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Static Relative Permittivities of Water + Ethane-1,2-diol and Water + Propane-1,2,3-triol under Pressures up to 300 MPa at 298.15 K

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Static relative permittivities (ϵ_r) of water + ethane-1,2-diol and water + propane-1,2,3-triol mixtures were measured at the mole fraction of organic component (x_2) from 0 to 0.8 at 0.2 intervals under pressures up to 300 MPa at the temperature 298.15 K. The relative permittivities at 0.1 MPa ($\epsilon_r(P_0)$) against x_2 for both aqueous mixtures in this work were correlated with a polynomial equation of x_2 and were compared with the literature values. The relative permittivities at pressure P ($\epsilon_r(P_0)$) were also correlated with the polarization (p) for both aqueous mixtures, and reasonable correlations were obtained by use of only one adjustable parameter (k_{12}). The experimental ϵ_r results as a function of P for each mixture were fitted to a Tait-type equation, and the Tait-type parameters, A and B, were determined. A comparison between composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ at 0.1 MPa and 298.15 K, $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, calculated from values of $\epsilon_r(P_0)$ and the Tait-type parameters and that of the isothermal compressibility at 0.1 MPa, κ_{T,P_0}, was made for both aqueous polyhydric alcohol mixtures. In addition, composition dependence of $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ values at 0.1 MPa, $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$, evaluated from $\epsilon_r(P_0)$, A, and B values were correlated with a quadratic equation of x_2. An empirical equation by Marcus for estimating $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values was used, and the estimated results were compared with the experimental ones. Furthermore, a combination equation of the correlation equations for $\epsilon_r(P_0)$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ with x_2 was used to obtain $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values, and then it was found that the calculated values reproduce the composition dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ well.

Introduction

The static relative permittivities ϵ_r of water + polar organic mixtures under high pressures up to 300 MPa at 298.15 K have so far been measured as a function of composition in our laboratory.[1−5] Furthermore, compressions of binary aqueous polar organic mixtures at various compositions have been measured under pressures up to 200 MPa at 298.15 K, and composition dependence of the isothermal compressibilites at 0.1 MPa determined from their compression data has been reported.[6]

Recently we have reported ϵ_r values for pure polyhydric alcohols,[7] three aqueous butanediol mixtures,[4] and two aqueous propanediol mixtures[5] under pressures up to 300 MPa at 298.15 K. The present paper reports ϵ_r for water + ethane-1,2-diol and water + propane-1,2,3-triol at the mole fraction of polyhydric alcohol x_2 from 0 to 0.8 at intervals of 0.2 under pressures up to 300 MPa at 298.15 K. Relative permittivity at $P = 0.1$ MPa $\epsilon_r(P_0)$ for both aqueous mixtures are fitted to a polynomial equation of x_2. Pressure and density dependence of ϵ_r are, respectively, correlated with a Tait-type equation and a quadratic equation of density. Dielectric parameters at $P_0 = 0.1$ MPa: $(\partial\epsilon_r/\partial P)_{T,P_0}$, $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ are calculated from values of $\epsilon_r(P_0)$ and the Tait-type parameters. Since the isothermal compressibilities κ_T at 0.1 MPa, κ_{T,P_0}, are available for both aqueous polyhydric alcohol mixtures over the whole composition range at 298.15 K, the composition dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, is compared with that of κ_T at 0.1 MPa. In addition, $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ is fitted to a quadratic equation of x_2. The experimental $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values are compared with the estimated values from not only an empirical equation by Marcus but also an equation derived from a combination of correlation equations for $\epsilon_r(P_0)$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$.

Experimental Section

Guaranteed reagent-grade ethane-1,2-diol and propane-1,2,3-triol were purchased from Wako Pure Chemical Industries Ltd. The purity of each compound was better than 99 % according to the supplier. Under a N_2 stream at reduced pressure, each compound was refluxed over CaH_2 for several hours and then distilled at least twice. Water was purified by the method described in the previous paper.[5] The refractive indices n_D were measured with an Abbe refractometer at 0.1 MPa and 298.15 K and the values for ethane-1,2-diol and propane-1,2,3-triol were 1.4304 and 1.4722, respectively. Corresponding n_D values from the literature[8] are 1.4306 for ethane-1,2-diol and 1.4730 for propane-1,2,3-triol. All the aqueous organic mixtures were prepared gravimetrically and their compositions were accurate to within ± 0.0001. Details of the procedure and apparatus for capacitance measurements have been described earlier.[1] In the capacitance measurements, temperature was thermostated at (298.15 ± 0.01) K and pressure was measured with a Bourdon gauge with an accuracy of 0.07 MPa. The uncertainty in ϵ_r is estimated to be less than 0.1 %. The ϵ_r measurements were carried out more than three times for each solution, and the ϵ_r values thus obtained were reproduced to within ± 0.09 %.

Results and Discussion

Composition Dependence of $\epsilon_r(P_0)$. The averaged experimental ϵ_r values for water + ethane-1,2-diol and water + propane-1,2,3-triol under high pressure at 298.15 K are listed in Table 1, where x_2 is the mole fraction of organic component.

