

Effect of Pressure on the Static Relative Permittivities of Alkan-1-ols at 298.15 K

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Static relative permittivities ϵ_r were measured for alkan-1-ols from methanol to octan-1-ol under pressures up to 300 MPa at 298.15 K. A Tait-type equation was used to represent pressure P dependence of ϵ_r values for each alkan-1-ol, and the Tait-type parameters A and B were determined. By using the static relative permittivity at $P_0 = 0.1$ MPa $\epsilon_r(P_0)$ and the Tait-type parameters, dielectric parameters at P_0 [$(\partial\epsilon_r/\partial P)_{T,P_0}$, $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$] for alkan-1-ols were calculated at 298.15 K. Values of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ for each alkan-1-ol from methanol to heptan-1-ol were correlated with the temperature T by a combination of the present values at 298.15 K and those evaluated from $\epsilon_r(P)$ data at various temperatures from the literature. Effect of carbon number n in alkan-1-ol on the dielectric parameters was also examined at 298.15 K. The $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values in this work were compared with those calculated from some relationships between $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and the isothermal compressibility at P_0 [κ_{T,P_0}].

Introduction

The knowledge of dielectric parameters such as $(\partial \epsilon_r/\partial P)_T$ and $(\partial \ln \epsilon_r/\partial P)_T$ values of polar solvents at 0.1 MPa and 298.15 K is required to analyze some thermophysical properties of electrolytes in polar solvents.¹ Since information on pressure P dependence of the static relative permittivities ϵ_r is needed to obtain these dielectric parameters, measurements of ϵ_r under high pressure should be carried out. Although many studies on ϵ_r measurements of polar solvents under high pressure are found in the literature,^{2–11} most of them have mainly focused on the effect of pressure on the dielectric polarization or the structure of liquids from the Kirkwood correlation factor; the correlation factor gives useful information on the local structure of liquids.¹² However, systematic studies on the dielectric parameters of polar liquids have not been well-conducted.

In previous papers,^{13–15} we have so far measured ϵ_r values of some monohydric alkanols: alkan-2-ols,¹³ 2-methylalkan-1-ols,¹⁴ and 2-ethylalkan-1-ols,¹⁵ under high pressures up to 300 MPa at 298.15 K. It has been demonstrated that pressure dependence of ϵ_r for each alkanol was well-represented by a Tait-type equation. For alkan-2-ols, pressure dependence of the Kirkwood correlation factor for each alkan-2-ol has been studied to clarify the effect of the size of alkyl substituent on the local structure of liquids. Effect of carbon number on ϵ_r at various pressures has been analyzed for 2-methylalkan-1-ols and 2-ethylalkan-1-ols. The dielectric parameters at $P_0 = 0.1$ MPa and 298.15 K [$(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$] have been also determined for 2-ethylalkan-1-ols by making use of the values of the Tait-type parameters and the relative permittivity at P_0 [$\epsilon_r(P_0)$].

In continuation of our work on ϵ_r measurements for alkanols, the present paper reports ϵ_r values for alkan-1-ols from methanol to octan-1-ol under high pressures up to 300 MPa at 298.15 K. Dielectric parameters at P_0 [$(\partial\epsilon_r/\partial P)_{T,P_0}$, $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$] are evaluated for each alkan-1-ol at 298.15

K. Correlation equations for $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ with temperature T are given for each alkan-1-ol using the present values at 298.15 K and the evaluated ones at various temperatures from the literature. The effect of carbon number n in alkan-1-ol on $(\partial\epsilon_r/\partial P)_{T,P_0}$, $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ at 298.15 K is examined, and the correlation equations are given. In addition, the $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ values determined in this work are compared with those calculated from some relationships between $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and the isothermal compressibility at P_0 [κ_{T,P_0}].

Experimental Section

Methanol (>99.8 %), ethanol (>99.5 %), propan-1-ol (>99.5 %), butan-1-ol (>99.0 %), pentan-1-ol (>98.5 %), hexan-1-ol (>98.0 %), heptan-1-ol (>98.0 %), and octan-1-ol (98.0 %) were purchased from Kanto Chemical Co., Inc. Methanol, ethanol, and propan-1-ol were refluxed over Mg activated by I_2 for several hours and then fractionally distilled twice. Butan-1-ol and pentan-1-ol were refluxed over CaH_2 for a few hours and then fractionally distilled. Other alkan-1-ols were refluxed over CaH_2 for several hours and then distilled in a stream of N_2 at reduced pressure. The purity of each alkan-1-ol was analyzed by gas chromatography. Gas chromatographic analysis showed that the major peak areas are >99.9 % for methanol, ethanol, and propan-1-ol; >99.7 % for butan-1-ol and pentan-1-ol; and >99.3 % for hexan-1-ol, heptan-1-ol, and octan-1-ol. The refractive index n_D at atmospheric pressure was measured with an Abbe refractometer thermostated at (298.15 ± 0.05) K. The uncertainty in n_D in the present work is less than 0.0001.

Dielectric cells of a three-terminal capacitor having the cell constant of about 3.9 pF or 4.3 pF were used to measure the capacitance of alkan-1-ols. A high-pressure vessel with the dielectric cell was immersed in a thermostated water bath controlled at (298.15 ± 0.01) K. For pressure measurement, a Bourdon gauge was used with an uncertainty of ± 0.1 MPa. Details of the apparatus for capacitance measurements have been reported in a previous paper.¹⁶ The uncertainty in ϵ_r is estimated to be better than 0.1 %. The ϵ_r measurements were carried out

