
9.9	0.380	0.543	0.555	0.550	0.521	0.407	0.313
19.7	0.383	0.551	0.567	0.564	0.537	-.428	0.329
29.5	0.386	0.566	0.579	0.576	0.550	0.446	0.342
39.3	0.388	0.578	0.591	0.590	0.563	0.473	0.358
49.1	0.391	0.588	0.603	0.603	0.578	0.491	0.373
58.9	0.394	0.598	0.615	0.615	0.593	0.508	0.388
68.8	0.396	0.609	0.627	0.628	0.606	0.526	0.404

[a] Mole fraction of methanol.

Table II. Viscosity of (Water + Ethanol) Mixtures (η in mPa · s)

P (MPa)	x[a]						
	0.00	0.20	0.30	0.40	0.60	0.78	1.00
298.15 K							
0.1	0.891	2.334	2.313	2.147	1.739	1.423	1.087
9.9	0.888	2.399	2.406	2.248	1.847	1.517	1.169
19.7	0.887	2.459	2.479	2.350	1.940	1.613	1.245
29.5	0.886	2.504	2.557	2.437	2.049	1.702	1.325
39.3	0.885	2.565	2.636	2.525	2.135	1.799	1.396
49.1	0.885	2.600	2.701	2.609	2.218	1.874	1.474
58.9	0.885	2.664	2.775	2.700	2.328	1.965	1.546
68.8	0.886	2.701	2.843	2.778	2.388	2.051	1.612
78.6	0.887	2.770	2.938	2.883	2.530	2.106	1.693
323.15 K							
0.1	0.547	1.080	1.108	1.072	0.941	0.810[b]	0.669
9.9	0.549	1.134	1.155	1.146	1.029	0.856[b]	0.748
19.7	0.551	1.137	1.169	1.167	1.060	0.884[b]	0.779
29.5	0.553	1.176	1.212	1.215	1.114	0.941[b]	0.839
39.3	0.555	1.187	1.251	1.266	1.168	0.998[b]	0.881
49.1	0.557	1.202	1.277	1.300	1.184	1.020[b]	0.928
58.9	0.560	1.235	1.344	1.336	1.237	1.083[b]	0.970

[a] Mole fraction of ethanol.
[b] The composition is $x = 0.80$.

reference viscosity values of water of the International Association for the Properties of Steam [5] with the improved reference values of Watson et al. [3].

3.1. Comparison of Experimental Results with Literature Values

Only one set of experimental data is found in the literature for the viscosity of aqueous methanol solutions under high pressure, while three sets of measurements are found for pure methanol. That is, Isdale et al. [6] measured the viscosity of aqueous methanol solutions at 298–323 K up to 400 MPa with a falling-cylinder viscometer. The viscosity of pure methanol was measured by Bridgman [7] at 303 and 348 K up to 1177 MPa, by Golubev and Petrov [8] from 423 to 543 K up to 81 MPa, and by Isakova and Oshueva [9] from 293 to 433 K up to 24.5 MPa. Figure 1 illustrates the pressure dependences of the viscosity of pure alcohols at 323 K together with the reference viscosity value of water. Available literature values, some

Table III. Viscosity of (Water + 1-Propanol) Mixtures (η in mPa·s)

