

# Static Relative Permittivities of Three Water + Butanediol Mixtures under Pressures up to 300 MPa at 298.15 K

Yasuhiro Uosaki,\* Sunao Kitaura, Takashi Kita, and Takashi Moriyoshi

Department of Chemical Science and Technology, Faculty of Engineering, University of Tokushima, Tokushima 770-8506, Japan

Static relative permittivities  $\epsilon_r$  of water + butane-1,2-diol, water + butane-1,3-diol, and water + butane-1,4-diol in the liquid phase were determined from capacitance measurements over the entire composition range under pressures up to 300 MPa at 298.15 K. The Tait-type equation is applied to represent the pressure dependence of  $\epsilon_r$  for each solution. The Tait-type parameters,  $A$  and  $B$ , are determined from the nonweighted least-squares method. The composition dependence of  $\epsilon_r(0.1)$ ,  $(\partial \ln \epsilon_r / \partial P)_T$ , and  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  values at 0.1 MPa for the three binary aqueous butanediol mixtures are compared.

## Introduction

The static relative permittivities  $\epsilon_r$ , usually referred to as the dielectric constants, of many aqueous organic mixtures have been so far studied extensively as a function of composition at atmospheric pressure. There are limited values for aqueous organic mixtures under high pressure. The pressure dependence of  $\epsilon_r$  gives us not only useful some information on the molecular interactions between water and organic molecules but also important parameters such as  $(\partial \ln \epsilon_r / \partial P)_T$  and  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  at 0.1 MPa, which are important in theories of electrolytes as well as for many chemical reactions, especially those involving ionic or polar chemical species (Isaacs, 1981).

In previous papers (Uosaki et al., 1996, 1997), we have reported the pressure dependence of the static relative permittivities for some aqueous organic mixtures in the liquid phase over the entire mole-fraction range under pressures up to 300 MPa at 298.15 K and evaluated  $(\partial \ln \epsilon_r / \partial P)_T$  and  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  values at 0.1 MPa for each aqueous organic mixture as a function of composition. Moreover, the composition dependence of the isothermal compressibilities  $\kappa_T$  and  $(\partial \ln \epsilon_r / \partial P)_T$  values at 0.1 MPa were compared for some aqueous mixtures.

In continuation of our work on dielectric properties measurements for binary aqueous organic mixtures, the present paper reports the liquid-phase static relative permittivities of water + butane-1,2-diol, water + butane-1,3-diol, and water + butane-1,4-diol over the entire composition range under pressures up to 300 MPa at 298.15 K. High-pressure studies on physical properties of butanediols are quite few; density measurements of butane-1,3-diol up to 274.6 MPa over the temperature range of 213.15 K to 303.15 K (McDuffie et al., 1969) and expansivity measurements of butane-1,4-diol up to 385 MPa at 299.11 K and 312.92 K (Ter Minassian and Pruzan, 1977) have been reported. To correlate the experimentally obtained  $\epsilon_r$  values with pressure, the Tait-type equation is applied. We evaluate  $(\partial \ln \epsilon_r / \partial P)_T$  and  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  values at 0.1 MPa for three aqueous butanediol mixtures and then

compare the composition dependence of these values among these systems.

## Experimental Section

Guaranteed-reagent-grade butane-1,2-diol, butane-1,3-diol, and butane-1,4-diol were purchased from Wako Pure Chemical Industries Ltd. The purity of each compound was better than 99% according to the supplier. Under a N<sub>2</sub> stream at reduced pressure, each butanediol was refluxed over CaH<sub>2</sub> for several hours and then distilled at least twice. Water was purified by the method described earlier (Uosaki et al., 1996). The refractive indices  $n_D$  were measured with an Abbe refractometer at 0.1 MPa and 298.15 K, and their values for butane-1,2-diol, butane-1,3-diol, and butane-1,4-diol were 1.4364, 1.4382, and 1.4442, respectively. Corresponding recent literature values (Piekariski et al., 1995) are 1.4359 for butane-1,2-diol, 1.4389 for butane-1,3-diol, and 1.4444 for butane-1,4-diol. All the aqueous butanediol mixtures were prepared by mass, and their compositions were controlled to within  $\pm 5 \times 10^{-5}$  mole fraction of butanediol at the nominal values. Details of the procedure and apparatus for capacitance measurements have been described earlier (Moriyoshi et al., 1990). In the capacitance measurements, temperature was controlled to  $\pm 0.01$  K and pressure was measured with a Bourdon gauge with an accuracy of 0.35 MPa. The uncertainty in  $\epsilon_r$  is estimated to be less than 0.1%. The  $\epsilon_r$  measurements were carried out more than three times for each solution, and the  $\epsilon_r$  values thus obtained were reproduced to within  $\pm 0.1\%$ .