Figure 1, panels a and b, illustrates plots of the static relative permittivity at $P_0 = 0.1$ MPa $\epsilon_r(P_0)$ for water + ethane-1,2-diol and water + propane-1,2,3-triol against x_2 at 298.15 K, respectively. Available $\epsilon_r(P_0)$ data for each aqueous polyhydric alcohol mixture from the literature[9−15] are also plotted in each panel. Most of data are obtained from the tabulated data in the

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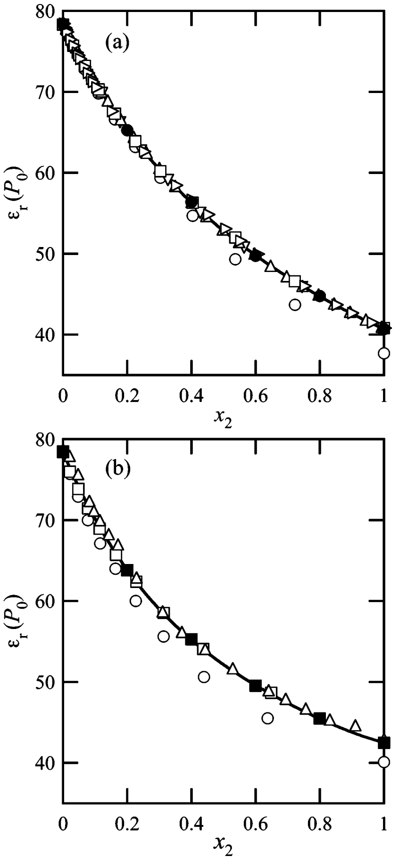

Figure 1. Static relative permittivities at 298.15 K and 0.1 MPa $\epsilon_r(P_0)$ against mole fraction of organic component x_2. (a) For water (1) + ethane-1,2-diol (2): ●, this work; ○, ref 9; □, ref 10; △, ref 11; ▽, ref 12; right-facing open triangle, ref 13. (b) For water + propane-1,2,3-triol (2): ■, this work; ○, ref 9; □, ref 14; △, ref 15. The smoothed curves are based on the values of A_i listed in Table 2.

Table 1. Static Relative Permittivities ϵ_r for Water + Ethane-1,2-diol and Water + Propane-1,2,3-triol as a Function of Pressure at 298.15 K

	ϵ_r at P/MPa						
x_2	0.1	50	100	150	200	250	300
	Water (1) + Ethane-1,2-diol (2)						
0.0000	78.39	80.18	81.88	83.47	85.01	86.48	87.94
0.2000	65.26	66.72	68.04	69.30	70.47	71.60	72.68
0.4000	56.38	57.74	58.96	60.14	61.19	62.23	63.22
0.6000	49.73	50.99	52.14	53.21	54.20	55.15	56.06
0.8000	44.76	45.95	47.04	48.05	49.00	49.89	50.72
1.0000[a]	40.70	41.80	42.83	43.77	44.65	45.48	46.27
	Water (1) + Propane-1,2,3-triol (2)						
0.2000	63.79	65.05	66.28	67.44	68.55	69.62	70.65
0.4000	55.26	56.37	57.44	58.46	59.43	60.37	61.28
0.6000	49.52	50.55	51.50	52.42	53.29	54.14	54.95
0.8000	45.48	46.43	47.33	48.18	48.99	49.77	50.53
1.0000[a]	42.49	43.39	44.24	45.04	45.80	46.54	47.25

[a] Ref 7.

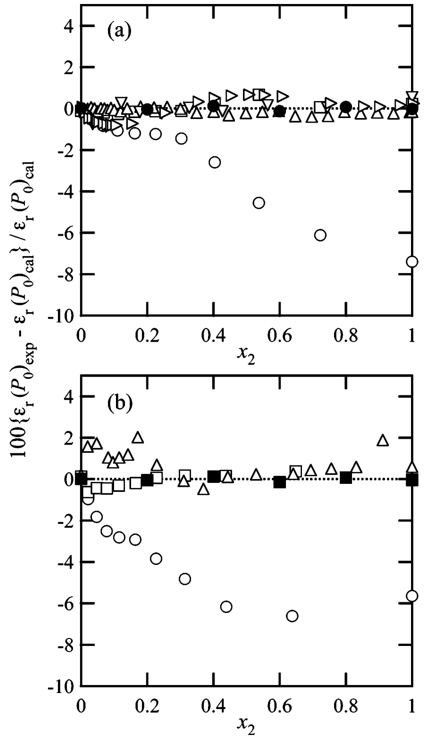

Figure 2. Relative deviation of $\epsilon_r(P_0)$ at 298.15 K from eq 1 against mole fraction of organic component x_2. (a) For water (1) + ethane-1,2-diol (2): ●, this work; ○, ref 9; □, ref 10; △, ref 11; ▽, ref 12; right-facing open triangle, ref 13. (b) For water + propane-1,2,3-triol (2): ■, this work; ○, ref 9; □, ref 14; △, ref 15.