P (MPa)	x^a 0.00	0.25	0.30	0.40	0.50	0.75	1.00
				283.15 K			
01	1.310	4.792	4.768	4.636	4.201	3.401	2.808
9.9	1.299	5.016	5.004	4.850	4.387	3.667	3.054
19.7	1.289	5.246	5.207	5.139	4.671	3.958	3.293
29.5	1.281	5.427	5.436	5.414	4.932	4.251	3.536
39.3	1.274	5.654	5.670	5.716	5.250	4.512	3.802
49.1	1.268	5.885	5.915	5.983	5.529	4.810	4.083
58.9	1.263	6.119	6.170	6.256	5.841	5.065	4.325
68.8	1.260	6.359	6.468	6.538	6.155	5.450	4.595
78.6	1.257	6.553	6.689	6.796	6.428	5.710	4.866
88.4	1.255	6.775	6.953	7.177	6.750	6.066	5.128
98.2	1.254	6.995	7.181	7.516	7.043	6.376	5.399
108.0	1.253	7.216	7.720	7.740	7.396	6.711	5.694
117.8	1.253	7.459	7.717	8.029	7.743	7.085	5.941
				298.15 K			
0.1	0.891	2.661	2.671	2.597	2.509	2.157	1.968
9.9	0.888	2.763	2.784	2.736	2.703	2.319	2.126
19.7	0.887	2.877	2.908	2.882	2.869	2.495	2.290
29.5	0.886	2.977	2.995	2.996	2.993	2.659	2.449
39.3	0.885	3.079	3.122	3.160	3.150	2.840	2.629
49.1	0.885	3.184	3.263	3.307	3.324	3.009	2.782
58.9	0.885	3.299	3.384	3.450	3.464	3.198	2.964
68.8	0.886	3.402	3.510	3.588	3.622	3.371	3.134
78.6	0.887	3.503	3.631	3.730	3.782	3.576	3.319
88.4	0.888	3.614	3.755	3.872	3.942	3.771	3.487
98.2	0.890	3.722	3.893	4.012	4.083	3.970	3.702
108.0	0.892	3.829	4.028	4.165	4.268	4.185	3.882
117.8	0.894	3.934	4.158	4.322	4.432	4.402	4.091
				323.15 K			
0.1	0.547	1.323	1.317	1.315	1.266	1.178	1.115
9.9	0.549	1.354	1.382	1.384	1.349	1.274	1.210
19.7	0.551	1.403	1.449	1.465	1.435	1.374	1.310
29.5	0.553	1.470	1.511	1.540	1.521	1.482	1.409
39.3	0.555	1.523	1.578	1.626	1.609	1.586	1.512
49.1	0.557	1.580	1.647	1.691	1.698	1.688	1.615
58.9	0.560	1.633	1.706	1.767	1.787	1.783	1.720
68.8	0.562	1.688	1.779	1.840	1.876	1.878	1.826
78.6	0.565	1.734	1.838	1.915	1.966	1.981	1.932
88.4	0.568	1.786	1.901	1.975	2.056	2.097	2.039
98.2	0.570	1.838	1.962	2.062	2.147	2.203	2.148
108.0	0.573	1.888	2.022	2.133	2.236	2.307	2.255
117.8	0.576	1.937	2.081	2.203	2.324	2.412	2.362

[a] Mole fraction of 1-propanol.

of which are obtained by interpolation, are also plotted for a comparison. For pure methanol at 323 K, the present results agree within the estimated uncertainty of ±2% with the measurements of both Isdale et al. [6] and Isakova and Oshueva [9]. For mixtures at 298 K, the agreement with the data of Isdale et al. is within the combined uncertainty of 4%.

For ethanol systems under high pressure, two sets of measurements have been reported for mixtures and for pure ethanol, respectively. Abaszade et al. [10] measured the viscosity of aqueous ethanol solutions

Table IV. Viscosity of (Water + 2-Propanol) Mixtures (η in mPa · s)