## Results and Discussion

The averaged experimental  $\epsilon_r$  values for water + butane-1,2-diol, water + butane-1,3-diol, and water + butane-1,4-diol in the liquid phase under high pressure at 298.15 K are listed in Table 1, where  $x_2$  is the mole fraction of butanediol. Table 1 also lists some literature values of the static relative permittivities at 0.1 MPa and 298.15 K,  $\epsilon_r(0.1)$ , for pure butanediols for comparison. The present  $\epsilon_r(0.1)$  value for butane-1,2-diol agrees with that by Sagal (1962) and is 1.4% lower than that by Bald et al. (1992b). For butane-1,3-diol, the literature values (Sagal, 1962; Piekariski et al., 1995; Grineva and Zhuravlev, 1996) are

\* To whom correspondence should be addressed. E-mail: uosaki@chem.tokushima-u.ac.jp.

**Table 1. Static Relative Permittivities  $\epsilon_r$  for Water + Butanediols as a Function of Pressure at 298.15 K**

$x_2$	P/MPa												
	0.1	10	20	25	30	40	50	75	100	150	200	250	300
Water (1) + Butane-1,2-diol (2)													
0.200	48.49						49.94		51.28	52.46	53.57	54.60	55.56
0.400	35.62						36.88		37.96	38.93	39.83	40.68	41.46
0.600	29.13						30.19		31.16	32.02	32.78	33.50	34.17
0.800	25.17						26.14		26.98	27.73	28.40	29.05	29.65
1	22.40						23.30		24.07	24.76	25.39	25.97	26.52
	22.4 <sup>a</sup>												
	22.71 <sup>b</sup>												
Water (1) + Butane-1,3-diol (2)													
0.200	52.40						53.68		54.84	55.90	56.88	57.81	58.67
0.400	41.34						42.45		43.43	44.32	45.16	45.92	46.66
0.600	35.49						36.45		37.30	38.05	38.75	39.40	40.01
0.800	31.68						32.52		33.25	33.91	34.49	35.04	35.56
1	28.68						29.41		30.05	30.61	31.11	31.59	32.03
	28.8 <sup>a</sup>												
	28.48 <sup>c</sup>												
	28.43 <sup>d</sup>												
Water (1) + Butane-1,4-diol (2)													
0.200	53.43						54.68		55.84	56.90	57.89	58.80	59.68
0.400	43.36						44.45		45.44	46.35	47.19	47.96	48.70
0.600	37.83						38.78		39.64	40.41	41.14		
0.800	33.99				34.41		34.80	35.19	35.55				
1	30.99	31.14	31.29		31.43	31.57							
	30.8 <sup>a</sup>												
	31.9 <sup>e</sup>												
	30.33 <sup>f</sup>												
	30.84 <sup>d</sup>												
	31.4 <sup>g</sup>												

<sup>a</sup> Sagal, 1962. <sup>b</sup> Bald et al., 1992b. <sup>c</sup> Piekarski et al., 1995. <sup>d</sup> Grineva and Zhuravlev, 1996. <sup>e</sup> Safonova et al., 1980. <sup>f</sup> Bald et al., 1992a. <sup>g</sup> Wang et al., 1997.

in agreement with ours within  $\pm 0.9\%$ . Our  $\epsilon_r(0.1)$  value for butane-1,4-diol also agrees with the literature values (Sagal, 1962; Grineva and Zhuravlev, 1996) within  $\pm 0.6\%$ , but those by Safonova et al. (1980), Bald et al. (1992a), and Wang et al. (1997) are, respectively, 2.9% larger, 2.1% smaller, and 1.3% larger than the present value. Grineva and Zhuravlev (1996) have discussed reasons for the slightly large differences in  $\epsilon_r(0.1)$  for butane-1,4-diol among their value and those reported by Safonova et al. (1980) and Bald et al. (1992a).