Table 2. Coefficients A_i and Standard Deviation $\sigma(\epsilon_r(P_0))$ for Least-Squares Representations of $\epsilon_r(P_0)$ by Equation 1 at 298.15 K

A_0	A_1	A_2	A_3	A_4	$\sigma(\epsilon_r(P_0))$
Water (1) + Ethane-1,2-diol (2)					
78.38	−79.24	79.08	−53.79	16.28	0.01
Water (1) + Propane-1,2,3-triol (2)					
78.38	−94.06	125.26	−101.33	34.25	0.01

literature. Since the $\epsilon_r(P_0)$ data for water + propane-1,2,3-triol by Saleh et al.[15] were given only in their figure, the data extracted from the scanned figure were included in Figure 1b. Repeated scanning and digitized values of $\epsilon_r(P_0)$ and x_2 are reproduced respectively within ± 0.01 and ± 0.001. Our $\epsilon_r(P_0)$ data are fitted to the following equation by a method of least squares:

$$\epsilon_r(P_0) = \sum_{i=0}^{N} A_i x_2^{\,i} \qquad (1)$$

where A_i values are the coefficients and are tabulated in Table 2, where the standard deviations of the fit $\sigma(\epsilon_r)$ by eq 1 are also listed. Relative $\epsilon_r(P_0)$ deviations, $100\{\epsilon_r(P_0)_{exp} - \epsilon_r(P_0)_{calc}\}/\epsilon_r(P_0)_{calc}$, of the experimental values $\epsilon_r(P_0)_{exp}$ from the calculated values $\epsilon_r(P_0)_{calc}$ by use of eq 1 and A_i values are illustrated as a function of x_2 in Figure 2. For water + ethane-1,2-diol, the experimental data from the literature except those by Åkerlöf[9] are in agreement with the calculated values by eq 1 within ± 0.8 %; the average absolute deviation by Morenas and Douhéret,[10] Douhéret and Pal,[11] Corradini et al.,[12] and George and Sastry[13] are 0.2 %, 0.2 %, 0.3 %, and 0.5 %, respectively. The data by Åkerlöf below $x_2 = 0.303$ agree with the calculated ones within 1.5 %, but the deviation above $x_2 = 0.404$ becomes larger in magnitude with an increase in composition; $\epsilon_r(P_0)$ at $x_2 = 1$ is 7.4 % smaller than the calculated one. For water + propane-1,2,3-triol, the average absolute deviation by Albright[14] from the calculated values by eq 1 is 0.3 %. The average absolute deviation by Saleh et al.[15] is as high as 1.9 % below $x_2 = 0.171$, and a maximum deviation is found to be 1.9 % at $x_2 = 0.171$, while the average deviation in the range of $x_2 = (0.229$ to $1)$ except at $x_2 = 0.911$ is only 0.3 %; the deviation at $x_2 = 0.911$ is 1.8 %. The absolute relative deviation for water + propane-1,2,3-triol by Åkerlöf,[9] in general, becomes larger with x_2 as well as found in the composition dependence of the deviation for water + ethane-1,2-diol; his $\epsilon_r(P_0)$ data are smaller than ours over the composition range with a maximum deviation of −6.6 % at $x_2 = 0.638$.

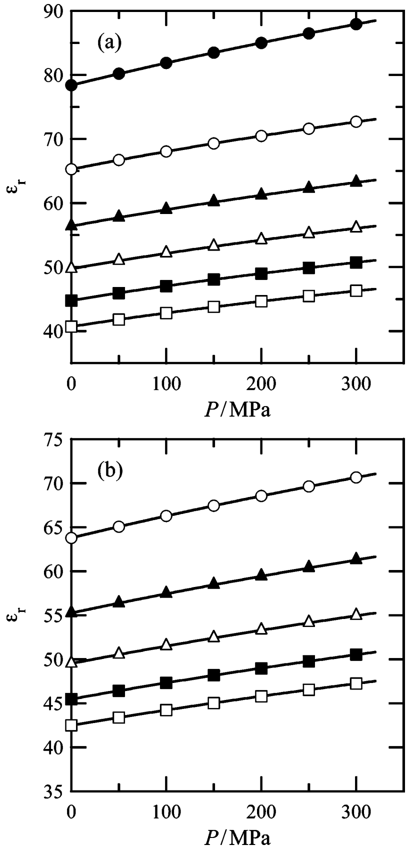

Figure 3. Pressure dependence of the static relative permittivities ϵ_r for (a) water (1) + ethane-1,2-diol (2) and (b) water (1) + propane-1,2,3-triol (2) at 298.15 K: ●, $x_2 = 0.0000$; ○, $x_2 = 0.2000$; ▲, $x_2 = 0.4000$; △, $x_2 = 0.6000$; ■, $x_2 = 0.8000$; □, $x_2 = 1.0000$.[7] The smoothed curves are based on the values of $\epsilon_r(P_0)$, *A*, and *B* listed in Table 3.

Pressure and Density Dependence of ϵ_r. The ϵ_r results for each aqueous polyhydric alcohol mixture are plotted as a function of pressure in Figure 3. Although ϵ_r values increase with pressure, $(\partial\epsilon_r/\partial P)_T$ becomes smaller with increasing pressure in each solution. Such pressure dependences of ϵ_r are usually found as long as the solution is in the liquid phase. The dependence of ϵ_r values on pressure for each mixture is correlated with the following Tait-type equation, usually known as the Owen−Brinkley equation:[16]

$$1 - \frac{\epsilon_r(P_0)}{\epsilon_r(P)} = A \ln\left(\frac{B + P}{B + P_0}\right) \qquad (2)$$

In this equation, $\epsilon_r(P)$ is the static relative permittivity at the pressure *P*. Table 3 summarizes the Tait-type parameters, *A* and *B*, for each solution determined from a nonweighted least-squares method together with the standard deviations $\sigma(\epsilon_r)$ of the fit. The largest $\sigma(\epsilon_r)$ value obtained in this work is 0.02, so the value is within the uncertainty in ϵ_r. Consequently, $\epsilon_r(P)$ value at any pressure up to 300 MPa can be calculated using eq 2 with $\epsilon_r(P_0)$, *A*, and *B* values in Table 3 with a good accuracy.

