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Static Dielectric Constants of Water + Ethanol and Water + 2-Methyl-2-propanol Mixtures from 0.1 to 300 MPa at 298.15 K

Takashi Moriyoshi,* Tetsuro Ishii, Yoshihisa Tamai, and Masafumi Tado

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

The static dielectric constants ϵ of water + ethanol and water + 2-methyl-2-propanol mixtures have been measured as a function of composition at 298.15 K and pressures up to 300 MPa. The measurements were carried out by means of a transformer ratio-arm bridge with a three-terminal dielectric cell placed in a pressure vessel for frequencies in the range 10–50 kHz. The uncertainty of the experimental ϵ values obtained was estimated to be within ±0.1%, and the reliability of the values was checked by comparison with available data in the literature. The results for ϵ as a function of pressure were well represented by the Tait-type equation.

Introduction

The static dielectric constant of liquids is a measure of the polarization character, and, in particular, the measurements for polar liquids provide valuable information about the local structure due to the molecular orientation and interactions (*1*). In addition, the dielectric data at high pressures for pure liquids and the mixtures as a solvent are required to estimate the volume change arising from electrostatic ion–solvent interactions, based on the electrostriction theory for ionic solutions (*2*) and the Debye–Hückel limiting-law parameters for volumes and other thermodynamic properties (*3*).

Although the dielectric constants as a function of pressure have so far been measured on various liquids, there are few reliable experimental data for polar liquids and data are extremely scarce for binary mixtures of water with liquids (*4*, *5*).

The present study was designed to measure precise static dielectric constants as functions of composition and pressure for aqueous alcohol mixtures. In this paper, we describe the measuring bridge and dielectric cell used and present the measurements for water + ethanol and water + 2-methyl-2-propanol mixtures from 0.1 to 300 MPa at 298.15 K. Measurements at the same temperature have been made previously at 0.1 MPa for the present two mixtures (*6*–*13*) and at pressures up to 300 MPa for the pure liquids (water and ethanol) (*14*–*17*).

Experimental Section

***Materials*.** The best grade alcohols (Wako Chemical Co.) were dried by refluxing over CaO and then were distilled twice. Ethanol was further purified by the Lund–Bjerrum magnesium method and then redistilled. Deionized water was distilled from alkaline $KMnO_4$ and redistilled. The purities of the materials were checked by measuring their refractive indices; these agreed to within 0.0001 with those in the literature (*18*). The mixtures were prepared by weighing the pure liquids; the compositions were controlled to ±0.0001 mole fraction of alcohol at the nominal values.

***Apparatus and Procedure*.** The bridge and cell for measuring the dielectric constant of polar liquids and the mixtures at high pressures have been newly designed and constructed. Figure 1 shows the circuit diagram of a transformer ratio-arm bridge used, which is essentially the same type as that reported by Cole and Gross (*19*). A precision capacitor (Yokogawa–Hewlett-Packard, Ltd., Model CDS-500), modified to the three-terminal type, was calibrated against a capacitance bridge (General Radio Type 1615-A); it is capable of measuring up to 500 pF with a precision of 0.001 pF. A modified oscillator (Ando Electric Co., Ltd., Model WBG-9) and a tuned detector (Ando Model BDA-9) were used in conjunction with the bridge.