Figure 1a depicts a variation of  $\epsilon_r(0.1)$  with  $x_2$  for water + butane-1,2-diol and water + butane-1,3-diol. A similar plot for water + butane-1,4-diol is shown in Figure 1b. Available literature  $\epsilon_r(0.1)$  data for each aqueous butanediol mixture are also plotted in each figure. In any aqueous butanediol systems,  $\epsilon_r(0.1)$  values decrease with  $x_2$ ; a marked decrease in  $\epsilon_r(0.1)$  is observed, especially at lower mole fractions of butanediol. The present  $\epsilon_r(0.1)$  values for water + butane-1,2-diol are slightly lower than those by Bald et al. (1992b) over the entire composition range but agree within 0.9%. Our  $\epsilon_r(0.1)$  values for water + butane-1,3-diol are in agreement with the literature values (Grineva and Zhuravlev, 1996; Piekarski et al., 1995) within  $\pm 0.6\%$ . For water + butane-1,4-diol, the reported values by Safonova et al. (1980) are 2.4% larger than ours. However, the values by Bald et al. (1992a), Grineva and Zhuravlev (1996), and Wang et al. (1997) coincide with ours within  $\pm 1.2\%$ ,  $\pm 0.5\%$ , and  $\pm 0.7\%$ , respectively.

Figure 2 shows the experimental  $\epsilon_r$  results for each aqueous butanediol mixture as a function of pressure. With a rise in pressure,  $\epsilon_r$  values in the liquid phase increase, but a rate of increase in  $\epsilon_r$  with pressure becomes smaller in every solutions. These  $\epsilon_r$  behaviors with pressure are usually found in the liquid phase (Moriyoshi et al., 1990; Uosaki et al., 1996, 1997). In water + butane-1,4-diol, some solutions solidified at high pressure. Solidi-

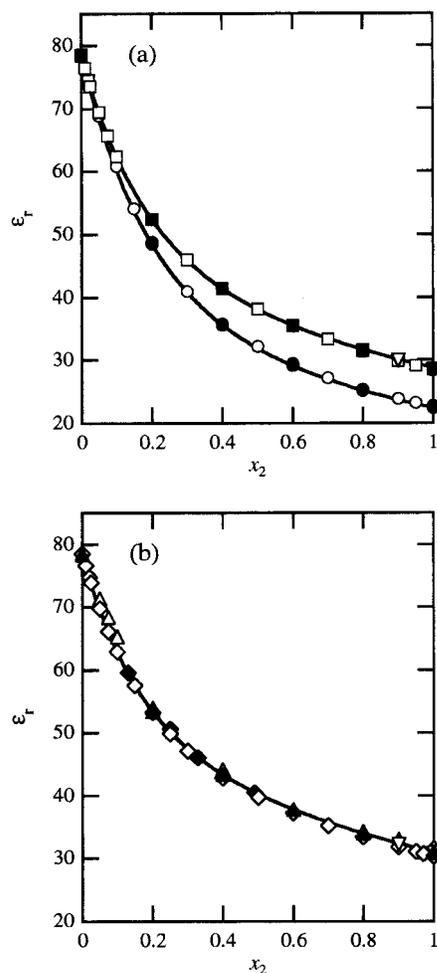
fication of solution can be easily detected by a sudden pressure drop and/or a sudden decrease in capacitance of solution. Pure butane-1,4-diol froze near 50 MPa. The freezing pressure for pure butane-1,4-diol at 298.15 K well corresponds with that at 299.11 K, 40–70 MPa, estimated from the high-pressure expansivity measurement (Ter Minassian and Pruzan, 1977). Aqueous butane-1,4-diol mixtures of the composition  $x_2 = 0.800$  and  $x_2 = 0.600$  also solidified around 125 MPa and 240 MPa, respectively. No other aqueous butanediol mixtures was found to be frozen up to 300 MPa at 298.15 K.

The following Tait-type equation is applied to correlate the pressure dependence of the  $\epsilon_r$  data for each solution in the liquid phase:

$$1 - \frac{\epsilon_r(0.1)}{\epsilon_r(P)} = A \ln \left( \frac{B + P/\text{MPa}}{B + 0.1} \right) \quad (1)$$

In this equation,  $\epsilon_r(P)$  is the static relative permittivity at the pressure  $P$ . The Tait-type parameters,  $A$  and  $B$ , for each solution were determined from the nonweighted least-squares method and are summarized in Table 2, along with the standard deviations  $\sigma(\epsilon_r)$  of the fit. The results for pure water (Moriyoshi et al., 1990) are also included in Table 2. The  $\sigma(\epsilon_r)$  values are less than 0.01 for each aqueous butanediol mixture.