In the previous paper,[5] it has been shown that $\epsilon_r(P)$ for water + propane-1,2-diol and water + propane-1,3-diol was well-represented by the following equation, which passed through the point $(\rho(P_0), \epsilon_r(P_0))$:

$$\epsilon_r(P) = \epsilon_r(P_0) + a\{\rho(P) - \rho(P_0)\} + b\{\rho(P) - \rho(P_0)\}^2 \quad (3)$$

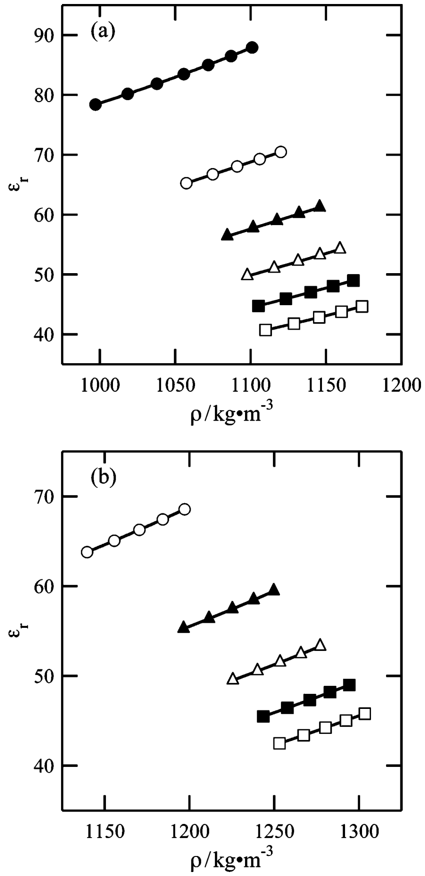

Figure 4. Density dependence of ϵ_r at 298.15 K for (a) water (1) + ethane-1,2-diol (2) and (b) water (1) + propane-1,2,3-triol (2): ●, $x_2 = 0.0000$; ○, $x_2 = 0.2000$; ▲, $x_2 = 0.4000$; △, $x_2 = 0.6000$; ■, $x_2 = 0.8000$; □, $x_2 = 1.0000$. The smoothed curves are based on the values of $\epsilon_r(P_0)$ in Table 3 and $\rho(P_0)$, *a*, and *b* in Table 4.

Table 3. Static Relative Permittivity at 0.1 MPa $\epsilon_r(P_0)$, Parameters of the Tait-Type Equation *A* and *B*, and Standard Deviations of Fit by Equation 2 $\sigma(\epsilon_r)$ at 298.15 K

x_2	$\epsilon_r(P_0)$	*A*	*B*/MPa	$\sigma(\epsilon_r)$
		Water (1) + Ethane-1,2-diol (2)		
0.0000	78.39	0.2166	461.3	0.01
0.2000	65.26	0.1758	381.4	0.01
0.4000	56.38	0.1737	347.6	0.02
0.6000	49.73	0.1741	329.0	0.01
0.8000	44.76	0.1742	310.9	0.00
1.0000[a]	40.70	0.1790	312.6	0.01
		Water (1) + Propane-1,2,3-triol (2)		
0.2000	63.79	0.2118	515.4	0.00
0.4000	55.26	0.2147	516.9	0.02
0.6000	49.52	0.2029	478.0	0.00
0.8000	45.48	0.2019	468.6	0.00
1.0000[a]	42.49	0.1992	456.0	0.01

[a] Ref 7.

where *a* and *b* are the adjustable parameters, and $\rho(P)$ and $\rho(P_0)$ are the density at pressure *P* and 0.1 MPa, respectively. The $\rho(P)$ values up to 200 MPa were calculated from the Tait equation with the aid of the Tait parameters determined from the compression measurements[6] at pressures up to 200 MPa and available $\rho(P_0)$ data for water + ethane-1,2-diol[11,13,17] and water + propane-1,2,3-triol[18,19] at 298.15 K. Plots of ϵ_r against ρ thus determined at various compositions for each aqueous polyhydric alcohol mixture up to 200 MPa are depicted in Figure 4, where ϵ_r data for water were plotted against density up to 300 MPa available from the NIST Chemistry WebBook.[20] Table 4 lists $\rho(P_0)$, $\epsilon_r(P_0)$, *a*, and *b* values determined by a least-squares method for both aqueous polyhydric alcohols along with the standard deviation $\sigma(\epsilon_r)$ of the fit by eq 3. There is a general