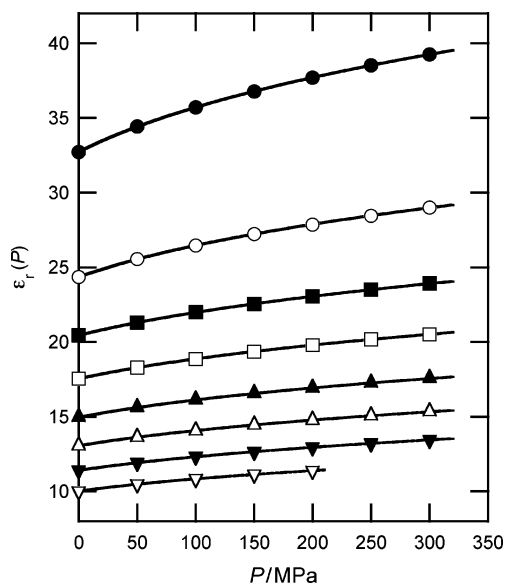
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Table 1. Refractive Indices n_D and Static Relative Permittivities $\epsilon_r(P_0)$ for Alkan-1-ols at 0.1 MPa and 298.15 K

alkan-1-ol	n_D			$\epsilon_r(P_0)$				
	this work	lit.		this work	lit.			
methanol	1.3266	1.32652, ¹⁷	1.3268, ¹⁸	32.72	32.65, ⁹	32.62, ²²	32.64 ¹⁹	
ethanol	1.3596	1.35941, ¹⁷	1.3595, ¹⁸	24.35	24.37, ⁹	24.33, ²²	24.55 ¹⁹	
propan-1-ol	1.3833	1.38370, ¹⁷	1.3834 ¹⁸	20.45	20.33, ²³	20.34, ⁹	20.44 ²²	
butan-1-ol	1.3972	1.3971, ^{16,17}	1.3973 ¹⁸	17.54	17.43, ²³	17.54, ²²	17.10 ¹⁹	
pentan-1-ol	1.4078	1.4080, ^{17,18}	1.40767, ²⁰	14.96	15.13, ²³	15.03, ²²	15.04, ²⁰	15.558 ²¹
hexan-1-ol	1.4157	1.4161, ¹⁷	1.4160 ^{18,21}	13.06	13.28, ²³	13.325 ²¹		
heptan-1-ol	1.4219	1.4223, ¹⁷	1.4227, ¹⁸	11.41	11.793 ²¹			
octan-1-ol	1.4275	1.4276, ¹⁷	1.4284, ¹⁹	10.01	10.02, ¹⁹	9.858 ²¹		

Table 2. Static Relative Permittivities $\epsilon_r(P)$ for Alkan-1-ols as a Function of Pressure P at 298.15 K

alkan-1-ol	$\epsilon_r(P)$ at P/MPa						
	0.1	50	100	150	200	250	300
methanol	32.72	34.43	35.70	36.77	37.70	38.52	39.25
ethanol	24.35	25.56	26.46	27.22	27.86	28.45	29.00
propan-1-ol	20.45	21.30	21.98	22.55	23.05	23.50	23.91
butan-1-ol	17.54	18.29	18.87	19.36	19.79	20.17	20.52
pentan-1-ol	14.96	15.62	16.12	16.55	16.92	17.25	17.56
hexan-1-ol	13.06	13.63	14.07	14.45	14.77	15.06	15.33
heptan-1-ol	11.41	11.92	12.32	12.65	12.95	13.21	13.45
octan-1-ol	10.01	10.48	10.84	11.13	11.39		

**Figure 1.** Pressure dependence of the static relative permittivities ϵ_r for alkan-1-ols at 298.15 K: ●, methanol; ○, ethanol; ■, propan-1-ol; □, butan-1-ol; ▲, pentan-1-ol; △, hexan-1-ol; ▼, heptan-1-ol; ▽, octan-1-ol. The smoothed curves are based on the values of $\epsilon_r(P_0)$, A , and B listed in Table 3.

more than three times for each alkan-1-ol, and the ϵ_r values thus determined were reproduced to within $\pm 0.08\%$.

Results and Discussion

The measured refractive indices n_D and static relative permittivities at $P_0 = 0.1$ MPa [$\epsilon_r(P_0)$] at 298.15 K are listed in Table 1, where the literature values^{9,17–23} are also tabulated. Our n_D values for alkan-1-ols agree with the literature ones. The present $\epsilon_r(P_0)$ values for methanol, ethanol, propan-1-ol, butan-1-ol, and octan-1-ol are generally in good agreement with those found in the literature, but the values for pentan-1-ol, hexan-1-ol, and heptan-1-ol are a few percent smaller than those reported in the literature.

The ϵ_r values determined for alkan-1-ols as a function of pressure at 298.15 K are listed in Table 2 and illustrated in Figure 1. Alkan-1-ols except octan-1-ol at 298.15 K were in

the liquid state even at 300 MPa. After the capacitance measurement of octan-1-ol at 200 MPa, pressure was increased with a rate of ca. 3 MPa·min⁻¹ using a high-pressure hand pump up to 225 MPa, and then a sudden drop in pressure was observed, accompanied by a decrease in capacitance. About 30 min later, the gauge showed a pressure of around 210 MPa, and there was no further change in pressure with time. The fact that the capacitance of octan-1-ol was very low at this pressure strongly indicates that octan-1-ol was still in the solid state. An averaged freezing pressure P_f from three dielectric measurements for octan-1-ol under high pressure at 298.15 K is found to be (210 ± 2) MPa, while the freezing pressure at 298.15 K extrapolated from the results of solid–liquid equilibrium study in the temperature range of (263.2 to 293.2) K by Yang et al.²⁴ is determined to be (211.3 ± 0.3) MPa. The agreement between two P_f values is excellent.

As found in Table 2 and Figure 1, $(\partial\epsilon_r/\partial P)_T$ becomes smaller with pressure in any alkan-1-ol. Pressure dependence of ϵ_r for each alkan-1-ol is well-correlated with the Tait-type equation, usually referred to as the Owen–Brinkley equation:²⁵

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

In this equation, $\epsilon_r(P)$ is the static relative permittivity at the pressure P . By using a nonweighted least-squares method, the Tait-type parameters A and B were determined for each alkan-1-ol. Table 3 summarizes $\epsilon_r(P_0)$, A , and B values thus determined and the standard deviations $\sigma(\epsilon_r)$ of the fit by eq 1. The corresponding values for some alkan-1-ols at various temperatures reported or calculated from the $\epsilon_r(P)$ data in the literature^{2–10,16} are also given in Table 3. Since the $\sigma(\epsilon_r)$ values in this work are less than 0.01, ϵ_r values for alkan-1-ols at any pressure up to the maximum pressure P_{\max} can be interpolated with a good accuracy using $\epsilon_r(P_0)$, A , and B values with the aid of eq 1. The A value for alkan-1-ols from methanol to octan-1-ol measured in this work is in the range of (0.109 to 0.119), while that for alkan-2-ols,¹³ 2-methylalkan-1-ols,¹⁴ and 2-ethylalkan-1-ols¹⁵ (except for octan-2-ol and 2-ethylhexan-1-ol) has been reported to be in the range of (0.102 to 0.132). Hence it is considered that the A value for alkanols is not so much variable with the chain length in alkan-2-ols and the methyl or ethyl substituent in alkan-1-ols.