Details of the dielectric cell are illustrated in Figure 2. The cell was of a three-terminal type and consisted of a concentric rod (the low-potential electrode), cylinder (the high-potential electrode), and sleeve (the guard electrode), which are made of Type 304 stainless steel. The low-potential electrode, 12 mm in diameter and 13 mm in length, is separated by 1 mm from the inner wall of the high-potential electrode, and the lower end of the former electrode is remote more than 20 mm from the bottom surface of the latter electrode; hence, the cell can be substantially regarded as a coaxial cylinder-type capacitor in which any end correction is negligible. The electrodes were electrically insulated with glass fiber reinforced Teflon. A thin-walled Teflon case containing the dielectric cell served as a diaphragm separating the sample liquid from the pressure-transmitting fluid (kerosene) and responding sensitively to pressure when being compressed. Figure 3 shows the manner in which the assembled cell is installed in the pressure vessel (about 220-cm^3 capacity, 12-cm diameter, and 29.5-cm length), built of a Ni–Cr–Mo steel. The electrodes were connected to two terminals extending into the closure head of the pressure vessel, with a BNC connector for the low-potential electrode and a piece of shielded wire for the high-potential electrode. The terminals consist of steel cones that are electrically insulated with conical sleeves made of pyrophyllite from the seat; a thin layer of epoxy resin was used on the mating surfaces to make the initial seal. The closure head was sealed by means of a Bridgman packing with use of Teflon and copper rings. After assembly, the pressure vessel was immersed in a thermostat bath controlled to 298.15 ± 0.01 K. Pressure was generated by means of a high-pressure screw pump and measured with an accuracy of 0.35 MPa with a Heise Bourdon gauge that was calibrated against a pressure balance.

The lead capacitance C_L between the bridge and cell is given by a difference of the capacitances measured, when the cell is plugged into the bridge terminals with and without two coaxial lead wires of the closure head; the capacitance determined was 0.006 pF. The cell constant C_0 at atmospheric pressure (0.1 MPa) was determined according to the manner described below, from capacitance measurements of the cell filled with dry air (ϵ = 1.000 527) (*20*) at 50 kHz, because in this case no frequency dependence of the capacitances was observed; the values of C_0 for the two cells used in the present study were about 3.9 and 4.3 pF.

The electric capacitance C_x of the cell containing sample liquid was measured in the frequency range 10–50 kHz; the values of C_x obtained were plotted against the reciprocal frequency f^{-1} and extrapolated according to a linear relationship to infinite frequency to eliminate the effect of electrode polarization. In the graphs for any of the liquids studied, good linear relationship was obtained over the frequency range used. The most serious sources of error for the measured capacitances are the capacitances associated with the resistors used in the bridge to balance the conductance of the liquids. Although the magnitude of this correction was checked by measuring ca-

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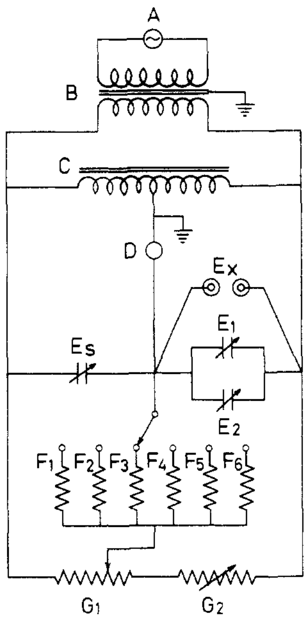

Figure 1. Schematic diagram of bridge circuit: A, oscillator; B, coupling transformer; C, ratio-arm transformer; D, detector; E_s, standard precision capacitor (500 pF); E_x, measuring cell; E_1 and E_2, zero balance capacitors (10 pF and 200 pF); F_1–F_6, metal film resistors (1, 2, 5, 10, and 20 kΩ, and 1 MΩ); G_1 and G_2, potentiometers (100 Ω).

