Effect of Pressure on the Static Relative Permittivities of 2-Methyl-1-alkanols at 298.15 K

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Static relative permittivities, ϵ_r, were measured for 2-methyl-1-propanol, 2-methyl-1-butanol, 2-methyl-1-pentanol, and 2-methyl-1-hexanol under pressures up to 300 MPa at 298.15 K. Values of ϵ_r increase with pressure for each 2-methyl-1-alkanol and are well-fitted with the Tait-type equation. In addition, a good correlation equation of static relative permittivities, $\epsilon_r(P, n)$, for 2-methyl-1-alkanols with pressure P and the number n in $H(CH_2)_{n-2}CH(CH_3)CH_2OH$ (n = 3 to 6) is given.

Introduction

The static relative permittivities, ϵ_r, for polar liquids under high pressure give us not only useful information on the liquid structure but also useful parameters such as the pressure P coefficient of ϵ_r at 0.1 MPa, $(\partial\epsilon_r/\partial P)_T$, to analyze some physical properties of electrolyte solutions and to estimate a contribution of electrostriction to the activation or reaction volume in the ionic chemical reactions. Among many polar liquids, ϵ_r values for alkanols under high pressure have been extensively measured. Nevertheless, systematic studies on the static relative permittivities for alkanols have not been fully performed to understand intermolecular interactions such as hydrogen bonding.

In a previous paper (Uosaki et al., 1998), we have reported the ϵ_r values for 2-alkanols from 2-propanol to 2-octanol under pressures up to 300 MPa and 298.15 K and have found the different pressure dependence of the Kirkwood correlation factor, g, among 2-alkanols; g values for 2-propanol and 2-butanol decrease with pressure, while those for 2-pentanol and 2-octanol increase with pressure.

The present work reports ϵ_r values of 2-methyl-1-alkanols, $H(CH_2)_{n-2}CH(CH_3)CH_2OH$ (n = 3 to 6), from 2-methyl-1-propanol to 2-methyl-1-hexanol under high pressure up to 300 MPa at 298.15 K. Therefore n corresponds to the number of carbons in key 1-alkanols. Only two studies on ϵ_r values for 2-methyl-1-alkanols under high pressure have been reported: 2-methyl-1-propanol up to 1215.9 MPa at 273.15 K and 303.15 K (Danforth, 1931) and 2-methyl-1-butanol up to 392.3 MPa in the temperature range of 293.15 K to 323.15 K (Bennett et al., 1973). The ϵ_r values obtained as a function of pressure in this work are fitted with the Tait-type equation. A comparison between the present data and the literature ones is made. Furthermore, we provide a good correlation equation of ϵ_r values under high pressure for 2-methyl-1-alkanols at 298.15 K.

Experimental Section

2-Methyl-1-propanol (>99%), 2-methyl-1-pentanol (>99%), and 2-methyl-1-hexanol (>97%) were purchased from Tokyo Kasei Kogyo Co., Ltd. 2-Methyl-1-butanol (>99%) was obtained from Aldrich Chemical Co., Inc. 2-Methyl-1-propanol was refluxed over CaH_2 for several hours and then distilled twice. Other alkanols were refluxed over CaH_2 for several hours and then distilled at least twice under N_2 stream at reduced pressure. The refractive indices, n_D, measured with an Abbe refractometer and the static relative permittivities, $\epsilon_r(0.1)$, at 0.1 MPa and 298.15 K are listed in Table 1, together with those found in the literature. Uncertainty in n_D is less than 0.0001. Our n_D values for 2-methyl-1-propanol, 2-methyl-1-butanol, and 2-methyl-1-pentanol agree with the literature ones. The n_D value for 2-methyl-1-hexanol is, however, in poor agreement with the reported one. The $\epsilon_r(0.1)$ values for 2-methyl-1-propanol and 2-methyl-1-butanol obtained in this work agree with those found in the literature within ±1.1%.

Table 1. Refractive Indices, n_D, and Static Relative Permittivities, $\epsilon_r(0.1)$, for 2-Methyl-1-alkanols at 0.1 MPa and 298.15 K

	n_D		$\epsilon_r(0.1)$	
alkanol	this work	lit.	this work	lit.
2-methyl-1-propanol	1.3938	1.3938,[a] 1.3939[b]	17.73	17.93[b]
2-methyl-1-butanol	1.4087	1.4086,[a] 1.4087[b]	15.50	15.63,[c] 15.44[d]
2-methyl-1-pentanol	1.4172	1.4172,[a] 1.4172[b]	12.93	
2-methyl-1-hexanol	1.4231	1.421[a]	10.65	

[a] Wilhoit and Zwolinski, 1973. [b] Riddick et al., 1986. [c] D'Aprano et al., 1973. [d] Calculated from an empirical equation by Bennett et al. (1973).