Values of dielectric parameters at 0.1 MPa [$(\partial\epsilon_r/\partial P)_{T,P_0}$, $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$, and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$] are useful quantities for analyzing the thermophysical data in electrolyte solutions and the activation volumes determined from pressure dependence of rate constants in inorganic chemical reactions.^{1,26} These dielectric parameters are easily evaluated from the following relations using $\epsilon_r(P_0)$ and the Tait-type parameters:

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

Table 3. Static Relative Permittivities at 0.1 MPa $\epsilon_r(P_0)$, Tait-type Parameters A and B , and Standard Deviation $\sigma(\epsilon_r)$ of Fit by Equation 1 at 298.15 K

alkan-1-ol	T/K	$\epsilon_r(P_0)$	A	B/MPa	$\sigma(\epsilon_r)$	$P_{\text{max}}^a/\text{MPa}$	reference	
methanol	283.15	35.70	0.11698 ^b	107.74 ^b	0.03	300.0	Srinivasan and Kay ⁹	
	293.15	33.60	0.1109	94.3	0.01	182.4	Hartmann et al. ⁵	
	293.15	33.79	0.1352	132.1	0.02	294.2	Kyropoulos ²	
	298.15	32.72	0.1175	96.1	0.01	300.0	this work	
	298.15	32.65	0.11486 ^b	93.43 ^b	0.02	300.0	Srinivasan and Kay ⁹	
	308.15	30.83	0.1032	76.2	0.01	182.4	Hartmann et al. ⁵	
	313.15	29.85	0.11223 ^b	80.12 ^b	0.01	300.0	Srinivasan and Kay ⁹	
	323.15	28.24	0.1037	67.4	0.01	182.4	Hartmann et al. ⁵	
	ethanol	273.15	27.8	0.1384	219.9	0.04	1215.9	Danforth ³
		283.15	26.78	0.10965 ^b	107.01 ^b	0.01	300.0	Srinivasan and Kay ⁹
293.15		25.71	0.1277	140.5	0.03	294.2	Kyropoulos ²	
298.15		24.35	0.1158	100.7	0.01	300.0	this work	
298.15		24.37	0.10916 ^b	92.80 ^b	0.01	300.0	Srinivasan and Kay ⁹	
298.15		24.36	0.1154	101.0	0.01	300.0	Moriyoshi et al. ¹⁶	
303.15		23.2	0.1290	118.3	0.12	1215.9	Danforth ³	
303.15		23.73	0.09798	78.3	0.02	182.4	Hartmann et al. ⁶	
313.15		22.15	0.12111 ^b	87.92 ^b	0.02	300.0	Srinivasan and Kay ⁹	
323.15		20.84	0.09657	59.3	0.03	182.4	Hartmann et al. ⁶	
propan-1-ol	208.0	37.42	0.1068	234.7	0.00	150.0	Chen et al. ⁷	
	216.0	35.36	0.1012	245.9	0.01	200.0	Chen et al. ⁷	
	224.8	33.22	0.1231	267.3	0.02	250.0	Chen et al. ⁷	
	244.5	29.22	0.0969	152.8	0.02	300.0	Chen et al. ⁷	
	273.1	24.21	0.1240	177.6	0.02	300.0	Chen et al. ⁷	
	283.15	22.49	0.10607 ^b	126.41 ^b	0.01	300.0	Srinivasan and Kay ⁹	
	298.15	20.45	0.1177	124.0	0.01	300.0	this work	
	298.15	20.34	0.10687 ^b	110.42 ^b	0.01	300.0	Srinivasan and Kay ⁹	
	303.15	19.70	0.1128	109.5	0.03	300.0	Chen et al. ⁷	
	313.15	18.43	0.10912 ^b	92.93 ^b	0.01	300.0	Srinivasan and Kay ⁹	
butan-1-ol	361.3	12.06	0.1733	121.8	0.06	300.0	Chen et al. ⁷	
	287.35	18.50	0.7186	719.9	0.00	20.44	Harris et al. ⁴	
	298.15	17.54	0.1138	116.3	0.00	300.0	this work	
	300.15	16.84	0.1463	144.9	0.01	18.16	Harris et al. ⁴	
	313.15	15.36	0.1347	107.1	0.01	20.91	Harris et al. ⁴	
pentan-1-ol	293.15	15.37 ^c	0.1126 ^c	111.1 ^c	0.02	392.3	Bennett et al. ⁸	
	298.15	14.96	0.1145	113.8	0.01	300.0	this work	
	298.15	14.76 ^c	0.1143 ^c	108.4 ^c	0.02	392.3	Bennett et al. ⁸	
	303.15	14.15 ^c	0.1158 ^c	105.5 ^c	0.01	392.3	Bennett et al. ⁸	
	313.15	12.93 ^c	0.1185 ^c	98.5 ^c	0.00	392.3	Bennett et al. ⁸	
	323.15	11.72 ^c	0.1211 ^c	91.1 ^c	0.01	392.3	Bennett et al. ⁸	
hexan-1-ol	298.15	13.06	0.1156	115.6	0.00	300.0	this work	
	303.15	12.90	0.1811	334.9	0.01	405.3	Danforth ³	
	348.15	8.55	0.09037	65.8	0.03	810.6	Danforth ³	
heptan-1-ol	262.6	15.22	0.07038	92.9	0.00	150.0	Vij et al. ¹⁰	
	272.8	14.125	0.08744	117.0	0.01	250.0	Vij et al. ¹⁰	
	283.0	13.12	0.1836	324.7	0.02	350.0	Vij et al. ¹⁰	
	293.2	11.906	0.1204	127.7	0.02	350.0	Vij et al. ¹⁰	
	298.15	11.41	0.1187	116.0	0.01	300.0	this work	
	298.15	11.35 ^d	0.1082 ^d	91.7 ^d	0.03	350.0	Vij et al. ¹⁰	
	323.2	9.07	0.1262	86.6	0.02	350.0	Vij et al. ¹⁰	
	348.6	7.14	0.1561	91.5	0.03	350.0	Vij et al. ¹⁰	
373.8	5.75	0.1500	66.7	0.02	300.0	Vij et al. ¹⁰		
octan-1-ol	298.15	10.01	0.1091	98.2	0.01	200.0	this work	

