International Journal of Thermophysics, Vol. 9, No. 4, 1988

Viscosity of Aqueous Solutions of 1,2-Ethanediol and 1,2-Propanediol Under High Pressures

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

Received May 4, 1988

New experimental data on the viscosity of aqueous solutions of 1,2-ethanediol (ethylene glycol) and 1,2-propanediol (propylene glycol) are presented at 298 and 323 K under pressures up to 120 MPa. The measurements were performed by a falling-cylinder viscometer on a relative basis with an uncertainty of less than ±2%. The viscosity of these aqueous solutions at a constant temperature and pressure increases monotonously with increasing concentrations of diols (glycols) and is slightly lower than the mole fraction average value at each composition. The viscosity also increases almost linearly with pressure at a constant temperature and composition. The pressure coefficient of the viscosity, $(\partial\eta/\partial P)_{T,x}$, increases with decreasing temperature and increasing concentrations of diols. The experimental results are correlated with pressure, density, and composition by several empirical equations.

KEY WORDS: aqueous alcohol solution; ethanediol; ethylene glycol; falling-cylinder viscometer; free-volume theory; high pressure; pressure effect; propanediol; propylene glycol; viscosity; water.

1. INTRODUCTION

Recently aqueous solutions of polyhydric alcohols have been noticed as ones of nonflammable water-soluble lubricants. The behavior of water–alcohol mixtures is also interesting theoretically due to some anomalies in the composition dependences of thermodynamic and transport properties, since the alcohol molecules have both hydrophilic hydroxy groups and hydrophobic alkyl groups. In order to understand the molecular aspects of these anomalies, it is necessary to measure thermophysical properties accurately over a wide range of temperature and

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

pressure. The present investigation was undertaken to obtain precise viscosity data of aqueous solutions of 1,2-ethanediol (ED; ethylene glycol) and 1,2-propanediol (PD; propylene glycol) under high pressures as one of series of studies on the viscosity of (water + alcohol) mixtures [1–3].

2. EXPERIMENTAL

The viscosity measurements were performed by a falling-cylinder viscometer on a relative basis described in detail elsewhere [1]. The instrument constant and its temperature and pressure dependences were calibrated by distilled water and the viscosity standard liquid JS10 provided from the National Research Laboratory of Metrology, Japan. The reference data of viscosity and density of water were cited from Sengers and Watson [4] and Kestin and Sengers [5], respectively. The densities of the sample solutions were measured by a high-pressure burette method [2]. Extrapure reagents were obtained from commercial sources and were used after degassing in as-received condition. Their purities should be better than 99.8 wt%. The mixtures were prepared by weighing using an analytical balance within ±0.005%. The final uncertainty of the viscosity obtained is estimated to be less than ±2%, while the precision of measurements is ±0.5%.

3. EXPERIMENTAL RESULTS

The experimental results are presented in Tables I and II for 1,2-ethanediol and 1,2-propanediol solutions, respectively, as functions of temperature, pressure, and composition.

3.1. Comparison with Literature Values

No experimental data are found in the literature for the viscosity of these systems under high pressure, although four sets of measurements [6–9] are available only for ED solutions at atmospheric pressure. It is found that the present results agree quite well with those values within a maximum deviation of 2%. As no experimental data are available for PD solutions even at atmospheric pressure, the present experimental data at atmospheric pressure were compared with those measured by an Ostwald-type viscometer. It is confirmed that both results agree well within 1.5%.

3.2. Composition Dependence of Viscosity

The isobaric composition dependences of the viscosity of a (water + PD) mixture at 298.15 K are shown in Fig. 1. Similar behaviors are observed in the case of an ED solution. The viscosity of the PD solution varies significantly with composition and pressure from 0.9 to 115 mPa · s under the present experimental conditions, while that of the ED solution varies covering from 0.9 to 29 mPa · s under the same conditions. As illustrated in Fig. 2, it should be noted that the viscosity of monohydric