The ϵ_r measurements were carried out at least three times for each alkanol by means of a transformer ratio-arm bridge with a three-terminal dielectric cell. The frequency range was from 10 kHz to 50 kHz. Pressure was measured with a Bourdon gauge with an accuracy of 0.35 MPa, and temperature was controlled to ±0.01 K in ϵ_r measurements. The apparatus and experimental procedure for the ϵ_r measurements were described in detail earlier (Moriyoshi et al., 1990). Uncertainty in ϵ_r is estimated to be within ±0.1%. The ϵ_r values were reproduced to within ±0.1%.

Results and Discussion

The present experimental ϵ_r values for 2-methyl-1-alkanols as a function of pressure are given in Table 2.

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Table 2. Static Relative Permittivities, ϵ_r, for 2-Methyl-1-alkanol as a Function of Pressure at 298.15 K

	P/MPa						
alkanol	0.1	50	100	150	200	250	300
2-methyl-1-propanol	17.73	18.50	19.08	19.56	19.97	20.33	20.66
2-methyl-1-butanol	15.50	16.26	16.81	17.29	17.68	18.04	18.36
2-methyl-1-pentanol	12.93	13.67	14.23	14.67	15.07	15.41	15.72
2-methyl-1-hexanol	10.65	11.41	11.98	12.45	12.85	13.19	13.50

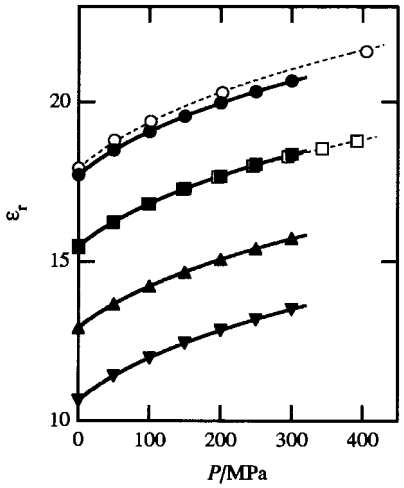

Figure 1. Pressure dependence of the static relative permittivities, ϵ_r, for 2-methyl-1-propanol (●, this work; ○, Danforth, 1931), 2-methyl-1-butanol (■, this work; □, Bennett et al., 1973), 2-methyl-1-pentanol (▲), and 2-methyl-1-hexanol (▼) at 298.15 K. The smoothed full or broken curves are based on the values of $\epsilon_r(0.1)$, *A*, and *B* given in Table 3.

Values of ϵ_r are plotted against pressure in Figure 1 and are fitted by the nonweighted least-squares method to the Tait-type equation

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

where $\epsilon_r(P)$ represents the static relative permittivity at the pressure *P* in MPa at 298.15 K and *A* and *B* are the Tait-type parameters. Figure 1 also includes the ϵ_r values up to around 400 MPa for 2-methyl-1-propanol interpolated from the measured values at 273.15 K and 303.15 K (Danforth, 1931) and for 2-methyl-1-butanol evaluated from an empirical equation (Bennett et al., 1973). The interpolated values for 2-methyl-1-propanol are larger than ours at each pressure, and its deviation becomes larger with pressure: 0.20 at 0.1 MPa and 0.37 at 300 MPa. Although the evaluated values for 2-methyl-1-butanol agree with the present ϵ_r values within ±0.06 over the investigated pressure ranges, a slight difference in pressure dependence of ϵ_r is observed. The Tait-type parameters thus obtained are summarized in Table 3, along with the $\epsilon_r(0.1)$ values and the standard deviations $\sigma(\epsilon_r)$ of the fit. Since the $\sigma(\epsilon_r)$ values for 2-methyl-1-alkanols in this work are less than 0.01, we can obtain the $\epsilon_r(P)$ value under pressure up to 300 MPa and 298.15 K from $\epsilon_r(0.1)$, *A*, and *B* values.

To establish an estimation method of ϵ_r value at any pressure, it is important to understand the contribution of the $-CH_2-$ group to the ϵ_r value in a series of 2-methyl-1-alkanols. Figure 2 shows plots of ϵ_r values at 0.1 MPa and 300 MPa as a function of *n*. A good linear relationship exists between ϵ_r and *n* values at any pressure. A decrement of ϵ_r per $-CH_2-$ group at any pressure is ca. −2.4 for 2-methyl-1-alkanols and decreases slightly with pressure.

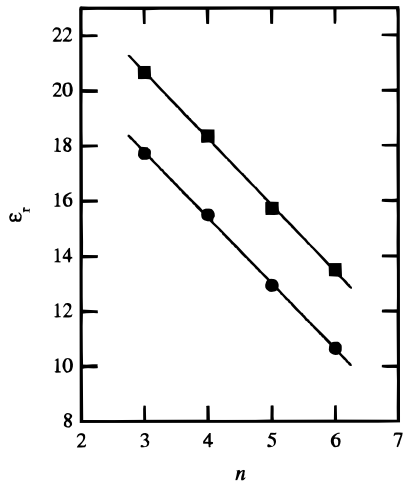

Figure 2. Effect of *n* in $H(CH_2)_{n-2}CH(CH_3)CH_2OH$ on the static relative permittivities, ϵ_r, under two pressures, 0.1 MPa (●) and 300 MPa (■), at 298.15 K.