To obtain the partial molar volume of electrolytes at infinite dilution from the apparent partial molar volume calculated from density measurements,  $(\partial \ln \epsilon_r / \partial P)_T$  values are required from a theoretical point of view. Furthermore,  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  values are needed to analyze the contribution of the electrostriction not only to the partial molar volume of an individual ion but also in the chemical reactions including ionic species. Since these volumetric properties are usually determined at 0.1 MPa, the  $(\partial \ln \epsilon_r / \partial P)_T$  and

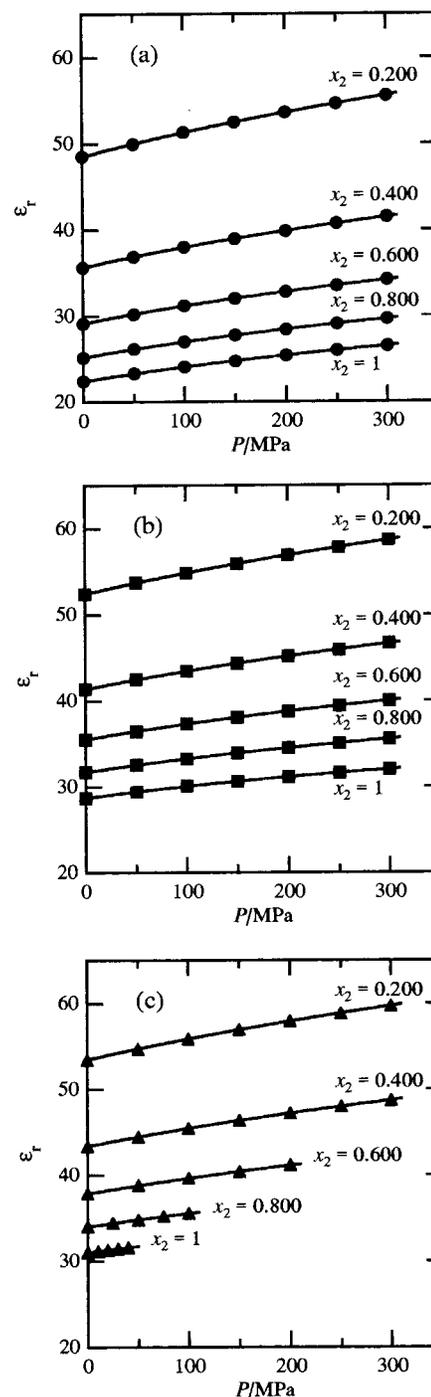


**Figure 1.** Static relative permittivities at 0.1 MPa and 298.15 K,  $\epsilon_r(0.1)$ , against mole fraction,  $x_2$ , for (a) water (1) + butane-1,2-diol (2) (●, this work; ○, Bald et al., 1992b) and water (1) + butane-1,3-diol (2) (■, this work, □, Piekarski et al., 1995; ▽, Grineva and Zhuravlev, 1996) and (b) water (1) + butane-1,4-diol (2) (▲, this work; △, Safonova, 1980; ◆, Bald et al., 1992a; ▽, Grineva and Zhuravlev, 1996; ◇, Wang et al., 1997).

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

$x_2$	$\epsilon_r(0.1)$	$A$	$B$	$\sigma(\epsilon_r)$	$P_{\max}^a/\text{MPa}$
Water (1) + Butane-1,2-diol (2)					
0 <sup>b</sup>	78.41	0.2185	463.6	0.02	300.0
0.200	48.49	0.1631	253.5	0.01	300.0
0.400	35.62	0.1601	212.8	0.01	300.0
0.600	29.13	0.1637	204.8	0.01	300.0
0.800	25.17	0.1624	195.7	0.01	300.0
1	22.40	0.1623	187.1	0.00	300.0
Water (1) + Butane-1,3-diol (2)					
0.200	52.40	0.1521	294.1	0.00	300.0
0.400	41.34	0.1508	265.9	0.01	300.0
0.600	35.49	0.1403	242.8	0.01	300.0
0.800	31.68	0.1290	225.9	0.01	300.0
1	28.68	0.1221	221.7	0.01	300.0
Water (1) + Butane-1,4-diol (2)					
0.200	53.43	0.1566	315.0	0.01	300.0
0.400	43.36	0.1527	285.3	0.00	300.0
0.600	37.83	0.1482	277.5	0.01	200.0
0.800	33.99	0.1611	318.8	0.01	100.0
1	30.99	0.1110	221.6	0.00	40.0

<sup>a</sup> Maximum pressure applicable to estimate  $\epsilon_r(P)$  values from the values of  $\epsilon_r(0.1)$ ,  $A$ , and  $B$  by the Tait-type equation. <sup>b</sup> The data for pure water are cited from the literature (Moriyoshi et al., 1990).