Table I. Viscosity of (Water + 1,2-Ethanediol) Mixtures in mPa · s

P (MPa)	Mole fraction of 1,2-ethanediol					
	0.00	0.20	0.40	0.60	0.80	1.00
			298.15 K			
0.1	0.891	2.925	5.764	9.207	13.10	16.99
9.9	0.888	2.959	5.899	9.540	13.65	17.87
19.7	0.887	2.995	6.040	9.848	14.20	18.68
29.5	0.886	3.031	6.185	10.17	14.75	19.54
39.3	0.885	3.065	6.315	10.49	15.31	20.42
49.1	0.885	3.102	6.460	10.81	15.93	21.33
58.9	0.885	3.137	6.607	11.14	16.51	22.28
68.8	0.886	3.176	6.758	11.48	17.15	23.30
78.6	0.887	3.213	6.908	11.84	17.79	24.27
88.4	0.888	3.252	7.059	12.18	18.45	25.21
98.2	0.890	3.289	7.212	12.54	19.12	26.37
108.0	0.892	3.323	7.368	12.92	19.80	27.41
117.8	0.894	3.362	7.523	13.28	20.47	28.55
			323.15 K			
0.1	0.547	1.468	2.638	3.948	5.303	6.588
9.9	0.549	1.493	2.697	4.068	5.505	6.884
19.7	0.551	1.514	2.758	4.187	5.681	7.173
29.5	0.553	1.535	2.820	4.309	5.888	7.471
39.3	0.555	1.555	2.881	4.435	6.097	7.776
49.1	0.557	1.575	2.948	4.561	6.305	8.073
58.9	0.560	1.594	3.004	4.688	6.514	8.353
68.8	0.562	1.614	3.068	4.816	6.739	8.660
78.6	0.565	1.633	3.130	4.945	6.952	8.932
88.4	0.568	1.655	3.192	5.081	7.191	9.260
98.2	0.570	1.673	3.259	5.219	7.422	9.545
108.0	0.573	1.695	3.320	5.360	7.631	9.893
117.8	0.576	1.717	3.386	5.500	7.889	10.22

alcohol solutions investigated previously [1–3] is relatively lower than that of the present diols (glycols).

The viscosity of ED and PD systems at a constant temperature and pressure increases monotonously with increasing diol concentrations. Each isobar has no viscosity extreme throughout the whole range of compositions, while a maximum is observed in the isobars of monohydric alcohol solutions [1–3] near a mole fraction of 0.3, and the viscosity

Table II. Viscosity of (Water + 1,2-Propanediol) Mixtures in mPa · s[a]

P (MPa)	Mole fraction of 1,2-propanediol					
	0.00	0.20	0.40	0.60	0.80	1.00
			298.15 K			
0.1	0.891	5.452	12.77	21.63	32.85	44.39
9.9	0.888	5.606	13.38	23.14	35.44	48.57
19.7	0.887	5.757	14.03	24.69	38.20	52.66
29.5	0.886	5.898	14.70	26.24	41.14	57.31
39.3	0.885	6.050	15.38	27.78	44.24	62.25
49.1	0.885	6.208	16.10	29.49	47.54	67.57
58.9	0.885	6.379	16.83	31.25	50.93	72.79
68.8	0.886	6.543	17.58	33.07	54.61	78.96
78.6	0.887	6.680	18.34	35.03	58.43	84.89
88.4	0.888	6.809	19.16	37.00	62.43	91.54
98.2	0.890	6.953	20.00	39.10	66.65	98.69
108.0	0.892	7.108	20.86	41.28	71.12	106.0
117.8	0.894	7.294	21.75	43.60	75.96	114.0
			323.15 K			
0.1	0.547	2.308	4.700	7.261	9.984	12.51
9.9	0.549	2.367	4.909	7.673	10.69	13.51
19.7	0.551	2.426	5.118	8.116	11.44	14.57
29.5	0.553	2.486	5.333	8.561	12.19	15.70
39.3	0.555	2.548	5.551	9.033	12.98	16.86
49.1	0.557	2.607	5.767	9.507	13.79	18.09
58.9	0.560	2.668	5.997	9.996	14.65	19.37
68.8	0.562	2.731	6.222	10.50	15.56	20.70
78.6	0.565	2.793	6.466	11.01	16.48	22.12
88.4	0.568	2.858	6.685	11.61	17.45	23.59
98.2	0.570	2.920	6.954	12.15	18.47	25.11
108.0	0.573	2.984	7.213	12.82	19.52	26.72
117.8	0.576	3.048	7.465	13.40	20.66	28.45