P (MPa)	x^a						
	0.10	0.25	0.40	0.50	0.80	0.90	1.00
			298.15 K				
0.1	2.440	3.049	2.865	2.630	2.104	2.031	2.036
9.9	2.488	3.182	3.038	2.824	2.311	2.240	2.257
19.7	2.543	3.326	3.221	3.023	2.516	2.450	2.470
29.5	2.591	3.469	3.406	3.217	2.726	2.667	2.692
39.3	2.639	3.608	3.592	3.422	2.941	2.886	2.916
49.1	2.688	3.754	3.781	3.621	3.160	3.112	3.145
58.9	2.737	3.902	3.969	3.830	3.388	3.345	3.382
68.8	2.786	4.053	4.174	4.047	3.623	3.580	3.627
78.6	2.834	4.207	4.382	4.264	3.863	3.829	3.874
88.4	2.879	4.361	4.588	4.487	4.112	4.086	4.131
98.2	2.926	4.518	4.797	4.721	4.374	4.350	4.400
108.0	2.973	4.680	5.032	4.966	4.642	4.625	4.678
117.8	3.021	4.845	5.247	5.211	4.921	4.909	4.958
			323.15 K				
0.1	1.066	1.297	1.286	1.216	1.036	1.009	0.995
9.9	1.089	1.351	1.366	1.306	1.136	1.114	1.098
19.7	1.111	1.410	1.449	1.398	1.232	1.220	1.208
29.5	1.131	1.468	1.528	1.493	1.335	1.327	1.318
39.3	1.154	1.524	1.611	1.582	1.438	1.436	1.430
49.1	1.174	1.578	1.687	1.675	1.546	1.547	1.545
58.9	1.192	1.644	1.769	1.765	1.651	1.658	1.660
68.8	1.213	1.700	1.852	1.860	1.764	1.773	1.783
78.6	1.233	1.754	1.934	1.961	1.878	1.895	1.902
88.4	1.253	1.818	2.018	2.057	1.993	2.019	2.033
98.2	1.272	1.882	2.103	2.151	2.106	2.136	2.161
108.0	1.293	1.938	2.187	2.268	2.227	2.268	2.288
117.8	1.311	2.001	2.277	2.362	2.353	2.393	2.424

[a] Mole fraction of 2-propanol.

Table V. Viscosity of (Water + 2-Methyl-2-Propanol) Mixtures (η in mPa·s)

P (MPa)	x^a						
	0.10	0.25	0.30	0.40	0.50	0.75	1.00
			298.15 K				
0.1	3.149	4.729	4.782	4.889	4.646	4.225	4.396
9.9	3.233	5.026	5.188	5.365	5.196	4.962	
19.7	3.327	5.369	5.550	5.901	5.802	5.781	
29.5	3.422	5.704	5.971	6.488	6.444	6.689	
39.3	3.523	6.037	6.333	7.074	7.137	7.721	
49.1	3.606	6.382	6.814	7.628	7.817	8.830	
58.9	3.713	6.739	7.279	8.291	8.556	10.01	
68.8	3.812	7.112	7.751	8.878	9.401	11.38	
78.6	3.901	7.489	8.206	9.545	10.29	12.92	
88.4	4.006	7.886	8.690	10.29	11.19		
98.2	4.104	8.288	9.194	11.05	12.19		
108.0	4.191	8.656	9.700	11.84	13.17		
117.8	4.293	9.096	10.24	12.71	14.23		
			323.15 K				
0.1	1.273	1.801	1.834	1.833	1.696	1.429	1.418
9.9	1.301	1.911	1.988	2.006	1.881	1.656	1.683
19.7	1.337	2.027	2.117	2.178	2.067	1.887	1.966
29.5	1.365	2.127	2.259	2.358	2.271	2.141	2.322
39.3	1.396	2.266	2.401	2.539	2.497	2.422	2.704
49.1	1.430	2.379	2.538	2.729	2.731	2.692	3.122
58.9	1.463	2.506	2.684	2.928	2.949	3.054	3.599
68.8	1.494	2.629	2.835	3.126	3.189	3.444	4.106
78.6	1.527	2.747	2.991	3.331	3.449	3.776	
88.4	1.563	2.891	3.160	3.550	3.726	4.179	
98.2	1.592	3.008	3.319	3.766	3.993	4.578	
108.0	1.622	3.137	3.465	3.989	4.269	4.963	
117.8	1.655	3.257	3.634	4.229	4.568	5.394	
			348.15 K				
0.1	0.700	0.889	0.903	0.870	0.818	0.701	0.589
9.9	0.712	0.941	0.969	0.948	0.906	0.812	0.712
19.7	0.727	0.990	1.032	1.027	0.995	0.922	0.852
29.5	0.739	1.044	1.095	1.104	1.098	1.027	0.971
39.3	0.749	1.093	1.159	1.184	1.198	1.142	
49.1	0.762	1.145	1.226	1.268	1.286	1.262	
58.9	0.774	1.205	1.293	1.353	1.387	1.390	
68.8	0.789	1.251	1.358	1.435	1.486	1.519	
78.6	0.803	1.303	1.427	1.522	1.595	1.657	
88.4	0.819	1.358	1.499	1.613	1.700	1.814	
98.2	0.835	1.402	1.565	1.699	1.817	1.965	
108.0	0.849	1.463	1.635	1.797	1.920	2.125	
117.8	0.863	1.525	1.707	1.890	2.040	2.307	