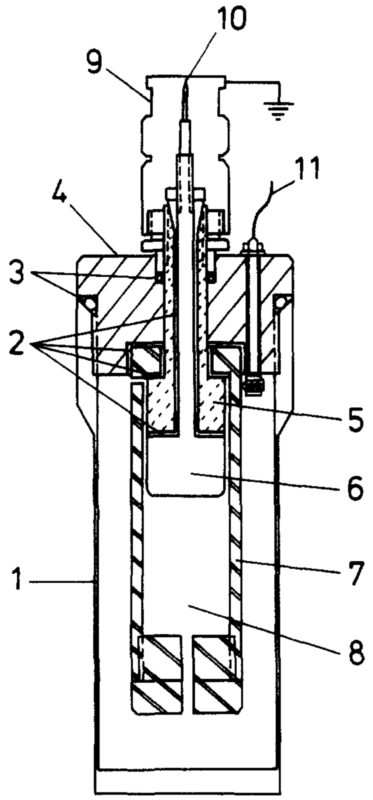

Figure 2. Dielectric cell: 1, Teflon case; 2, insulator (Teflon); 3, O-ring; 4, plug; 5, guard electrode; 6, low-potential electrode; 7, high-potential electrode; 8, sample liquid; 9, BNC connector; 10 and 11, connecting terminals.

pacitances for the cell filled with samples of water with different conductances up to $1 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, the variation of the values obtained for the extrapolated capacitance C_x^∞ was found to be within an experimental error of ±0.08%. Therefore, the value of C_x^∞ determined for a sample liquid was used without any correction, together with those values of C_0 and C_L to calculate the dielectric constant ϵ of the liquid from the equation

$$\epsilon = (C_x^\infty - C_f - C_L)/C_0 \qquad (1)$$

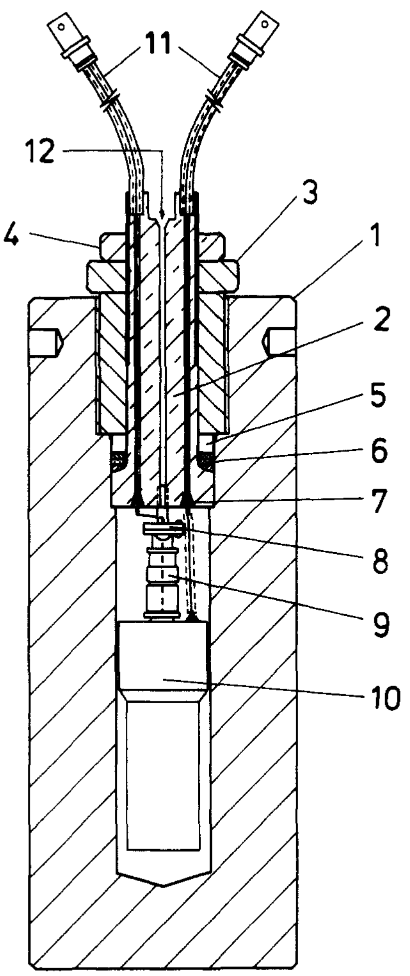

Figure 3. Pressure vessel with a dielectric cell: 1, pressure vessel; 2, closure; 3, nut; 4, closure nut; 5, ring; 6, packing; 7, cone; 8, holder; 9, BNC connector; 10, dielectric cell set in a Teflon case; 11, lead wire; 12, inlet of the pressure-transmitting fluid.

where C_f is the capacitance of the bridge balanced when no cell is connected. The cell constant $C_0(P)$ at any pressure P was calculated from the value $C_0(0.1)$ at 0.1 MPa by using the equation

$$C_0(P) = [C_0(0.1)](1 - k/3) \qquad (2)$$

where k is the compressibility of stainless steel, given by $k = 6.124 \times 10^{-6}\ P$ (*21*) with P in MPa. Measurements were made at 298.15 K and nine pressures up to 300 MPa. The uncertainty of the measurements obtained for ϵ was estimated to be within ±0.1%.

Results and Discussion

Experimental values of ϵ as a function of pressure for water + ethanol and water + 2-methyl-2-propanol mixtures are summarized in Table I, where X_2 is the mole fraction of the alcohol. The measurements for the former were made over the whole range of composition, while those for the latter were limited to the mixtures up to 0.2 mole fraction of 2-methyl-2-propanol. The data listed are the mean values obtained from measurements made more than two times on each of the pure liquids and the mixtures. The results at 0.1 MPa for the two mixtures are plotted against X_2 in Figures 4 and 5 together with values of other workers for comparison. For water + ethanol, the mean deviations from the values of Wyman (*6*), Graffunder and Heyman (*7*), Åkerlöf (*8*), Martin and Brown (*9*), and Heurou and Guerillot (*10*) are −0.17, 0.41, −0.07, −0.06, and 0.07 in ϵ, respectively. Our values for water + 2-methyl-2-propanol differ by −1.6, −0.46, 0.03, and −0.04 in ϵ on the average, respectively, from those of Åkerlöf (*8*), Brown and Ives (*11*),