[a] Other experimental data available from T. Makita on request are as follows: (298.15 K)$x = 0.10$, 0.70, 0.90; (323.15 K)$x = 0.10$, 0.30, 0.50, 0.70, 0.90.

maximum diminishes gradually with increasing pressures. The viscosity of diol solutions at each composition is slightly lower than the mole fraction average value, while that of monohydric alcohol solutions is always higher than the average value. The composition derivative of the viscosity at a given temperature and pressure, $(\partial\eta/\partial x)_{T,P}$, increases with increasing pressures and decreasing temperatures.

In order to compare the deviations from the mole fraction average values, a relative excess viscosity $\Delta\eta_r$ is defined as follows:

$$\Delta\eta_r = \frac{\eta - (x_1\eta_1 + x_2\eta_2)}{x_1\eta_1 + x_2\eta_2} \times 100\,\% \tag{1}$$

where η denotes the viscosity of alcohol solutions, and η_i and x_i are the viscosity and the mole fraction of the ith pure component, respectively. $\Delta\eta_r$ of ED and PD solutions at 298.15 K and 0.1 MPa are illustrated in Fig. 3,

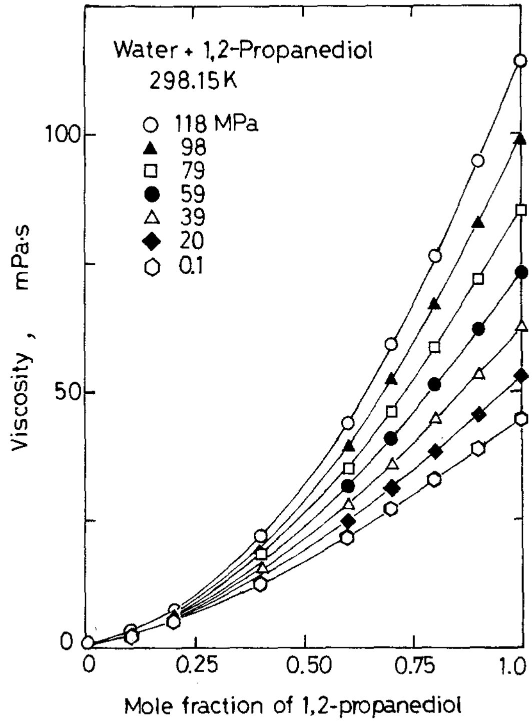

Fig. 1. Composition dependence of the viscosity of aqueous 1,2-propanediol solution at 298 K under high pressure.

together with those of five monohydric alcohol solutions investigated previously [1–3]. $\Delta\eta_r$ of diol solutions are always negative, while those of monohydric alcohol solutions are all positive. In both diol solutions a minimum in $\Delta\eta_r$ is observed near a mole fraction of 0.15. On the other hand, the monohydric alcohol solutions have maxima near mole fractions from 0.2 to 0.3. The compositions where the viscosity extreme is observed are almost constant independent of pressure. It should be noted that the absolute values of $\Delta\eta_r$ of both monohydric and polyhydric alcohol solutions increase with increasing sizes of the hydrophobic alkyl group in a molecule. However, the deviation of the viscosity of diol solutions from ideal behavior is smaller than those of monohydric alcohol solutions. It may be due to the fact that the interactions between the hydrophobic group of diols and water are not so strong as those between hydroxy groups in both glycols and water, that is, diols are quite hydrophilic due to their two hydroxy groups.