[a] Mole fraction of 2-methyl-2-propanol.

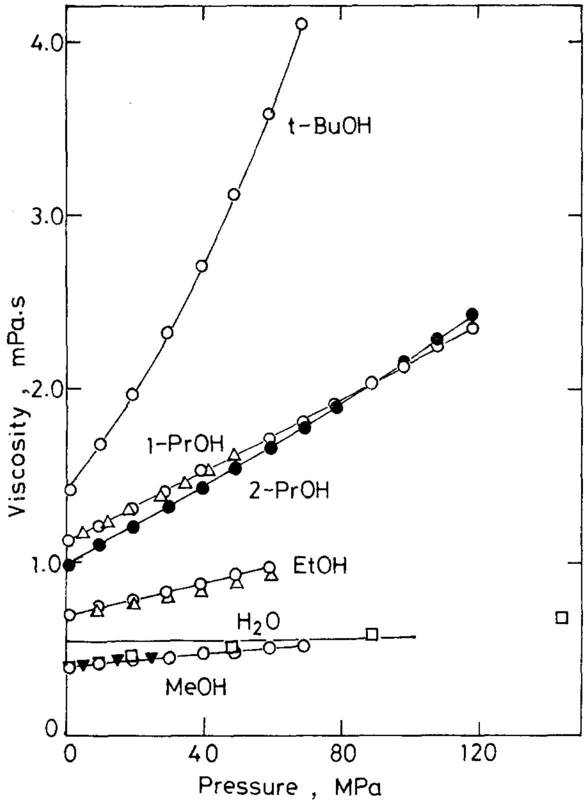

Fig. 1. Pressure dependences of the viscosity for pure alcohols and water at 323 K. (○, ●) This work; (□) Isdale et al. [6]; (▼) Isakova and Oshueva [9]; (△) Golubev et al. [8, 12].

at 303–473 K up to 118 MPa by a capillary method. The results of Yusa et al. [11], using a falling-cylinder method, cover the temperature range from 298 to 328 K and pressures up to 276 MPa. The viscosity of pure ethanol was measured by Bridgman [7] at 303 and 348 K up to 1177 MPa and by Golubev and Petrov [8] at 273–538 K up to 100 MPa. For pure ethanol at 323 K the present results agree with those of Golubev and Petrov [8] within 5%. However, a serious inconsistency is found at 298 K. In the results of Yusa et al. [11] the pressure coefficient of viscosity $(\partial\eta/\partial p)_T$ is quite small compared with the present data and those of Golubev and Petrov.

For the aqueous solutions of 1-propanol and 2-propanol there exist no experimental viscosity data under high pressure except for the results of Bridgman [7], Golubev and Petrov [8], and Golubev [12] for pure alcohols. Bridgman [7] measured these alcohols at 303 and 348 K up to 1177 MPa with a falling-cylinder viscometer, while Golubev [12] investigated 1-propanol at 323–553 K up to 49.4 MPa and Golubev and Petrov [8] investigated 2-propanol at 428–523 K up to 80 MPa by a capillary method. A direct comparison of the present results with these data is possible only for 1-propanol at 323 K. As shown in Fig. 1, the present data agree quite well with those of Golubev [12] within 0.5%.