Table I. Experimental Dielectric Constants, ϵ, of Two Water + Alcohol Mixtures as a Function of Pressure at 298.15 K

	ϵ as a function of P (MPa)								
X_2	0.1	20	60	100	140	180	220	260	300
				Water (1) + Ethanol (2)					
0	78.41	79.15	80.57	81.90	83.19	84.46	85.68	86.83	88.02
0.05	72.07	72.76	74.00	75.16	76.30	77.43	78.53	79.58	80.56
0.10	66.26	66.93	68.18	69.31	70.35	71.38	72.35	73.27	74.19
0.15	60.89	61.64	62.91	64.07	65.14	66.18	67.13	68.04	68.89
0.20	55.81	56.61	57.93	59.17	60.26	61.29	62.26	63.18	64.07
0.30	47.48	48.33	49.71	50.91	52.00	53.03	53.97	54.87	55.71
0.40	41.28	42.06	43.41	44.57	45.59	46.55	47.46	48.21	48.97
0.60	33.14	33.88	35.10	36.11	37.02	37.87	38.63	39.34	40.01
0.80	28.17	28.87	29.94	30.82	31.59	32.27	32.90	33.48	34.04
1	24.36	24.90	25.74	26.46	27.07	27.61	28.10	28.56	28.97
				Water (1) + 2-Methyl-2-propanol (2)					
0.02	73.14	73.78	75.17	76.40	77.57	78.67	79.80	80.82	81.80
0.04	68.32	68.97	70.25	71.44	72.58	73.65	74.66	75.68	76.63
0.07	60.70	61.54	63.10	64.44	65.64	66.78	67.79	68.77	69.67
0.10	53.59	54.54	56.29	57.65	59.10	60.19	61.41	62.34	63.44
0.15	43.84	44.87	46.55	48.10	49.30	50.63	51.61	52.80	53.64
0.20	36.38	37.46	39.12	40.50	41.75	42.86	43.90	44.84	45.74

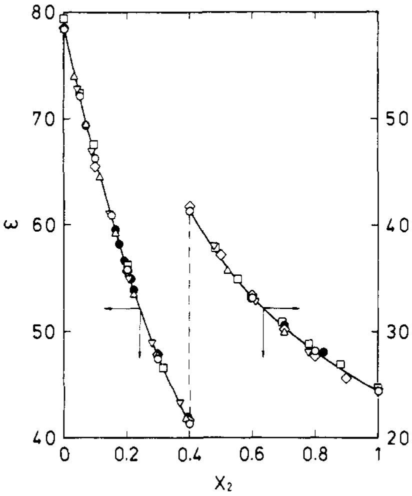

Figure 4. Dielectric constants as a function of composition for water (1) + ethanol (2) mixtures at 298.15 K and 0.1 MPa: ○, this work; △, ref 6; □, ref 7; ▽, ref 8; ◇, ref 9; ●, ref 10.

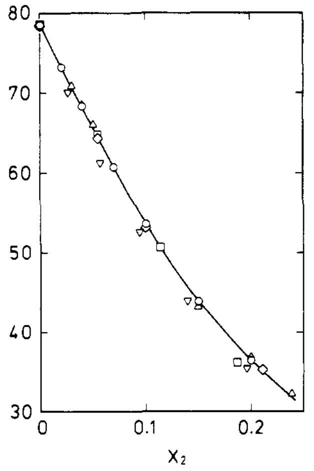

Figure 5. Dielectric constants as a function of composition for water (1) + 2-methyl-2-propanol (2) mixtures at 298.15 K and 0.1 MPa: ○, this work; ▽, ref 8; □, ref 11; △, ref 12; ◇, ref 13.