^a Maximum pressure applicable to calculate $\epsilon_r(P)$ values from the values of $\epsilon_r(P_0)$, A , and B by the Tait-type equation. ^b These values are taken from ref 9. ^c These values are based on the evaluated $\epsilon_r(P)$ values from an empirical equation in the temperature range of 293.15 K to 323.15 K.⁸ ^d These values are based on the evaluated $\epsilon_r(P)$ values from a cubic spline fit of $\epsilon_r(P)$ at other temperatures reported by Vij et al.¹⁰

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T,P_0} = \frac{A}{B + P_0} \quad (3)$$

$$\epsilon_r(P_0)^{-2} \left(\frac{\partial \epsilon_r}{\partial P}\right)_{T,P_0} = \frac{A}{\epsilon_r(P_0)(B + P_0)} \quad (4)$$

The $(\partial \epsilon_r / \partial P)_{T,P_0}$, $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$, and $\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T,P_0}$ values thus obtained for alkan-1-ols at 298.15 K are listed in Table 4 together with the reported isothermal compressibility at P_0 and 298.15 K [κ_{T,P_0}].²⁷

To check the reliability of our $\epsilon_r(P)$ data for each alkan-1-ol at 298.15 K, it is necessary not only to compare $\epsilon_r(P)$ data at each pressure with those from the literature but also to check the temperature dependence of $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T,P_0}$. It has been reported that these two dielectric parameters

for acetone at 298.15 K and other temperatures were represented well with a polynomial expression of temperature.²⁸ The differences $\Delta \epsilon_r(P)$ between the literature values $\epsilon_r(P)_{\text{lit}}$ and the present values $\epsilon_r(P)_{\text{obs}}$ at each pressure, given by

$$\Delta \epsilon_r(P) = \epsilon_r(P)_{\text{lit}} - \epsilon_r(P)_{\text{obs}} \quad (5)$$

are plotted against P for methanol, ethanol, propan-1-ol, pentan-1-ol, and heptan-1-ol at 298.15 K in Figure 2; $\epsilon_r(P)_{\text{lit}}$ values at 298.15 K are not available for other alkan-1-ols. The $\epsilon_r(P)_{\text{lit}}$ values at several pressures were estimated from $\epsilon_r(P_0)$, A , and B values listed in Table 3. For methanol and propan-1-ol, the present $\epsilon_r(P)_{\text{obs}}$ values are, respectively, 0.12 and 0.25 larger than those reported by Srinivasan and Kay,⁹ while our data for ethanol is in excellent agreement with their value⁹ and our

Table 4. 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} for Alkan-1-ols at a Temperature of 298.15 K

alkan-1-ol	$(\partial\epsilon_r/\partial P)_{T,P_0}$	$(\partial \ln \epsilon_r/\partial P)_{T,P_0}$	κ_{T,P_0}^a	$\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$	reference
	GPa ⁻¹	TPa ⁻¹	TPa ⁻¹	TPa ⁻¹	
methanol	40.0	1221	1248	37.3	this work
	40.1	1228		37.6	Srinivasan and Kay ⁹
ethanol	28.0	1149	1153	47.2	this work
	28.6	1175		48.2	Srinivasan and Kay ⁹
	27.8	1142		46.9	Moriyoshi et al. ¹⁶
	19.4	948		46.4	this work
propan-1-ol	19.7	967	1006	47.5	Srinivasan and Kay ⁹
	17.1	978		55.7	this work
butan-1-ol	15.0	1005	884	67.2	this work
	15.5	1053		71.4	Bennett et al. ⁸
hexan-1-ol	13.0	999	836	76.5	this work
	11.7	1022		89.6	this work
heptan-1-ol	13.4	1179	777	103.8	Vij et al. ¹⁰
	11.1	1110		110.9	this work

^a The values are taken from ref 27.

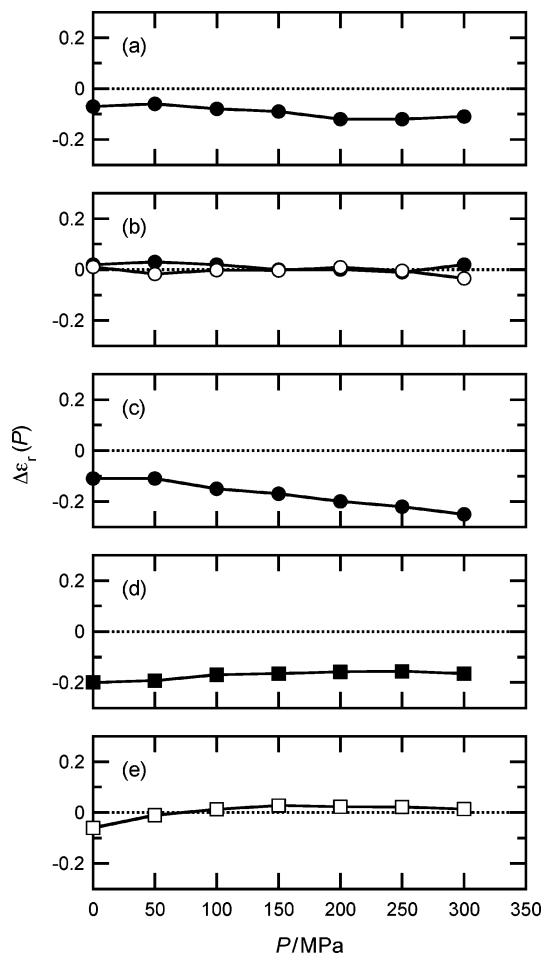


Figure 2. Plots of $\Delta\epsilon_r(P)$ against pressure P at 298.15 K for (a) methanol, (b) ethanol, (c) propan-1-ol, (d) pentan-1-ol, and (e) heptan-1-ol: ●, ref 9; ○, ref 16; ■, ref 8; □, ref 10.