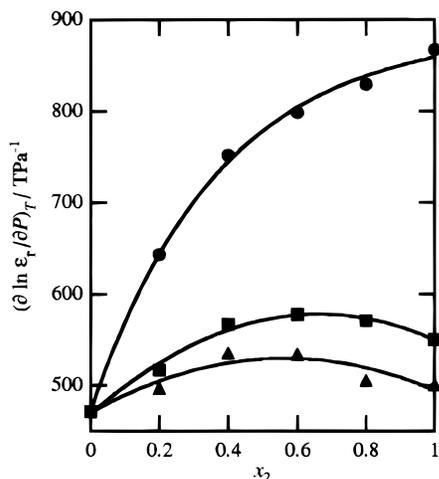
**Figure 2.** Pressure dependence of the static relative permittivities,  $\epsilon_r$ , at 298.15 K for (a) water (1) + butane-1,2-diol (2) (●), (b) water (1) + butane-1,3-diol (2) (■), and (c) water (1) + butane-1,4-diol (2) (▲). The smoothed curves are based on the values of  $\epsilon_r(0.1)$ ,  $A$ , and  $B$  given in Table 2.

$\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  values at 0.1 MPa are desired. Both parameters can be easily evaluated from  $\epsilon_r(0.1)$  and the Tait-type parameters by use of the following equations:

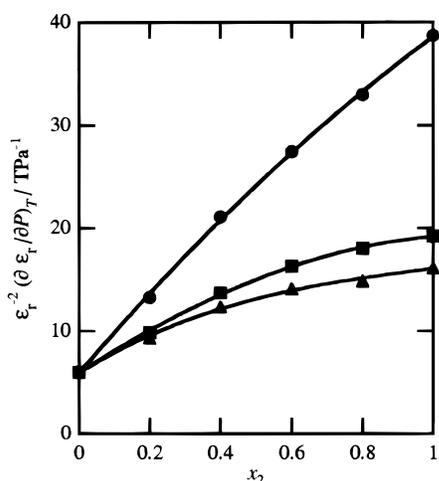
$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_T = \frac{A}{B + 0.1} \quad (2)$$

$$\epsilon_r^{-2} \left(\frac{\partial \epsilon_r}{\partial P}\right)_T = \frac{A}{\epsilon_r(0.1)(B + 0.1)} \quad (3)$$

We used  $\epsilon_r$  for  $\epsilon_r(P)$  in these equations for the sake of brevity.



**Figure 3.** Composition dependence of  $(\partial \ln \epsilon_r / \partial P)_T$  at 0.1 MPa and 298.15 K for water (1) + butane-1,2-diol (2) (●), water (1) + butane-1,3-diol (2) (■), and water (1) + butane-1,4-diol (2) (▲).



**Figure 4.** Composition dependence of  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  at 0.1 MPa and 298.15 K for water (1) + butane-1,2-diol (2) (●), water (1) + butane-1,3-diol (2) (■), and water (1) + butane-1,4-diol (2) (▲).

The composition dependences of  $(\partial \ln \epsilon_r / \partial P)_T$  at 0.1 MPa and 298.15 K for each aqueous butanediol mixture are presented in Figure 3. The  $(\partial \ln \epsilon_r / \partial P)_T$  values for water + butane-1,2-diol increase with  $x_2$ , while those for water + butane-1,3-diol and for water + butane-1,4-diol show a maximum around  $x_2 = 0.5$  and  $x_2 = 0.6$ , respectively. This maximum behavior for  $(\partial \ln \epsilon_r / \partial P)_T$  has not been found in aqueous organic mixtures studied so far; in water + 1,3-dimethyl-2-imidazolidinone, it has been observed that there was a shallow minimum in  $(\partial \ln \epsilon_r / \partial P)_T$  around  $x_2 = 0.2$ .

Figure 4 shows the  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  values at 0.1 MPa and 298.15 K for each aqueous butanediol mixture as a function of  $x_2$ . The values for each system increase with increasing the composition of organic component. Such a trend has been found in binary aqueous organic mixtures investigated so far (Moriyoshi et al., 1990; Uosaki et al., 1996, 1997).