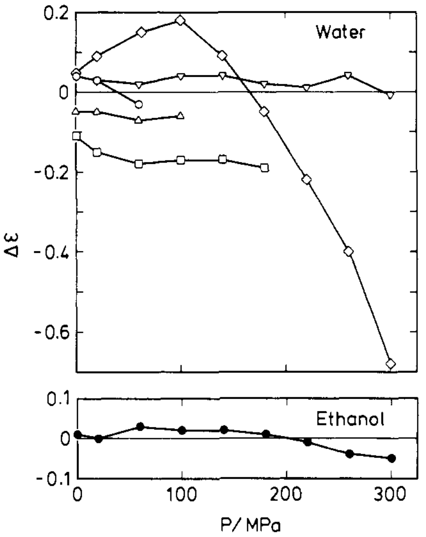

Figure 6. Comparison of our values with literature results for pure water and ethanol at 298.15 K: ○, ref 5; △, ref 14; □, ref 15; ▽, ref 16; ◇, ref 22; ●, ref 17.

Broadwater and Kay (*12*), and Winkelmann (*13*); the agreement between the experimental values and literature ones except for some data is generally good for both mixtures. Composition dependences of ϵ similar to those in Figures 4 and 5 were observed at pressures above 0.1 MPa for each of the mixtures; the values of ϵ increased with pressure, and the magnitude of the increase diminished as the mole fraction of alcohol increased.

The values obtained for pure ethanol and pure water are compared with those of earlier workers in Figure 6, where the differences between the literature values ϵ(lit.) and ours ϵ(obs) at each pressure, given by

$$\Delta\epsilon = \epsilon(\text{lit.}) - \epsilon(\text{obs}) \qquad (3)$$

are plotted against pressure. The values of ϵ(lit.) were calculated from the empirical equations presented in the literature. For water, the mean deviations from the values of Lührs and Schwitzgebel (*5*) up to 60 MPa, of Owen et al. (*14*) up to 100 MPa, and of Dunn and Stokes (*15*) up to 180 MPa are 0.02, -0.06, and -0.16 in ϵ, respectively. Recent data reported by Srinivasan and Kay for water (*16*) and ethanol (*17*) are consistent with our values to within maximum deviations of 0.04 and -0.05 in ϵ, respectively. An equation for ϵ of water and steam developed by Uematsu and Franck (*22*), based on selected literature data, gives calculated values that exhibit increasingly large negative deviations from our results for pressures above 150 MPa.

Experimental values of ϵ as a function of pressure at each composition were fitted by the method of least squares to the Tait-type equation

$$1 - \epsilon(0.1)/\epsilon(P) = A \ln [(B + P)/(B + 0.1)] \qquad (4)$$

Table II. Values of Constants in Equation 4 and Standard Deviations $\sigma(\epsilon)$ at 298.15 K

X_2	A	B/MPa	$\sigma(\epsilon)$
	Water (1) + Ethanol (2)		
0	0.2185	463.6	0.02
0.05	0.2109	462.0	0.02
0.10	0.1608	319.0	0.02
0.15	0.1444	243.0	0.02
0.20	0.1438	207.6	0.03
0.30	0.1414	163.4	0.04
0.40	0.1373	140.1	0.02
0.60	0.1389	123.1	0.02
0.80	0.1227	98.1	0.03
1	0.1154	101.0	0.01
	Water (1) + 2-Methyl-2-propanol (2)		
0.02	0.1808	376.1	0.03
0.04	0.1825	369.5	0.01
0.07	0.1309	179.2	0.01
0.10	0.1436	155.0	0.06
0.15	0.1508	126.6	0.06
0.02	0.1466	99.0	0.04

where $\epsilon(0.1)$ and $\epsilon(P)$ are the dielectric constants of pure liquid or mixture studied at 0.1 MPa and the experimental pressure P, respectively; A and B are empirical constants. The values of A and B from the fits are listed in Table II together with the standard deviation $\sigma(\epsilon)$. The maximum value of $\sigma(\epsilon)$ is 0.06, and the results in the table indicate that eq 4 can represent most of the observed values within the limits of experimental error for ϵ.