Table 4. Density at 0.1 MPa $\rho(P_0)$, Static Relative Permittivity at 0.1 MPa $\epsilon_r(P_0)$, Adjustable Parameters a and b in Equation 3, and Standard Deviation of Fit by Equation 3 $\sigma(\epsilon_r)$

x_2	$\rho(P_0)$/kg·m^{-3}	$\epsilon_r(P_0)$	a/kg^{-1}·m^3	10^5b/ kg^{-2}·m^6	$\sigma(\epsilon_r)$
		Water (1) + Ethane-1,2-diol (2)			
0.0000	997.05	78.39	0.08074	10.50	0.02
0.2000	1057.3	65.26	0.08201	1.608	0.01
0.4000	1084.5	56.38	0.07863	−0.158	0.01
0.6000	1097.8	49.73	0.07011	4.437	0.00
0.8000	1105.2	44.76	0.06424	4.819	0.00
1.0000	1109.9	40.70	0.05719	7.241	0.00
		Water (1) + Propane-1,2.3-triol (2)			
0.2000	1139.6	63.79	0.07769	8.885	0.01
0.4000	1196.6	55.26	0.07312	10.44	0.00
0.6000	1225.6	49.52	0.06921	7.898	0.01
0.8000	1243.5	45.48	0.06557	7.123	0.00
1.0000	1253.2	42.49	0.06308	5.392	0.00

tendency that a value decreases with an increase in x_2, as also found in water + propanediol systems.[5] Judging from the $\sigma(\epsilon_r)$ values, it is clear that eq 3 represents the density dependence of $\epsilon_r(P)$ very well (i.e., $\epsilon_r(P)$ is a quadratic equation of $\rho(P)$).

Correlation of Composition Dependence of $\epsilon_r(P)$ Using Polarization p. It is very important to predict composition dependence of $\epsilon_r(P)$ values for binary mixtures using only $\epsilon_r(P)$ and $\rho(P)$ data for pure components. Recently Wang and Anderko[21] have used a correlation equation for the composition dependence of the polarization per unit volume (p) at 0.1 MPa: $p_0 = (\epsilon_r(P_0) - 1)(2\epsilon_r(P_0) + 1)/9\epsilon_r(P_0)$ and have reported reasonable composition dependence of $\epsilon_r(P_0)$ for water + ethane-1,2-diol in the temperature ranges of (293.15 to 373.15) K using the $(\epsilon_r(P_0) - 1)(2\epsilon_r(P_0) + 1)/9\epsilon_r(P_0)$ data for pure components and only one adjustable parameter. Although they used their correlation equation to the data at atmospheric pressure, the equation can be applied to the data under high pressures. The correlation equation for binary mixtures is given as follows:

$$p(P) = \frac{\displaystyle\sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j \{p(P)M/\rho(P)\}_{ij}}{\displaystyle\sum_{i=1}^{2}\{x_i M_i/\rho_i(P)\}} \tag{4}$$

where

$$\{p(P)M/\rho(P)\}_{ij} = \frac{1}{2}\{p_i(P)M_i/\rho_i(P) + p_j(P)M_j/\rho_j(P)\}(1 + k_{ij}) \tag{5}$$

and k_{ij} is a adjustable parameter for $i \neq j$ and equal to zero for $i = j$. In eq 4, M_i and $\rho_i(P)$ are, respectively, the molar mass and the density at the pressure P for the component i, and $p_i(P)$ means the polarization per unit volume for the component i at the pressure P defined as follows:

$$p_i(P) = \frac{\{\epsilon_{ri}(P) - 1\}\{2\epsilon_{ri}(P) + 1\}}{9\epsilon_{ri}(P)} \tag{6}$$

where $\epsilon_{ri}(P)$ is $\epsilon_r(P)$ for the component i. By use of the $\epsilon_r(P)$ and $\rho(P)$ data as a function of x_2 for water + ethane-1,2-diol or propane-1,2,3-triol at pressures up to 200 MPa, k_{12} values for water + ethane-1,2-diol and water + propane-1,2,3-triol systems were determined. The values are listed in Table 5, where the standard deviations $\sigma(\epsilon_r)$ of the fit by eq 4 are also included. It is found that the $\sigma(\epsilon_r)$ values obtained from eq 4 are not so good as those values from the polynomial fit by eq 1, but the fact that use of only one adjustable parameter k_{12} gave a reasonable composition dependence of $\epsilon_r(P)$ is noteworthy.

Table 5. Adjustable Parameter k_{12} in Equation 4, Pressure Ranges, and the Standard Deviation of $\epsilon_r(P)$ of Fit by Equation 4 $\sigma(\epsilon_r)$

system	P^a/MPa	k_{12}	$\sigma(\epsilon_r)$
water (1) + ethane-1,2-diol (2)	0.1−200	0.123	0.29
water (1) + propane-1,2,3-triol (2)	0.1−200	0.115	0.43

[a] P means that k_{12} was determined from the $\epsilon_r(P)$ and $\rho(P)$ data in the pressure ranges of (0.1 to 200) MPa.

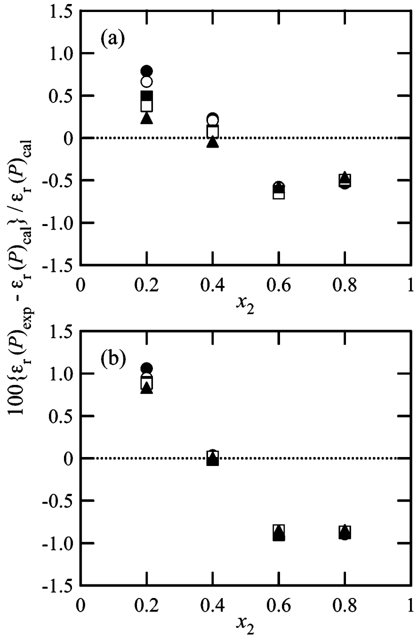

Figure 5. Relative deviation of $\epsilon_r(P)$ at 298.15 K from the calculated values from eq 4 using k_{12} listed in Table 5 against the mole fraction of organic component x_2 for (a) water (1) + ethane-1,2-diol (2) and (b) water + propane-1,2,3-triol (2): ●, 0.1 MPa; ○, 50 MPa; ■, 100 MPa; □, 150 MPa; ▲, 200 MPa.