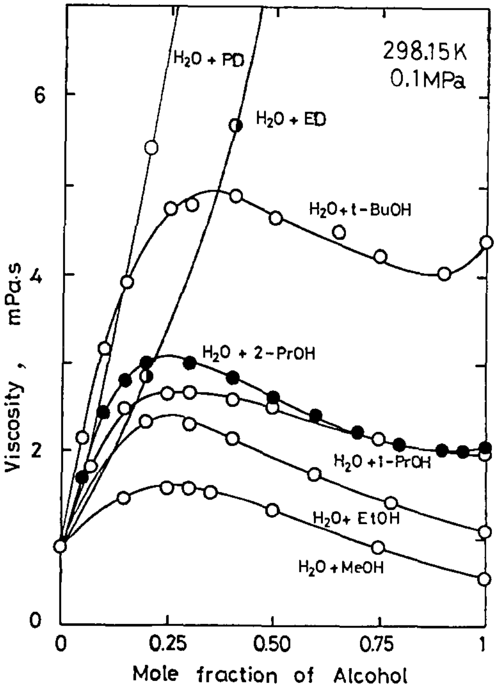

Fig. 2. Composition dependences of the viscosity of (water + alcohol) solutions at 298 K and 0.1 MPa.

3.3. Pressure and Density Dependences of Viscosity

The pressure dependences of the viscosity of PD solutions at 298.15 K are plotted in Fig. 4 as a function of composition. In concentrated solutions, the viscosity increases monotonously with increasing pressures having a small positive curvature, while that of pure water is substantially constant, and those of dilute solutions increases almost linearly. The pressure coefficient of the viscosity of aqueous diol solutions, $(\partial\eta/\partial P)_{T,x}$, increases with increasing concentrations of diols and decreasing temperatures. The viscosity isotherms of diol solutions change quite simply and systematically, although those of monohydric alcohol solutions intersect each other, which ascribes to the strong nonideality in the composition dependence of the viscosity due to the hydrogen bond.

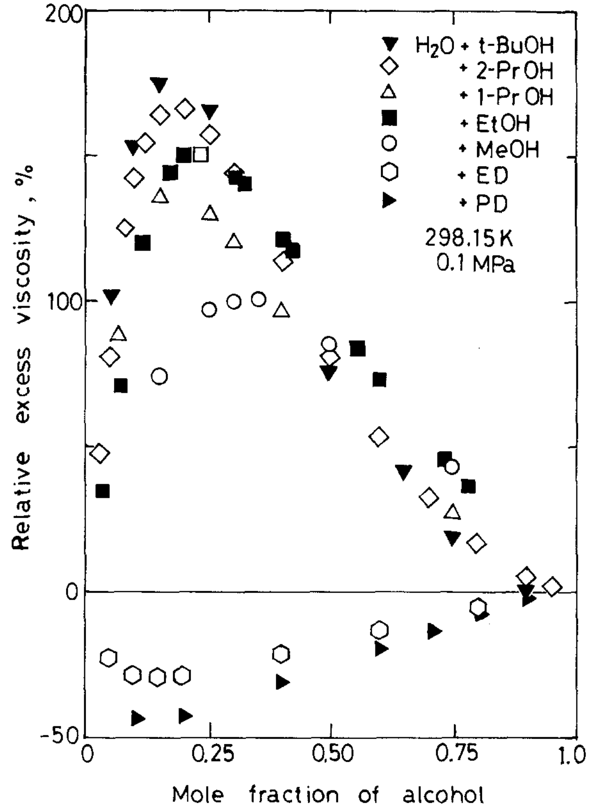

Fig. 3. Comparison of the relative excess viscosity of (water + alcohol) solutions at 298 K and 0.1 MPa.

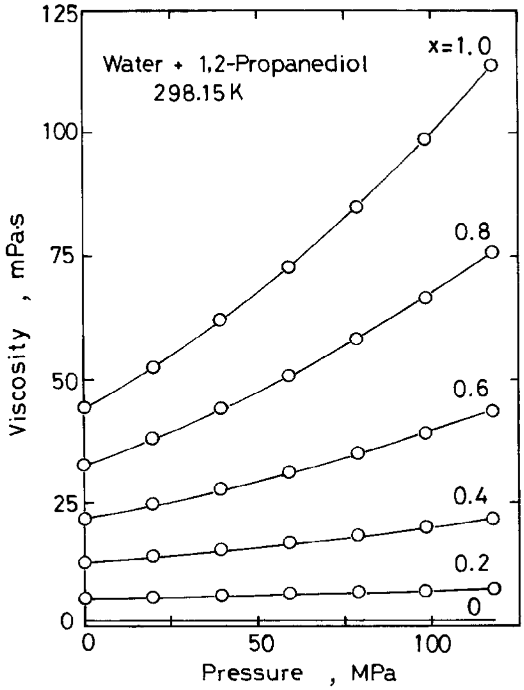

Fig. 4. Pressure dependence of the viscosity of aqueous 1,2-propanediol solution at 298 K.