No experimental viscosity data are found for 2-methyl-2-propanol system under high pressure.

In Fig. 2 the composition dependences of the viscosity obtained at 298 K under atmospheric pressure are shown for all alcohol mixtures

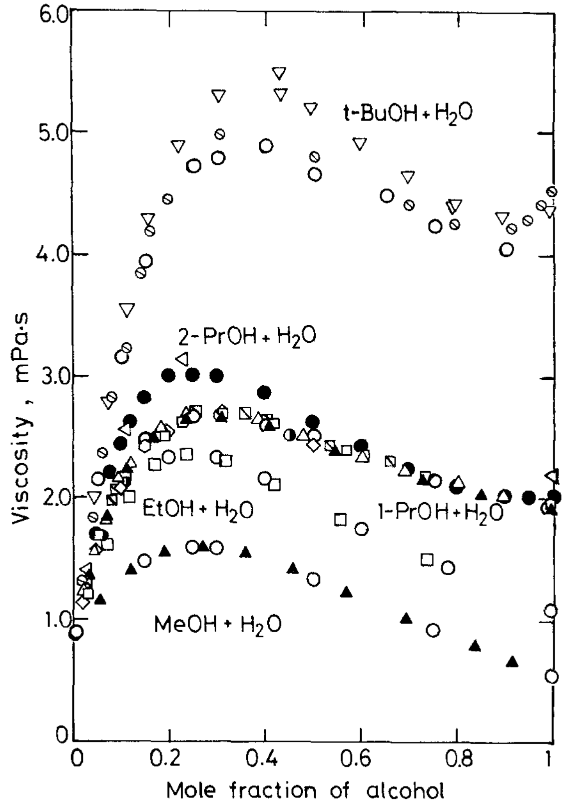

Fig. 2. Composition dependences of the viscosity for aqueous alcohol solutions at 298 K and atmospheric pressure. (○, ●) This work; (▲) Mikhail and Kimel [13, 15]; (□) Kikuchi and Oikawa [14]; (⧅) Dunstan [16]; (◑) Dunstan and Thole [17]; (○) Schott [18]; (△) Ratcliff and Khan [19]; (◇) Won et al. [20]; (◁) Traube [21]; (▽) Nakanishi and Ozasa [22]; (⊘) Broadwater and Kay [23].

studied together with literature values. For the systems of 1-PrOH, 2-PrOH, and t-BuOH, most of the literature values are plotted, while for the MeOH and EtOH systems only the results of Mikhail and Kimel [13] and Kikuchi and Oikawa [14] are shown besides the present results because these systems were described in detail previously [1, 2]. In the 1-PrOH and 2-PrOH systems the agreement of the present data with literature values is satisfactory within 3 %. However, the discrepancy is remarkable in the t-BuOH system. The largest deviation, about 12 %, is found near the maximum between the results of Nakanishi and Ozasa [22] and ours. On the other hand, the present data agree with those of Broadwater and Kay [3] within 3 %.

3.2. Composition Dependence of Viscosity

As shown in Fig. 2, the composition dependence of the viscosity deviates substantially from those calculated by a simple mole-fraction average method since aqueous alcohol solutions are highly associated due to the hydrogen bonds. Figure 3 shows the isobaric variations of viscosity for the 2-PrOH system at 323 K. Similar behaviors are found in other alcohol mixtures. Each isobar at low temperatures and low pressures has a viscosity maximum near a mole fraction of 0.3. The maximum diminishes gradually with increasing pressure. The isobars of 2-PrOH and t-BuOH mixtures have another shallow minimum near $x = 0.9$. This minimum diminishes gradually with rising temperature.