The pressure dependence of ϵ for a solvent is essential for evaluating the volume effect known as an electrostriction of the solvent resulting from ion–solvent interactions in the ionic solution. The Drude–Nernst equation (*23*) expressed by

$$\Delta V_{\mathrm{el}} = -\frac{Nz^2e^2}{2r\epsilon^2}\left\{\frac{\partial\epsilon}{\partial P}\right\}_T \qquad (5)$$

provides the volume change ΔV_{el} of the solvent, i.e., the electrostriction volume, when 1 mol of ions of radius r and charge ze are transferred from a vacuum into a solvent of dielectric constant ϵ. According to eq 5, the electrostriction for a given ion should increase in proportion to the value of $\epsilon^{-2}(\partial\epsilon/\partial P)_T$, which depends on the nature of the solvent. The values of $\epsilon^{-2}(\partial\epsilon/\partial P)_T$ for the mixtures studied can be calculated from the values of A and B in Table II. The values at 0.1 MPa are plotted against X_2 in Figure 7 together with those from the data reported for pure liquids. The value of 6.01 $\mathrm{TPa^{-1}}$ found for water is equal to the values of Owen et al. (*14*) and of Lührs and Schwitzgebel (*5*); furthermore, it is in good agreement with the values of 6.00 $\mathrm{TPa^{-1}}$ of Srinivasan and Kay (*16*) and of 5.90 $\mathrm{TPa^{-1}}$ of Dunn and Stokes (*15*). The value for ethanol is 46.9 $\mathrm{TPa^{-1}}$, comparable to 48.2 $\mathrm{TPa^{-1}}$ from the results of Srinivasan and Kay (*17*). The composition dependence of $\epsilon^{-2}(\partial\epsilon/\partial P)_T$ for the mixtures depends strongly on the nature of the alcohol and exhibits a sigmoid curve for water + ethanol, suggesting that the composition dependence of the electrostriction in the mixtures is complicated.

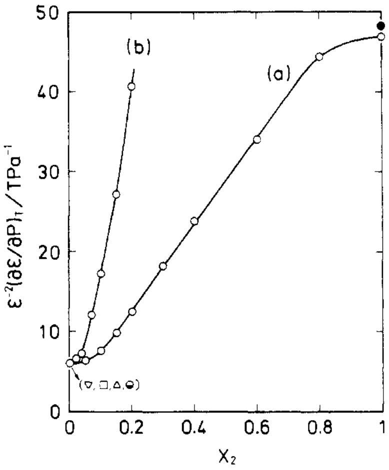

Figure 7. Composition dependence of $\epsilon^{-2}(\partial\epsilon/\partial P)_T$ at 298.15 K and 0.1 MPa: (a) water + ethanol; (b) water + 2-methyl-2-propanol. Key: ○, this work; ⊖, ref 5; △, ref 14; □, ref 15; ▽, ref 16; ●, ref 17.

Glossary

A,B	constants of eq 4
C	electric capacitance
C_0	cell constant
e	electronic charge
f	frequency
k	compressibility
N	Avogadro's number
P	pressure
r	ionic radius
T	temperature
ΔV_{el}	electrostriction volume
X	mole fraction
z	valency of ion

Greek Letters

ϵ	static dielectric constant
$\sigma(\epsilon)$	standard deviations, eq 4

Subscripts

1	water
2	alcohol

Registry No. Water, 7732-18-5; ethanol, 64-17-5; 2-methyl-2-propanol, 75-65-0.

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