Relative $\epsilon_r(P)$ deviations, $100\{\epsilon_r(P)_{exp} - \epsilon_r(P)_{calc}\}/\epsilon_r(P)_{calc}$, of the experimental values $\epsilon_r(P)_{exp}$ from the calculated values $\epsilon_r(P)_{calc}$ by use of eq 4 and k_{12} value are illustrated as a function of x_2 in Figure 5, where the values at $x_2 = (0$ and $1)$ are not plotted because relative $\epsilon_r(P)$ deviations are zero by definition. Composition dependence of relative deviations is very similar in both aqueous organic systems; large positive deviations are found at $x_2 = 0.2$, while the experimental values at $x_2 = 0.4$ are in excellent agreement with the calculated ones; slight negative deviations are found at $x_2 = (0.6$ and $0.8)$.

Dielectric Parameters at P_0. Values of $(\partial\epsilon_r/\partial P)_T$, $(\partial \ln \epsilon_r/\partial P)_T$, and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ at 0.1 MPa are required not only for analyzing electrolyte solution data at atmospheric pressure but also for estimating a volume contribution due to electrostriction to the standard partial molar volume of an individual ion by use of the Born equation. These values at 0.1 MPa can be easily evaluated from $\epsilon_r(P_0)$ and the Tait-type parameters as follows:

$$\left(\frac{\partial\epsilon_r}{\partial P}\right)_{T,P_0} = \frac{A\epsilon_r(P_0)}{B + P_0} \tag{7}$$

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T,P_0} = \frac{A}{B + P_0} \tag{8}$$

$$\epsilon_r(P_0)^{-2}\left(\frac{\partial\epsilon_r}{\partial P}\right)_{T,P_0} = \frac{A}{\epsilon_r(P_0)(B + P_0)} \tag{9}$$

Table 6 summarizes the values of $(\partial\epsilon_r/\partial P)_{T,P_0}$, $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ at selected compositions together with

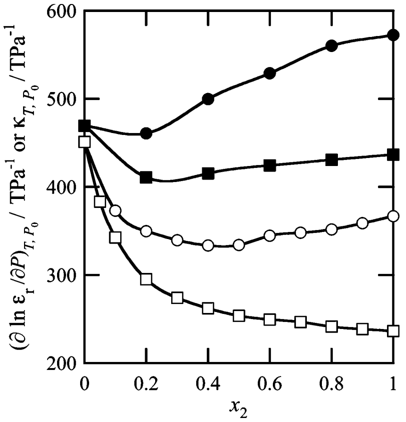

Figure 6. Composition dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ at 298.15 K: ●, water (1) + ethane-1,2-diol (2); ■, water (1) + propane-1,2,3-triol (2). The curves by a cubic-spline fit to data points are to guide to the eye.

Table 6. Dielectric Parameters at 0.1 MPa, $(\partial\epsilon_r/\partial P)_{T,P_0}$, $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$, and Isothermal Compressibility at 0.1 MPa κ_{T,P_0} at 298.15 K

x_2	$(\partial\epsilon_r/\partial P)_{T,P_0}$ / GPa^{-1}	$(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ / TPa^{-1}	κ_{T,P_0} / TPa^{-1}	$\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ / TPa^{-1}
		Water (1) + Ethane-1,2-diol (2)		
0.0000	36.80	469.4	451.2	5.99
0.2000	30.07	460.8	349.8	7.06
0.4000	28.17	499.6	333.5	8.86
0.6000	26.30	529.0	344.6	10.64
0.8000	25.07	560.1	351.8	12.51
1.0000	23.30	572.4	366.9	14.06
		Water (1) + Propane-1,2,3-triol (2)		
0.2000	26.20	410.9	295.1	6.44
0.4000	22.95	415.3	262.2	7.52
0.6000	21.02	424.4	249.5	8.57
0.8000	19.59	430.8	241.4	9.47
1.0000	18.56	436.7	236.3	10.28

the isothermal compressibility at 0.1 MPa, κ_{T,P_0}. Values of κ_{T,P_0} at other several compositions are also available in the previous paper.[6]

Figure 6 illustrates the composition dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and κ_{T,P_0} at 298.15 K for water + ethane-1,2-diol and water + propane-1,2,3-triol because it has been suggested that $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ has a close relationship with κ_{T,P_0}. For both aqueous systems, the $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values are larger than the κ_{T,P_0} values over the entire composition range and a shallow minimum in $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ is found around $x_2 = 0.2$. A shallow minimum in κ_{T,P_0} is also found for water + ethane-1,2-diol around $x_2 = 0.4$, while κ_{T,P_0} value for water + propane-1,2,3-triol show an abrupt decrease below $x_2 = 0.2$ and decreases gradually above the composition. As described in detail in the previous work,[5] it has been clarified that a ratio $(\partial \ln \epsilon_r/\partial P)_{T,P_0}/\kappa_{T,P_0}$ should be equal to $a\rho(P_0)/\epsilon_r(P_0)$ as far as density dependence of $\epsilon_r(P)$ is well-represented by eq 3. Although a comparison between both values are not shown here, it can be easily confirmed that the relationship also holds in the present water + polyhydric systems.