In all alcohol solutions studied, the viscosity of mixtures is always higher than the mole-fraction average value. The viscosity of primary alcohol mixtures increases with increasing molecular weight of alcohols. The composition where the viscosity maximum occurs moves gradually to a higher alcohol concentration. The viscosity of the t-BuOH system is remarkably higher than that of other alcohol solutions. The viscosity of the 2-PrOH system is also slightly higher than that of the 1-PrOH solution. These facts show that the viscosity of solutions including alcohols with side chains, secondary or tertiary alcohols, is generally higher than that of primary alcohol solutions.

3.3. Pressure Dependence of Viscosity

Pressure dependences of the viscosity for aqueous 2-PrOH solutions at 323 K are shown in Fig. 4. The viscosity of aqueous 2-PrOH solutions increases almost linearly with pressure. The pressure coefficients of viscosity increase with the concentration of alcohol. The isotherms of 2-PrOH solutions intersect each other, which ascribes to the strong nonideality in

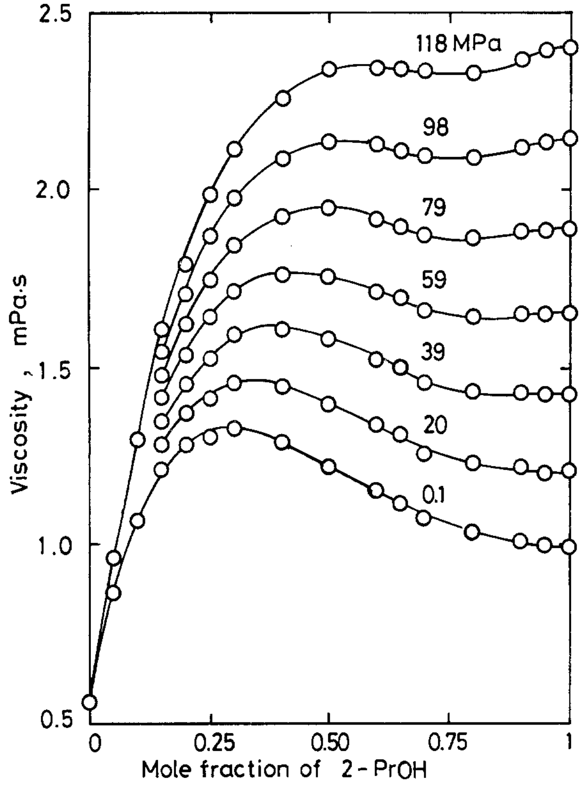

Fig. 3. Composition dependences of the viscosity for an aqueous 2-propanol solution at 323 K under high pressure.

the composition dependence of the viscosity due to the hydrogen bond. Similar behaviors are found in other alcohol solutions investigated.

3.4. Density Dependence of Viscosity

The density dependences of the viscosity for the aqueous 2-PrOH system at 323 K are illustrated in Fig. 5. The isotherms change more systematically with composition than the case in Fig. 4, and there is no intersection of isotherms in this expression. It is therefore more reasonable to express the change of viscosity as a function of density, instead of pressure, from a theoretical and an empirical point of view.

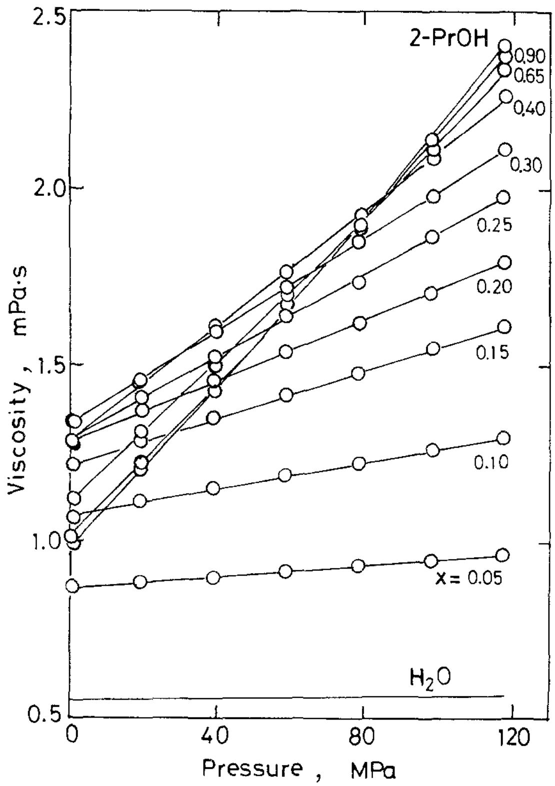

Fig. 4. Pressure dependences of the viscosity for an aqueous 2-propanol solution at 323 K.