As clarified in Figures 3 and 4, there is a resemblance between water + butane-1,3-diol and water + butane-1,4-diol not only in the composition dependence but also in the magnitude of  $(\partial \ln \epsilon_r / \partial P)_T$  and  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  values. The composition dependence of  $(\partial \ln \epsilon_r / \partial P)_T$  in water + butane-1,2-diol is different from the other two aqueous butanediol mixtures. Furthermore, the  $\epsilon_r^{-2}(\partial \epsilon_r / \partial P)_T$  values at higher mole fraction ( $x_2 \geq 0.6$ ) for water + butane-1,2-diol are about twice those obtained in other aqueous butanediols. It is considered that the different behavior of dielectric properties among aqueous butanediol mixtures results from the relative position of the OH groups in butanediols. Similar conclusions have been suggested; Piekarski et al. (1995) have reported that there was an appreciable similarity in some physical properties in water + butane-1,2-diol and water + butane-2,3-diol, and that an analogous similarity was also observed, but to a lower extent, in water + butane-1,3-diol and water + butane-1,4-diol.

### Literature Cited

- Bald, A.; Szejgis, A.; Woźnicka, J.; Józwiak, M. Physicochemical Properties of Butanediol–Water Systems. I. Densimetric, Viscosimetric and Dielectric Investigations of Butane-1,4-diol–Water Mixtures and Conductivity of Sodium Iodide in the Mixed Solvent. *J. Chem. Research (M)* **1992a**, 0923–0937.
- Bald, A.; Szejgis, A.; Woźnicka, J.; Józwiak, M. Physicochemical Properties of Butanediol – Water Systems. II. Densimetric, Viscosimetric and Dielectric Investigations of Butane-1,2-diol – Water Mixtures and Conductivity of Sodium Iodide in the Mixed Solvent. *J. Chem. Research (M)* **1992b**, 2201–2212.
- Grineva, O. V.; Zhuravlev, V. I. Densities and Dielectric Permittivities of Three Butanediols and Their Solutions with 10 mol % Water. *J. Chem. Eng. Data* **1996**, *41*, 604–607.
- Isaacs, N. I. *Liquid Phase High Pressure Chemistry*; John Wiley & Sons: Chichester, 1981.
- McDuffie, G. E.; Forbes, J. W.; Madigosky, W. M.; Von Bretzel, J. J. Density and Compressibility of Four Higher Alcohols for Pressures to 2800 kg per sq. cm. *J. Chem. Eng. Data* **1969**, *14*, 176–180.
- Moriyoshi, T.; Ishii, T.; Tamai, Y.; Tado, M. Static Dielectric Constants of Water + Ethanol and Water + 2-Methyl-2-propanol Mixtures from 0.1 to 300 MPa at 298.15 K. *J. Chem. Eng. Data* **1990**, *35*, 17–20.
- Piekarski, H.; Józwiak, M.; Woźnicka, J.; Bald, A.; Szejgis, A. Some Physicochemical Properties of Aqueous Solutions of Isomeric Butanediols. *Phys. Chem. Liq.* **1995**, *30*, 195–207.
- Safonova, L. P.; Egorova, I. V.; Krestov, G. A. Dielectric Constant of Aqueous Solutions of 1,3-Propanediol and 1,4-Butanediol at Different Temperatures. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1980**, *23*, 1563–1565 (in Russian).
- Sagal, M. W. Dielectric Relaxation in Liquid Alcohols and Diols. *J. Chem. Phys.* **1962**, *36*, 2437–2442.
- Ter Minassian, L.; Pruzan, P. High-pressure Expansivity of Materials Determined by Piezo-thermal Analysis. *J. Chem. Thermodyn.* **1977**, *9*, 375–390.
- Uosaki, Y.; Kawamura, K.; Moriyoshi, T. Static Relative Permittivities of Water + 1-Methyl-2-pyrrolidinone and Water + 1,3-Dimethyl-2-imidazolidinone Mixtures under Pressures up to 300 MPa at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1525–1528.
- Uosaki, Y.; Kitaura, S.; Moriyoshi, T. Static Relative Permittivities of Water + Acetone and Water + Dimethyl Sulfoxide under Pressures up to 300 MPa at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 580–584.
- Wang, F.; Pottel, R.; Kaatze, U. Dielectric Properties of Alkanediol/Water Mixtures. *J. Phys. Chem. B* **1997**, *101*, 922–929.

Received for review January 27, 1998. Accepted April 16, 1998.

JE9800353