Figure 7 depicts the composition dependence of $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ for the present and previous water + polyhydric alcohol mixtures at 298.15 K. In any mixture, $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ increases with x_2. Composition dependence of $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ is found to be well-correlated with the following equation:

$$\epsilon_r(P_0)^{-2}\left(\frac{\partial\epsilon_r}{\partial P}\right)_{T,P_0} = (1 - x_2)y_1 + x_2y_2 + C(1 - x_2)x_2(y_2 - y_1) \tag{10}$$

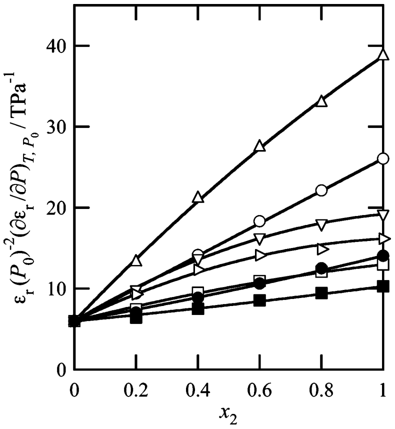

Figure 7. Composition dependence of $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ at 298.15 K: ●, water (1) + ethane-1,2-diol (2); ■, water (1) + propane-1,2,3-triol (2); ○, water (1) + propane-1,2-diol (2); □, water (1) + propane-1,3-diol (2); △, water (1) + butane-1,2-diol (2); ▽, water (1) + butane-1,3-diol (2); right-facing open triangle, water (1) + butane-1,4-diol (2). The curves are based on the values of $\{\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}\}_i$ and C in Table 7.

Table 7. Dielectric Parameter for the Component 2 $\{\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}\}_2$, Adjustable Parameter C, and the Standard Deviation $\sigma(\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0})$ of the Fit by Equation 7

system	$\{\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}\}_2$/TPa^{-1}	C^a	$\sigma(\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0})$
water (1) + ethane-1,2-diol (2)	14.06	−0.155	0.23
water (1) + propane-1,2,3-triol (2)	10.28	−0.141	0.19
water (1) + propane-1,2-diol (2)	26.05	0.008	0.33
water (1) + propane-1,3-diol (2)	12.98	0.376	0.19
water (1) + buane-1,2-diol (2)	38.70	0.214	0.32
water (1) + buane-1,3-diol (2)	19.19	0.723	0.17
water (1) + buane-1,4-diol (2)	16.16	0.800	0.33

[a] A value of $\{\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}\}_1$ was taken as 5.99 TPa^{-1} obtained in this work, and the C value was determined by using $\{\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}\}_i$ value for each component i.

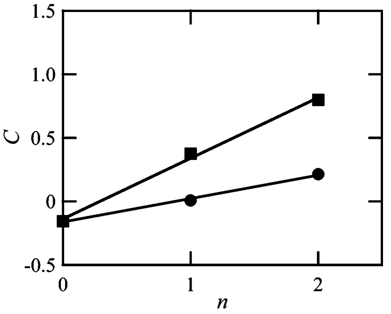

Figure 8. C values as a function of n in water (1) + alkanediol (2) at 298.15 K: ●, $HOCH_2-CH(OH)-(CH_2)_n-H$; ■, $HOCH_2-(CH_2)_n-CH_2-OH$. The straight lines are obtained by a least-squares method.

Here y_i is $\{\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}\}_i$ being $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ for component i, and C is the adjustable parameter. Table 7 summarizes values of C and standard deviation of fit $\sigma(\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0})$ by eq 10 for water + polyhydric alcohol mixtures. It is found that the C value for water + ethaner-1,2-diol is nearly equal to that for water + propane-1,2,3-triol. Figure 8 illustrates plots of C value against the number of methylene groups in alkanediol n for water + alkane-1,2-diol and for water + alkanediol whose OH groups exist at each terminal carbon atom. There is an approximate linear relationship between C and n in each water + alkanediol system, even though data points for C are few. The slope obtained for the group of water + alkane-1,2-diol is half of that for the group of water + alkanediol having OH groups at each terminal carbon. Moreover, the $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ values for water + ethaner-1,2-diol and water + propane-1,2,3-triol are smaller than those for water + butaneane-1,2-

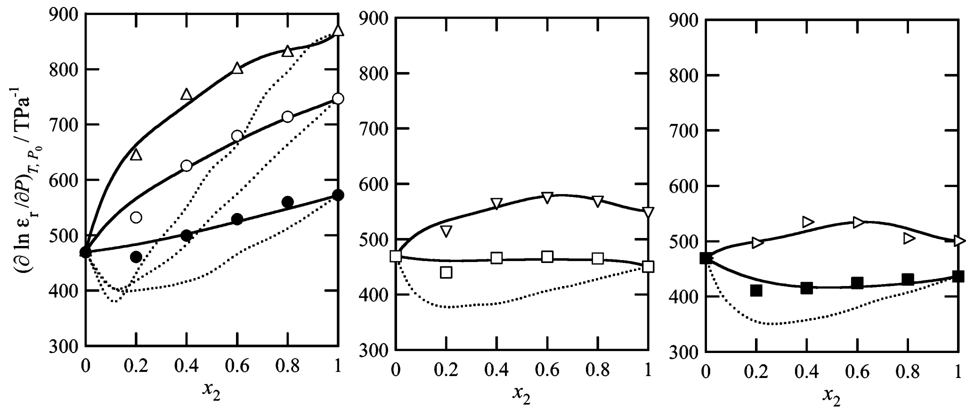

Figure 9. Comparison of the experimental $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values: ●, water (1) + ethane-1,2-diol (2); ■, water (1) + propane-1,2,3-triol (2); ○, water (1) + propane-1,2-diol (2); □, water (1) + propane-1,3-diol (2); △, water (1) + butane-1,2-diol (2); ▽, water (1) + butane-1,3-diol (2); right-facing open triangle, water (1) + butane-1,4-diol (2) with the evaluated $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ curves by eqs 11 and 12 at 298.15 K. The dotted and full curves are respectively based on eq 11 and eq 12.