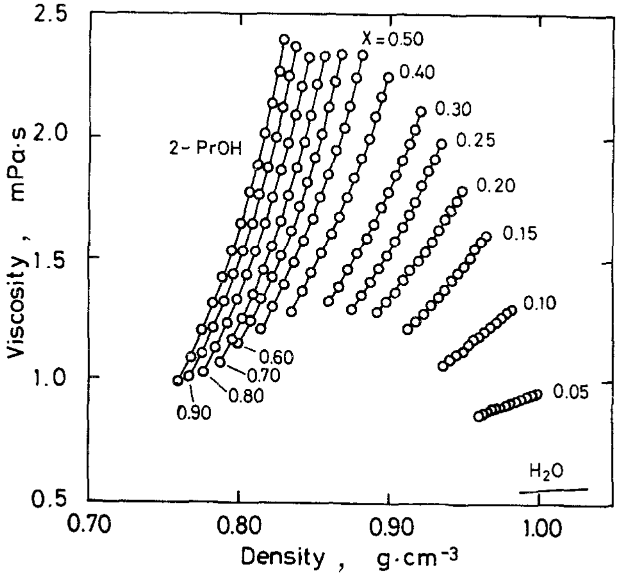

Fig. 5. Density dependences of the viscosity for an aqueous 2-propanol solution at 323 K.

4. CORRELATION OF VISCOSITY DATA

In order to correlate the viscosity data with pressure, density, and composition, some empirical and semitheoretical methods have been applied to the present experimental results.

4.1. Tait-Type Equation

An expression similar to the Tait equation, which is well known as a typical isothermal equation to represent the density of liquid under pressures, was applied to correlate the viscosity with pressure for a given temperature and composition:

$$(\eta - \eta_0)/\eta = A \ln[(B+P)/(B+P_0)] \tag{2}$$

where η and η_0 are the viscosities of mixtures at high pressure and atmospheric pressure P_0 in mPa · s, and P is the pressure in MPa. Empirical coefficients A and B were determined by the nonlinear regression method. In a typical case of 2-PrOH solutions, Eq. (2) reproduces the experimental data along each isotherm with a mean deviation of 0.14% and a maximum deviation of 1.04%. The composition dependences of A and B values, which are derived from the best fit to the experimental data, are found to be correlated well with mole fraction x above 0.1 by the following equations:

$$A = \sum_{i=0}^{6} a_i x^i \tag{3}$$

$$\ln B = \sum_{i=0}^{4} b_i x^{-i} \tag{4}$$

The viscosity at any composition and pressure can be calculated by Eqs. (2), (3), and (4) within the experimental uncertainty, if the value of η_0 is known.

4.2. Free-Volume Form of Equation

The free-volume form of equation was originally proposed by Dymond and Brawn [24] and shown to give a satisfactory fit of viscosity data for pseudospherical molecular liquids and rigid-ring hydrocarbons.

$$\ln(\eta V^{2/3}/\sqrt{MT}) = C + D[V_0/(V - V_0)] \tag{5}$$

where V is the molar volume in $\mathrm{cm^3 \cdot mol^{-1}}$, T is the temperature in K, and M is the molecular weight in $\mathrm{g \cdot mol^{-1}}$. C and D are adjustable parameters to take account of the effect of nonspherical molecular shape and of translational–rotational coupling. V_0 is the close-packed volume in the hard-sphere theory. Although the original model is quite far from that in aqueous alcohol solutions, the effectiveness of the equation in fitting viscosity data was tested using the present results. V_0 and the empirical coefficients C and D were determined by the method of least squares.