previous data;¹⁶ a maximum deviation $\Delta\epsilon_r(P)$ is only 0.03. For pentan-1-ol, the $\epsilon_r(P)$ data by Bennett et al.⁸ are 0.20 smaller than ours over the whole pressure range up to 300 MPa, but $\epsilon_r(P)$ data for heptan-1-ol by Vij et al.¹⁰ coincide within 0.03 with the present $\epsilon_r(P)$ data at high pressures except for $\epsilon_r(P_0)$: $\Delta\epsilon_r(P_0)$ is -0.06 . It seems that $\Delta\epsilon_r(P_0)$ for heptan-1-ol is small, but this $\Delta\epsilon_r(P_0)$ brings about a large difference in $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ values obtained from our $\epsilon_r(P)$ data and their data. Figures 3 and 4 show the temperature dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ values for each alkan-

1-ol from methanol to heptan-1-ol. To the best knowledge of the authors, no $\epsilon_r(P)$ measurement for octan-1-ol is reported in the literature. Temperature dependence of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ for each alkan-1-ol is fitted to the following polynomial equation of T :

$$X/TPa^{-1} = \sum_{i=0}^3 A_i(T/K)^i \quad (6)$$

Here X represents $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ or $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$. The $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ data for methanol at 293.15 K by Kyropoulos² and those for heptan-1-ol at 283.0 K by Vij et al.¹⁰ are omitted for the correlation by eq 6 because large deviations from other data are observed. Moreover, since the data for hexan-1-ol are few and scattered as found in Figures 3f and 4f, eq 6 is not applied for correlation. The coefficients A_i for each alkan-1-ol determined by a least-squares method are listed in Table 5 along with the standard deviation $\sigma(X)$ of the fit by eq 6.

Since the present $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ values obtained for methanol, ethanol, and propan-1-ol at 298.15 K are, respectively, 0.8 %, 2.3 % and 2.4 % smaller than those reported by Srinivasan and Kay,⁹ it is considered that the agreement between the present and literature values are fully satisfactory. Previous results for ethanol reported by our group¹⁶ agree with the present ones within 0.6 %. For pentan-1-ol, however, the present values are in poor agreement with the literature values. The present values are 6.3 % smaller than those for pentan-1-ol by Bennett et al.⁸ In addition, despite a fair agreement of $\epsilon_r(P)$ for heptan-1-ol up to 300 MPa except $\epsilon_r(P_0)$ as found in Figure 2e, the $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ values for heptan-1-ol by Vij et al.¹⁰ are 16 % larger than those obtained in this work; the reason is, needless to say, that $\epsilon_r(P_0)$ data extremely affect the values of the Tait-type parameters.

Figures 5 to 7 depict plots of these values obtained at 298.15 K in this work against carbon number n in alkan-1-ol. As shown in Figure 5, the $(\partial\epsilon_r/\partial P)_{T,P_0}$ value for alkan-1-ols decreases with an increase in n and is well-represented by the following equation:

$$\left(\frac{\partial\epsilon_r}{\partial P}\right)_{T,P_0}/GPa^{-1} = 10.92 + 50.26 \exp(-0.5483n) \quad (7)$$

with the standard deviation of 0.61 GPa⁻¹ from $n = (1$ to 8). The effect of n on the values of $(\partial \ln \epsilon_r/\partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial\epsilon_r/\partial P)_{T,P_0}$ for alkan-1-ols is fitted to the following

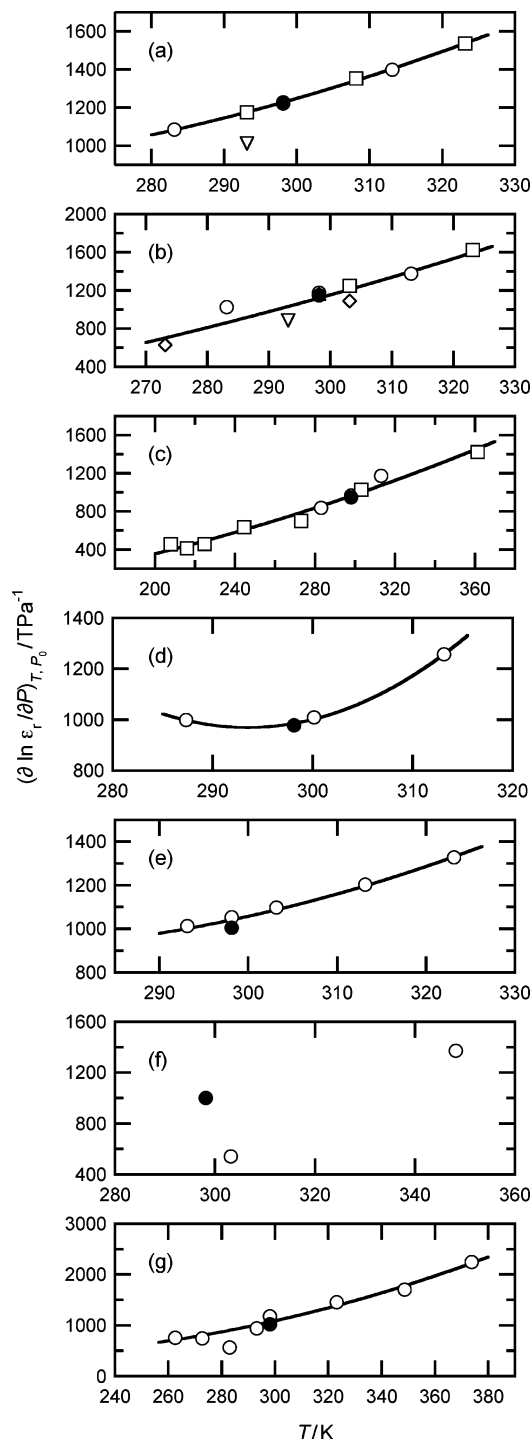


Figure 3. Temperature dependence of $(\partial \ln \epsilon_r / \partial P)_{T, P_0}$ for (a) methanol (●, this work; ▽, ref 2; □, ref 5; ○, ref 9), (b) ethanol (●, this work; ▽, ref 2; ◇, ref 3; □, ref 6; ○, ref 9; △, ref 16), (c) propan-1-ol (●, this work; ○, ref 9; □, ref 7), (d) butan-1-ol (●, this work; ○, ref 4), (e) pentan-1-ol (●, this work; ○, ref 8), (f) hexan-1-ol (●, this work; ○, ref 3), and (g) heptan-1-ol (●, this work; ○, ref 10).

polynomial of n :