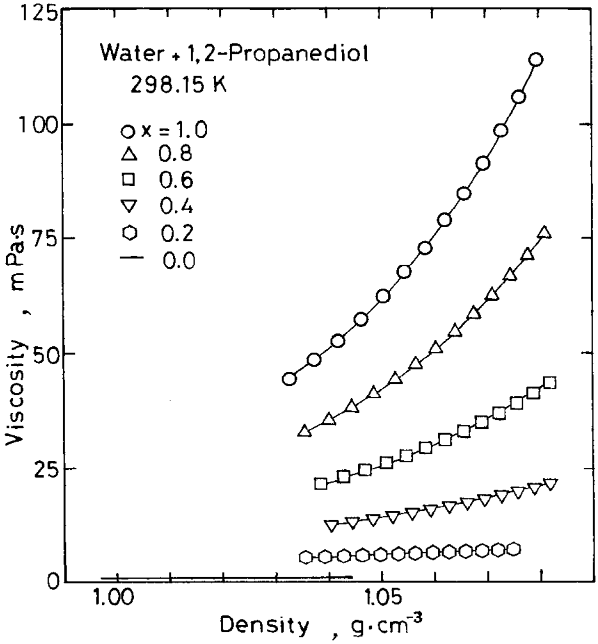

Fig. 5. Density dependence of the viscosity of aqueous 1,2-propanediol solution at 298 K.

The isothermal density dependences of the viscosity of PD solution at 298.15 K are illustrated in Fig. 5. The viscosity of dilute solutions increases almost linearly with density, while that of concentrated solutions increases with a positive curvature in the similar manner as the case of pressure dependence. The density derivative of the viscosity $(\partial\eta/\partial\rho)_{T,x}$ increases with diol concentration and decreases with temperature.

4. DISCUSSION

The present viscosity data have been correlated with pressure, density, and composition, by means of some empirical methods.

4.1. Tait-Type Equation

An empirical expression similar to the Tait equation, which is one of the good and simple equations to represent the isothermal variation of liquid density under high pressures, was applied to correlate the viscosity with pressure at a given temperature and composition:

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

Table III. Coefficients of Eq. (2) for 1,2-Ethanediol and 1,2-Propanediol Solutions: $A = 0.5576$ (298.15 K, 323.15 K)

	298.15 K			323.15 K		
Mole fraction of diols	B (MPa)	Mean dev. (%)	Max. dev. (%)	B (MPa)	Mean dev. (%)	Max. dev. (%)
			1,2-Ethanediol solution			
0.00	40020	0.50	0.83	1317	0.14	0.29
0.20	449.6	0.05	0.11	392.7	0.18	0.35
0.40	226.6	0.07	0.19	241.1	0.05	0.22
0.60	160.3	0.06	0.19	179.2	0.06	0.11
0.80	129.7	0.13	0.35	147.5	0.13	0.33
1.00	110.5	0.13	0.23	130.3	0.37	0.73
			1,2-Propanediol solution			
0.00	40020	0.50	0.83	1317	0.14	0.29
0.20	204.2	0.25	0.62	214.8	0.03	0.10
0.40	107.8	0.22	0.40	124.5	0.07	0.25
0.60	79.82	0.09	0.19	92.37	0.18	0.44
0.80	66.17	0.27	0.52	76.63	0.14	0.34
1.00	58.43	0.42	1.02	67.16	0.36	0.86

where η and η_0 are the viscosities of solution under pressure P and at atmospheric pressure P_0, respectively. The empirical coefficients A and B were determined by a nonlinear regression method. Although the optimum coefficients could be determined for each isotherm, it is found that the coefficient A is almost constant independent of temperature, composition, and type of diol solution under the present experimental conditions. Therefore, A is fixed to 0.5576, and B's are redetermined, as given in Table III, where the mean and the maximum deviations of experimental data from Eq. (2) are also listed. As the composition dependence of B is quite simple and systematic, B could be correlated satisfactorily with the mole fraction of diols x by the following equation:

$$B = \sum_{i=0}^{n} B_i x^{-i} \tag{3}$$

The viscosities at atmospheric pressure η_0 are also correlated as follows:

$$\eta_0 = \sum_{i=0}^{m} c_i x^{i/m} \tag{4}$$

The optimum coefficients of Eqs. (3) and (4) are given in Tables IV and V. Equations (2) to (4) enable us to calculate the viscosity of both diol solutions with the mean deviations of 0.51 and 0.53 % and the maximum deviations of 1.8 and 1.5 %, respectively.

4.2. Free-Volume Equation

The viscosities of organic liquids are expressed with molar volume by the free-volume equation proposed by Dymond and Brawn [10]:

$$\ln \eta' = D + EV_0/(V - V_0) \tag{5}$$

Table IV. Coefficients of Eq. (3) for 1,2-Ethanediol and 1,2-Propanediol Solutions

	1,2-Ethanediol solution		1,2-Propanediol solution	
B_i	298.15 K	323.15 K	298.15 K	323.15 K
B_0	40.918	47.589	27.113	30.809
B_1	66.840	84.751	31.256	36.391
B_2	2.9787	−3.1354	-9.8581×10^{-2}	3.1512×10^{-1}
B_3			2.1275×10^{-1}	-2.7176×10^{-2}
B_4			-5.3603×10^{-3}	2.8626×10^{-4}
Applicable range	$0.2 \leqslant x \leqslant 1.0$	$0.2 \leqslant x \leqslant 1.0$	$0.1 \leqslant x \leqslant 1.0$	$0.1 \leqslant x \leqslant 1.0$
Mean dev. (%)	0.17	0.55	0.14	0.43
Max. dev. (%)	0.41	0.86	0.40	1.22

Table V. Coefficients of Eq. (4) for 1,2-Ethanediol and 1,2-Propanediol Solutions

	1,2-Ethanediol solution		1,2-Propanediol solution	
c_i	298.15 K	323.15 K	298.15 K	323.15 K
c_0	0.8906	0.5470	0.8906	0.5470
c_1	6.63219	−0.0386072	−2.80974	11.5366
c_2	−26.5006	−2.03933	162.626	−44.5820
c_3	36.0081	8.1399	−314.9469	49.97173
c_4			224.1597	−4.897974
Applicable range	$0 \leqslant x \leqslant 1.0$	$0 \leqslant x \leqslant 1.0$	$0 \leqslant x \leqslant 1.0$	$0 \leqslant x \leqslant 1.0$
Mean dev. (%)	0.39	0.51	0.49	0.37
Max. dev. (%)	0.64	1.11	1.33	0.79

The quantity η' is the reduced viscosity defined as

$$\eta' = 100\eta V^{2/3}/(\mathrm{MT})^{1/2} \tag{6}$$

where η is the viscosity in mPa · s, V is the molar volume in $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, and M is the molecular weight in $10^{-3}\,\mathrm{kg} \cdot \mathrm{mol}^{-1}$. According to Dymond and Brawn [10], the free-volume equation gives a satisfactory representation of viscosity for pseudospherical molecular liquids and rigid-ring hydrocarbons. The coefficients D and E are adjustable parameters to take account of the effect of nonspherical molecular shape and of translational-rotational coupling. V_0 is the closed-packing volume in the hard-sphere theory. The coefficient D is found to be temperature independent and equal to -1.0. The value of V_0 varies linearly with the mole fraction over the whole composition range in nonassociated liquid mixtures [11].

The applicability of this equation to the associated diol solutions has been examined. The empirical coefficients D and E, and V_0, were determined by the method of least squares for each solution at a given temperature and composition. The optimum coefficients of Eq. (5) are given in Table VI for both diol solutions, as well as the deviations of $\ln \eta'$ from Eq. (5). The derived values of the coefficients and V_0 in the present work are considerably different from those for nonassociated organic mixtures. The variations of D, E, and V_0 with the diol concentration are not so systematic. It may be due to the fact that the original model is quite far from that in aqueous alcohol solutions. Equation (5), however, provides an estimation method of the viscosity under other conditions of density and composition with a mean deviation of 2%.