For nonassociated liquid mixtures, it was found [25] that C was temperature independent and equal to -1.0, and the values of V_0 varied linearly with the mole fraction over the whole composition range at each temperature. However, the derived values of V_0, C, and D in the present work are considerably different from those for nonassociated organic liquid mixtures, especially in dilute aqueous solutions below $x = 0.2$. The variations of empirical coefficients with composition are not so systematic, and it is quite difficult to obtain physically meaningful coefficients for associated liquids. However, Eq. (5) provides a convenient way of summarizing the experimental data and provides a very reliable estimation of viscosity under other conditions of density and composition.

5. DISCUSSION

No one has yet proposed a quantitative theory of aqueous alcohol solutions. Therefore we can discuss only a qualitative interpretation on the variation of viscosity with temperature, pressure, and composition.

The nonideal behavior of the viscosity observed in Figs. 2 and 3 may be closely related to the structure formation due to hydrogen bonds in aqueous solutions [26]. According to Frank and Wen [27], liquid water consists of ice-like open-structured clusters of hydrogen-bonded molecules and monomeric aggregates of unbonded high-coordinated water. The clusters are short-lived in the equilibrium with unbonded water. On the other hand, alcohols have both a hydrophilic hydroxyl group and a hydrophobic alkyl group in a molecule. In contrast to water, three-dimensional association is precluded in liquid alcohols due to the unfavorable steric effect of the alkyl group. The association in liquid alcohols is described in terms of equilibria between polymeric species consisting of five to seven molecules, or fewer for sterically hindered alcohols. The association of alcohols tends to decrease with increasing molecular weight, and in the sequence primary, secondary, tertiary. The hydroxyl group of the alcohol forms hydrogen bonds with the surrounding water molecules, while the hydrocarbon tail promotes increased order of the adjacent water molecules, similar to that around inert molecules [28]. When a small amount of alcohol is added, it enhances the structure of the total system and causes the viscosity to increase rapidly. This process competes with the opposite process in which the degree of structure is reduced as a result of solute–solvent interaction as the alcohol concentration in the mixture increases. This gradual breakdown in the liquid structure is accompanied by a monotonic decrease in viscosity. The appearance of a viscosity maximum is to be expected as a result of these competing processes.

According to the investigation of Wolf and Kudish [29] of the viscosity of methanol solutions with D_2O^{16} and D_2O^{18} at 298 K, the viscosity maximum is larger than that in a normal water solution and the maximum shifts slightly to a lower alcohol concentration. This shift can be explained by the fact that heavy water is more structured than normal water, and therefore the structure formation is achieved more rapidly in methanol + heavy water mixtures.

Heating may weaken or break the hydrogen bond in the aqueous solution and decrease the structure formation. Compression would also suppress the bulky three-dimensional structure. Thus, the viscosity maximum tends to diminish at higher temperatures and pressures.

6. CONCLUSIONS

New experimental viscosity data are presented for completely miscible aqueous alcohol solutions of methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol, covering temperatures from 283 to 348 K and pressures up to 120 MPa. The experimental results are correlated with pressure, density, and composition by empirical and semitheoretical equations over the entire range of this work. The authors hope that this basic information on the viscosity of aqueous alcohol solutions under high pressure may contribute to solving the complicated behaviors of aqueous solutions of hydroxyl compounds.[2]

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[2] Other experimental data available from T. Makita on request are as follows: Table I (water + methanol)—$x = 0.15$; Table III (water + 1-propanol)—$x = 0.15$; Table IV (water + 2-propanol)—$x = 0.03$, 0.05, 0.08, 0.12, 0.15, 0.20, 0.30, 0.60, 0.70, and 0.95; and Table V (water + 2-methyl-2-propanol)—$x = 0.05$, 0.15, 0.65, and 0.90.

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