diol, + propane-1,2-diol, + butane-1,3-diol, and + butane-1,4-diol over the whole composition range. The values for water + propane-1,3-diol are nearly equal to those for water + propane-1,2,3-triol. These results suggest that the $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ values strongly influence not only the relative position of the OH groups and a size of alkyl substituent at terminal group but also the number of the OH group in polyhydric alcohols.

Composition Dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$. Limited dielectric parameters given in eqs 7 to 9 are reported for binary water + polar organic solvent systems as a function of x_2 at 298.15 K, so it is very important to find out a simple method to estimate those values for water + organic solvent at any composition by use of as little information as possible. Recently an attempt for estimating $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values for aqueous mixtures of organic solvents was made by Marcus.[22] He has used the following equation to represent the composition dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ for binary aqueous mixtures:

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T,P_0} = \left[(1-x_2)\left\{\frac{(\partial \ln \epsilon_r/\partial P)_{T,P_0}}{\kappa_{T,P_0}}\right\}_1 + x_2\left\{\frac{(\partial \ln \epsilon_r/\partial P)_{T,P_0}}{\kappa_{T,P_0}}\right\}_2\right]\kappa_{T,P_0} \qquad (11)$$

Here $\{(\partial \ln \epsilon_r/\partial P)_{T,P_0}/\kappa_{T,P_0}\}_i$ means $(\partial \ln \epsilon_r/\partial P)_{T,P_0}/\kappa_{T,P_0}$ for component i ($i = 1, 2$). Equation 11 has no theoretical background and is only empirically proposed. Marcus has applied the equation to water + 1-methyl-2-pyrrolidinone system and described that the equation was approximately the case for the system. To check its versatility, eq 11 is applied to the following water + polyhydric alcohol mixtures: water + ethane-1,2-diol,[6] + propane-1,2,3-triol,[6] + propane-1,2-diol,[6] + propane-1,3-diol,[6] and + butane-1,2-diol[23] because κ_{T,P_0} values are available at selected mole fractions for those mixtures. Values of κ_{T,P_0} at any composition over the whole composition range were interpolated by a cubic spline fit of experimental data. Figure 9 shows a comparison of the estimated $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values from eq 11 as a function of x_2 for the aqueous polyhydric alcohol systems with the experimental results. In any mixture, the calculated curves show a minimum at lower mole fraction range of (0.1 to 0.3), and poor agreement between the calculated and experimental values were found, as can be judged from the magnitude of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and its composition dependence. Hence it is concluded that eq 11 by Marcus[22] is not useful for estimating $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values for water + polyhydric alcohol mixtures over the whole mole fraction range.

The following equation can be derived from a combination of eqs 1 and 10:

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T,P_0} = \left(\sum_{i=0}^{N} A_i x_2^{\,i}\right)\{(1-x_2)y_1 + x_2 y_2 + C(1-x_2)x_2(y_2-y_1)\} \qquad (12)$$

As described earlier in the present work, composition dependence of $\epsilon_r(P_0)$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ is well-represented respectively by eq 1 and eq 10. Hence the $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values obtained by using eq 12 are expected to reproduce the experimental ones over the whole composition range fairly well. Actually it is clear that the calculated values plotted as full curves in Figure 9 coincide satisfactorily with the experimental results for aqueous mixtures of polyhydric alcohol. The calculated $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ value at $x_2 = 0.2$ is, however, larger than the experimental one at the same composition in many water + polyhydric alcohol systems. This is mainly caused by limited applicability of eq 10 at lower mole fraction range.

Composition dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ is not simple, as shown in Figure 9. Hence there is a limitation to correlate $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ with x_2 by a polynomial equation of x_2 as well as the equation by Marcus. In contrast, it is easy to represent composition dependence of $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ by a simple equation such as eq 10. For example, there is a possibility to estimate $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values for water + pentane-1,2-diol and water + pentane-1,5-diol over the composition range at 298.15 K by use of the estimated C value from Figure 8, the $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ value for pentane-1,2-diol and pentane-1,5-diol, and the coefficients A_i in eq 1. In fact, since $\epsilon_r(P_0)$ data as a function of x_2 is available for only water + pentane-1,5-diol[24] and the $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ value for pentane-1,5-diol can be estimated from $\epsilon_r(P_0)$ data for pentane-1,5-diol by a correlation equation for monohydric and polyhydric alcohols given in the previous paper,[7] $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ values can be evaluated as a function of composition using the estimated C value: 0.391. However, there is no experimental $\epsilon_r(P)$ data available for water + pentane-1,5-diol at present. It is impossible to confirm applicability of eq 12.

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