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T, P_0} / \text{TPa}^{-1} = 1436.4 - 236.45n + 36.035n^2 - 1.4646n^3 \quad (8)$$

$$\epsilon_r(P_0)^{-2} \left(\frac{\partial \epsilon_r}{\partial P}\right)_{T, P_0} / \text{TPa}^{-1} = 38.993 - 0.36310n + 1.1369n^2 \quad (9)$$

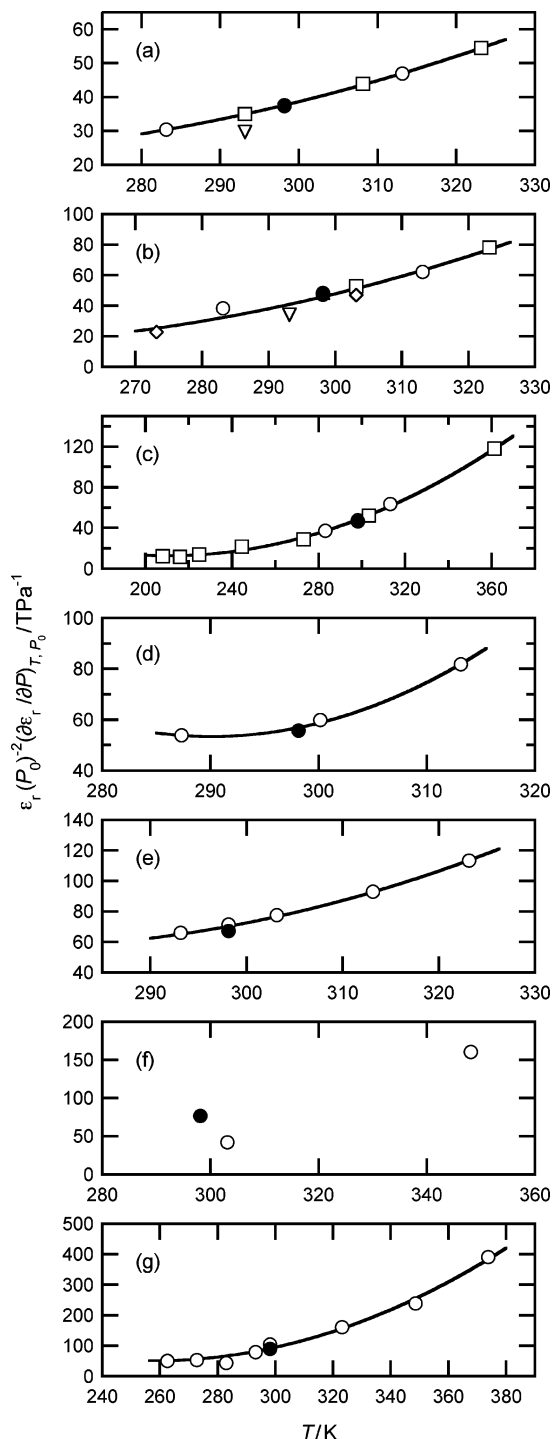


Figure 4. Temperature dependence of $\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T, P_0}$ for (a) methanol (●, this work; ▽, ref 2; □, ref 5; ○, ref 9), (b) ethanol (●, this work; ▽, ref 2; ◇, ref 3; □, ref 6; ○, ref 9; △, ref 16), (c) propan-1-ol (●, this work; ○, ref 9; □, ref 7), (d) butan-1-ol (●, this work; ○, ref 4), (e) pentan-1-ol (●, this work; ○, ref 8), (f) hexan-1-ol (●, this work; ○, ref 3), and (g) heptan-1-ol (●, this work; ○, ref 10).

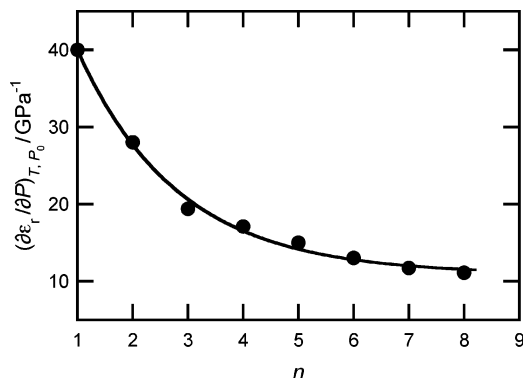
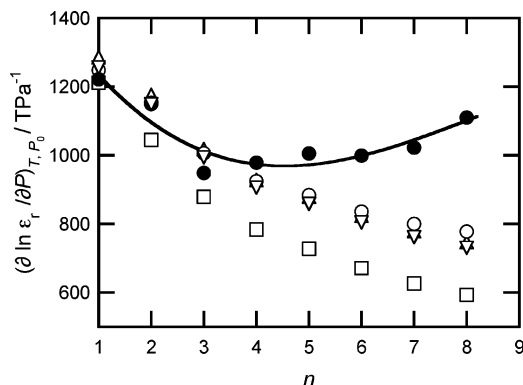
The standard deviations of the fit by eqs 8 and 9 are, respectively, 33 TPa^{-1} and 2.3 TPa^{-1} . The smoothed curves calculated by eqs 7, 8, and 9 are also depicted in Figures 5 to 7.

Since limited ϵ_r measurements of polar liquids under high pressure have so far been made at 298.15 K, reliable $(\partial \epsilon_r / \partial P)_{T, P_0}$, $(\partial \ln \epsilon_r / \partial P)_{T, P_0}$, and $\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T, P_0}$ data at 298.15 K have not been available. Hence it is important to construct simple equations to estimate these values by use of easily measurable

Table 5. Coefficients A_i and Standard Deviation $\sigma(X)$ for Least-Squares Representation of $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T,P_0}$ for Alkan-1-ols by Equation 6