Table VI. Coefficients of Eq. (5) for 1,2-Ethanediol and 1,2-Propanediol Solutions

Temperature (K)	Mole fraction of alcohols	D	E	V_0 ($cm^3 \cdot mol^{-1}$)	Mean dev. (as $\ln \eta'$) (%)	Max. dev. (as $\ln \eta'$) (%)
		1,2-Ethanediol solution				
298.15	0.20	2.538	0.3293	17.98	0.018	0.039
	0.40	1.881	1.183	21.35	0.011	0.033
	0.60	1.088	2.306	24.30	0.014	0.038
	0.80	1.408	1.826	31.72	0.019	0.029
	1.00	0.6109	2.658	35.44	0.018	0.060
323.15	0.20	0.7920	2.628	10.57	0.030	0.098
	0.40	−0.4816	6.035	12.63	0.019	0.039
	0.60	1.037	1.363	26.64	0.007	0.017
	0.80	0.8873	1.602	31.75	0.021	0.054
	1.00	0.1617	2.558	34.32	0.066	0.16
		1,2-Propanediol solution				
298.15	0.20	0.5886	3.519	14.08	0.049	0.13
	0.40	1.166	1.756	26.96	0.010	0.026
	0.60	0.04127	3.118	32.33	0.017	0.048
	0.80	0.4543	2.642	41.97	0.010	0.022
	1.00	0.1753	3.028	49.18	0.022	0.046
323.15	0.20	0.5754	1.963	16.39	0.008	0.022
	0.40	0.4982	1.970	25.49	0.018	0.071
	0.60	0.9414	1.462	36.77	0.028	0.076
	0.80	0.4133	2.129	42.40	0.017	0.033
	1.00	−0.3838	3.124	47.36	0.008	0.015

5. CONCLUSIONS

New experimental viscosity data are presented for aqueous 1,2-ethanediol and 1,2-propanediol solutions at temperatures of 298 and 323 K and pressures up to 120 MPa. The experimental results are correlated with pressure, molar volume, and composition by some empirical and theoretical equations over the entire range of this work. The viscosity of these diol solutions varies with temperature, pressure, and composition more simply than the cases of aqueous solutions of monohydric alcohols previously investigated. An expression similar to the Tait equation, Eq. (2), gives a good representation for the present results except for the quite dilute solutions. The free-volume equation, Eq. (5), is also found to reproduce the present experimental data reasonably within the uncertainty of the present measurements.

REFERENCES

1. Y. Tanaka, T. Yamamoto, Y. Satomi, H. Kubota, and T. Makita, *Rev. Phys. Chem. Jpn.* **47**:12 (1977).
2. H. Kubota, S. Tsuda, M. Murata, T. Yamamoto, Y. Tanaka, and T. Makita, *Rev. Phys. Chem. Jpn.* **49**:59 (1979).
3. Y. Tanaka, Y. Matsuda, H. Fujiwara, H. Kubota, and T. Makita, *Int. J. Thermophys.* **8**:147 (1987).
4. J. V. Sengers and J. T. R. Watson, *J. Phys. Chem. Ref. Data* **15**:1291 (1986).
5. J. Kestin and J. V. Sengers, *J. Phys. Chem. Ref. Data* **15**:305 (1986).
6. F. S. Jerome, J. T. Tseng, and L. T. Fan, *J. Chem. Eng. Data* **13**:496 (1968).
7. W. Hayduk and V. K. Malik, *J. Chem. Eng. Data* **16**:143 (1971).
8. Y. S. Won, D. K. Chung, and A. F. Mills, *J. Chem. Eng. Data* **26**:140 (1981).
9. D. Bohne, S. Fisher, and E. Obermeier, *Ber. Bunsenges. Phys. Chem.* **88**:739 (1984).
10. J. H. Dymond and T. A. Brawn, *Proc. 7th Symp. Thermophys. Prop.* (ASME, New York, 1977), p. 660.
11. J. H. Dymond, K. J. Young, and J. D. Isdale, *Int. J. Thermophys.* **1**:345 (1980).