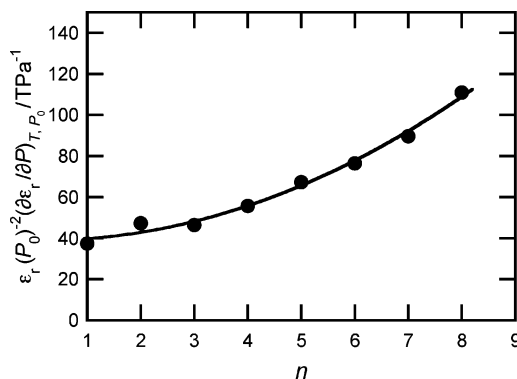
alkan-1-ol	A_0	A_1	A_2	$\sigma(X)^a$
	$(\partial \ln \epsilon_r / \partial P)_{T,P_0}$			
methanol	4012.0	-29.356	0.067143	5
ethanol	-93.385	-9.7567	0.046370	83
propan-1-ol	-267.42	1.0584	0.010285	49
butan-1-ol	65353	-438.72	0.74739	5
pentan-1-ol	9161.2	-63.052	0.12013	17
heptan-1-ol	1907.7	-17.261	0.048438	66
	$\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T,P_0}$			
methanol	299.08	-2.3080	0.0047993	0.2
ethanol	475.38	-3.9154	0.0083002	3.1
propan-1-ol	217.11	-1.9438	0.0046197	1.6
butan-1-ol	4576.0	-31.177	0.053731	0.8
pentan-1-ol	1786.0	-12.660	0.023159	1.7
heptan-1-ol	1690.1	-12.724	0.024687	7.9

^a X is $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ or $\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T,P_0}$.

**Figure 5.** Plots of $(\partial \epsilon_r / \partial P)_{T,P_0}$ against carbon number n in alkan-1-ol at 298.15 K. The smoothed curve is based on eq 7.**Figure 6.** Plots of $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ against carbon number n in alkan-1-ol at 298.15 K: ●, this work ○, eq 10; □, eq 11; △, eq 12; ▽, eq 13. The smoothed curve is based on eq 8.

physical properties at P_0 ; the property is usually the isothermal compressibility at 0.1 MPa κ_{T,P_0} . Some relationships between $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ and κ_{T,P_0} have been proposed^{11,29-32} because ϵ_r and density ρ show similar pressure dependence; ϵ_r for liquids is usually well-represented by a quadratic function of ρ .^{33,34}

Côté et al.¹¹ have attempted to correlate $\epsilon_r(P_0)(\partial \ln \epsilon_r / \partial P)_{T,P_0} / \{\epsilon_r(P_0) - 1\}$ with κ_{T,P_0} for aprotic or protic solvents and have reported that there were good correlations between these quantities for both solvent systems. It seems that the correlation for protic solvents can be applied for the present data for alkan-1-ols. Since a definite correlation equation was not given and the correlation was done for limited data for protic solvents, no further exploration of their treatment is considered in this work.

**Figure 7.** Plots of $\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T,P_0}$ against carbon number n in alkan-1-ol at 298.15 K. The smoothed curve is based on eq 9.

The simplest equation suggested by Kawaizumi and Zana²⁹ is given by the following equation:

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T,P_0} / \kappa_{T,P_0} \approx 1 \quad (10)$$

Marcus and co-workers^{30,31} have proposed a semiempirical relationship between $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ and κ_{T,P_0} values at 298.15 K for primary, secondary, straight-chain, and branched alkanols as follows:

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T,P_0} / \kappa_{T,P_0} = \frac{\{\epsilon_r(P_0) - 1\}\{2.974 + 0.0257\epsilon_r(P_0)\}}{3.81\epsilon_r(P_0)} \quad (11)$$

Recently, Marcus and Hefter³² have suggested the following equations for many liquids at 298.15 K:

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T,P_0} / \kappa_{T,P_0} = (1.057 \pm 0.031) - \frac{(1.057 \pm 0.031)}{\epsilon_r(P_0)} \quad (12)$$

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_{T,P_0} / \kappa_{T,P_0} = (1.039 \pm 0.033) - \frac{(0.920 \pm 0.094)}{\epsilon_r(P_0)} \quad (13)$$

Figure 6 also plots the values of $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ for each alkan-1-ol evaluated from eqs 10 to 13 using κ_{T,P_0} values²⁷ listed in Table 4. The coefficients in eqs 12 and 13 are almost the same, and the calculated results for each alkan-1-ol by eqs 12 and 13 coincide each other within 1.5%. The $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ values calculated from eqs 10 to 13 decrease with an increase in n , while the experimentally obtained $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ values show a minimum around $n = (3 \text{ to } 5)$. Therefore, it is found that no equation reproduces the carbon number n dependence of $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ well. Nonetheless the estimated $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ values for methanol, ethanol, propan-1-ol, and butan-1-ol from eqs 10, 12, and 13 are, respectively, in agreement with those obtained in this work with an average deviation of 4.3%, 5.1%, and 4.7%; eq 11 is only applicable for methanol, ethanol, and propan-1-ol with an average deviation of 5.7%.

Conclusions

Pressure dependence of ϵ_r at 298.15 K for alkan-1-ols from methanol to octan-1-ol obtained in this work was well-represented by the Tait-type equation. Values of $(\partial \ln \epsilon_r / \partial P)_{T,P_0}$ and $\epsilon_r(P_0)^{-2}(\partial \epsilon_r / \partial P)_{T,P_0}$ for alkan-1-ols from methanol to heptan-1-ol except hexan-1-ol were correlated with temperature by a quadratic expression. Correlation equations for the dielectric parameters at 298.15 K were given as a function of carbon

number n in alkan-1-ol. By comparison of the $(\partial \ln \epsilon_r / \partial P)_{T, P_0}$ values calculated from some relationships between $(\partial \ln \epsilon_r / \partial P)_{T, P_0}$ and κ_{T, P_0} with the values obtained in this work, it was found that most of relationships can be applied only for lower alkan-1-ols.

Literature Cited

- (1) Marcus, Y. *Ion Solvation*; John Wiley & Sons: Chichester, 1985.
- (2) Kyropoulos, S. The influence of pressure up to 300 kg/cm² upon the dielectric constant of some liquids. *Z. Phys.* **1926**, *40*, 507–520 (in German).
- (3) Danforth, W. E., Jr. The dielectric constant of liquid under high pressure. *Phys. Rev.* **1931**, *38*, 1224–1235.
- (4) Harris, F. E.; Haycock, E. W.; Alder, B. J. Dielectric polarization and structure of polar liquids under pressure. *J. Chem. Phys.* **1953**, *21*, 1943–1948.
- (5) Hartmann, H.; Neumann, A.; Rinck, G. Pressure dependence of the dielectric constants of organic liquids. *Z. Phys. Chem. N.F.* **1965**, *44*, 204–217 (in German).
- (6) Hartmann, H.; Engelmann, R.; Neumann, A. Pressure dependence of dielectric constants of benzene–ethanol and cyclohexane–ethanol mixtures. *Z. Phys. Chem. N.F.* **1969**, *66*, 298–307 (in German).
- (7) Chen, T.; Dannhauser, W.; Johari, G. P. Study of the pressure dependence of dielectric polarization. *J. Chem. Phys.* **1969**, *50*, 2046–2052.
- (8) Bennett, R. G.; Hall, G. H.; Calderwood, J. H. The pressure dependence of the static permittivity of pentanol isomers. *J. Phys. D: Appl. Phys.* **1973**, *6*, 781–789.
- (9) Srinivasan, K. R.; Kay, R. L. Structural considerations from dielectric measurements on the aliphatic alcohols. *J. Solution Chem.* **1975**, *4*, 299–310.
- (10) Vij, J. K.; Scaife, W. G.; Calderwood, J. H. The pressure and temperature dependence of the static permittivity and density of heptanol isomers. *J. Phys. D: Appl. Phys.* **1978**, *11*, 545–559.
- (11) Côté, J.-F.; Brouillette, D.; Desnoyers, J. E.; Rouleau, J.-F.; St-Arnaud, J.-M.; Perron, G. Dielectric constants of acetonitrile, γ -butyrolactone, propylene carbonate, and 1,2-dichloroethane as a function of pressure and temperature. *J. Solution Chem.* **1996**, *25*, 1163–1173.
- (12) Böttcher, C. J. F. *Theory of Electric Polarization. Vol. 1 Dielectrics in Static Field*; Elsevier: Amsterdam, 1973.
- (13) Uosaki, Y.; Kitaura, S.; Moriyoshi, T. Effect of pressure on the static relative permittivities of alkan-2-ols. *Rev. High Pressure Sci. Technol.* **1998**, *7*, 1216–1218.
- (14) Uosaki, Y.; Kitaura, S.; Kita, T.; Moriyoshi, T. Effect of pressure on the static relative permittivities of 2-methyl-1-alkanols at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 868–870.
- (15) Uosaki, Y.; Kitaura, S.; Kita, T.; Moriyoshi, T. Effect of pressure on the static relative permittivities of 2-ethyl-1-alkanols at 298.15 K. In *Science and Technology of High Pressure*; Manghnani, M. H., Nellis, W. J., Nicol, M. F., Eds.; University Press: Hyderabad, India, 2000; Vol. 2, pp 836–839.
- (16) 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.
- (17) Wilhoit, R. C.; Zwolinski, B. J. Physical and thermodynamic properties of aliphatic alcohols. *J. Phys. Chem. Ref. Data* **1973**, *2*, Suppl. 1.
- (18) Aminabhavi, T. M.; Aralaguppi, M. I.; Harogoppad, S. P.; Balundgi, R. H. Densities, viscosities, refractive indices, and speeds of sound for methyl acetoacetate + aliphatic alcohols (C1–C8). *J. Chem. Eng. Data* **1993**, *38*, 31–39.
- (19) Ritzoulis, G.; Missopolinou, D.; Doulami, S.; Panayiotou, C. Relative permittivities, densities, refractive indices and ultrasound velocities of the binary systems of γ -butyrolactone with methanol, ethanol, 1-butanol, and 1-octanol. *J. Chem. Eng. Data*, **2000**, *45*, 636–641.
- (20) D'Aprano, A.; Dorina D, I. Dielectric polarization and polarizability of 1-pentanol + n -octane mixtures from static dielectric constant and refractive index data at 0, 25 and 45 °C. *J. Solution Chem.* **1990**, *19*, 883–892.
- (21) Sastry, N. V.; Valand, M. K. Dielectric constants, refractive indexes and polarizations for 1-alcohol + heptane mixtures at 298.15 and 308.15 K. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 243–250.
- (22) Bezman, R. D.; Casassa, E. F.; Kay, R. L. The temperature dependence of the dielectric constants of alkanols. *J. Mol. Liq.* **1997**, *73–74*, 397–402.
- (23) D'Aprano, A.; Donato, D. I.; Caponetti, E. The static dielectric constant of solutions of water in n -alcohols at 15, 25, 35, and 45 °C. *J. Solution Chem.* **1979**, *8*, 135–146.
- (24) Yang, M.; Terakawa, E.; Tanaka, Y.; Sotani, T.; Matsuo, S. Solid–liquid phase equilibria in binary (1-octanol + n -alkane) mixtures under high pressure. Part 1. (1-Octanol + n -tetradecane or n -hexadecane) systems. *Fluid Phase Equilib.* **2002**, *194–197*, 1119–1129.
- (25) Owen, B. B.; Brinkley, S. R. Jr. The effect of pressure upon the dielectric constants of liquids. *Phys. Rev.* **1943**, *64*, 32–36.
- (26) Isaacs, N. S. *Liquid Phase High Pressure Chemistry*; John Wiley & Sons: Chichester, 1981.
- (27) Díaz Peña, M.; Tardajos, G. Isothermal compressibilities of n -1-alcohols from methanol to 1-dodecanol at 298.15, 308.15, 318.15, and 333.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 441–445.
- (28) 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.
- (29) Kawaizumi, F.; Zana, R. Partial molar volumes of ions in organic solvents from ultrasonic vibration potentials and density measurements. II. Ethanol and dimethylformamide. *J. Phys. Chem.* **1974**, *78*, 1099–1105.
- (30) Marcus, Y.; Ben-Zwi, N.; Shiloh, I. Molar volumes and ion pairing of lithium halides in alcohols. *J. Solution Chem.* **1976**, *5*, 87–106.
- (31) Marcus, Y. The volume change on ion-pairing of symmetrical electrolytes. *Z. Naturforsch.* **1983**, *38a*, 247–251.
- (32) Marcus, Y.; Hefter, G. On the pressure and electric field dependencies of the relative permittivity of liquids. *J. Solution Chem.* **1999**, *28*, 575–592.
- (33) Uosaki, Y.; Kitaura, S.; Moriyoshi, T. Static relative permittivities of water + propane-1,2-diol and water + propane-1,3-diol under pressures up to 300 MPa at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 2008–2012.
- (34) Uosaki, Y.; Kitaura, S.; Moriyoshi, T. 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. *J. Chem. Eng. Data* **2006**, *51*, 423–429.

Received for review June 4, 2006. Accepted July 18, 2006.

JE060248P