Accordingly, the static relative permittivity for $H(CH_2)_{n-2}CH(CH_3)CH_2OH$ ($n = 3$ to 6) at pressure *P*, $\epsilon_r(P, n)$, is well-represented by

$$\epsilon_r(P, n) = \epsilon_r(P, 2) - [2.380 + 1.00 \times 10^{-4}(P/\mathrm{MPa})](n - 2) \quad (2)$$

It is considered that the first term, $\epsilon_r(P, 2)$, corresponds to the static relative permittivity at pressure *P* of $HCH(CH_3)CH_2OH$: 1-propanol. However, since a slight difference in steric hindrance around the −OH group is expected between 1-propanol and other 2-methyl-1-alkanols, it should be noticed that $\epsilon_r(P, 2)$ values in this work are nothing but the hypothetical ones for 1-propanol. To correlate the obtained $\epsilon_r(P, 2)$ values with pressure, we also used the Tait-type equation (eq 1) and then found the following relation

$$\epsilon_r(P, 2) = \frac{20.16}{1 - 0.0950 \ln[(107.3 + P/\mathrm{MPa})/107.4]} \quad (3)$$

with a standard deviation of 0.01. With the aid of eqs 2 and 3, we can get reliable ϵ_r values for 2-methyl-1-alkanols, $H(CH_2)_{n-2}CH(CH_3)CH_2OH$ ($n = 3$ to 6), under any pressure up to 300 MPa at 298.15 K; an average of the absolute error is 0.45%, and the maximum absolute error is 0.89%.

The dielectric parameter, $(\partial\epsilon_r/\partial P)_T$, at 0.1 MPa is needed to get $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ values at 0.1 MPa. The $(\partial\epsilon_r/\partial P)_T$ value at 0.1 MPa for each 2-methyl-1-alkanol can be easily evaluated from the $\epsilon_r(0.1)$ value and the Tait-type parameters by

$$\left(\frac{\partial\epsilon_r}{\partial P}\right)_T = \frac{A\epsilon_r(0.1)}{B + 0.1} \quad (4)$$

where we used ϵ_r for $\epsilon_r(P)$ for brevity. The $(\partial\epsilon_r/\partial P)_T$ value at 0.1 MPa for each 2-methyl-1-alkanol calculated from eq 4 by use of the parameters in Table 3 is plotted against *n* in Figure 3. On the basis of eqs 2 and 3, we can evaluate the $(\partial\epsilon_r/\partial P)_T$ values at 0.1 MPa for 2-methyl-1-alkanols as a function of *n* as follows:

$$\left(\frac{\partial\epsilon_r}{\partial P}\right)_T \Big/ \mathrm{GPa}^{-1} = 17.83 - 0.10(n - 2) \quad (5)$$

Figure 3 also shows the $(\partial\epsilon_r/\partial P)_T$ values at 0.1 MPa from eq 5 and the calculated ones for 2-methyl-1-propanol

Table 3. Static Relative Permittivity at 0.1 MPa and 298.15 K, $\epsilon_r(0.1)$, Parameters of the Tait-type Equation, *A* and *B*, for 2-Methyl-1-alkanols, and Standard Deviations of Fit of Eq 1, $\sigma(\epsilon_r)$

alkanol	$\epsilon_r(0.1)$	*A*	*B*	$\sigma(\epsilon_r)$	P_{max}[a]/MPa	ref
2-methyl-1-propanol	17.73	0.1020	99.6	0.00	300.0	this work
	17.93[b]	0.1044[b]	96.3[b]	0.05[b]	1215.9	Danforth (1931)
2-methyl-1-butanol	15.50	0.1092	94.9	0.01	300.0	this work
	15.44[c]	0.0962[c]	72.9[c]	0.01[c]	392.3	Bennett et al. (1973)
2-methyl-1-pentanol	12.93	0.1183	86.1	0.00	300.0	this work
2-methyl-1-hexanol	10.65	0.1317	75.2	0.01	300.0	this work

[a] Maximum pressure applicable to evaluate $\epsilon_r(P)$ values from the values of $\epsilon_r(0.1)$, *A*, and *B* by the Tait-type equation. [b] These values are based on the interpolated ϵ_r values from the reported ϵ_r values at 273.15 K and 303.15 K, assuming that the relation $\epsilon_r = a + bT$ is valid at each pressure, where *T* is the temperature and *a* and *b* are the coefficients. [c] These values are based on the evaluated ϵ_r values from an empirical equation in the temperature range of 293.15 K to 323.15 K.

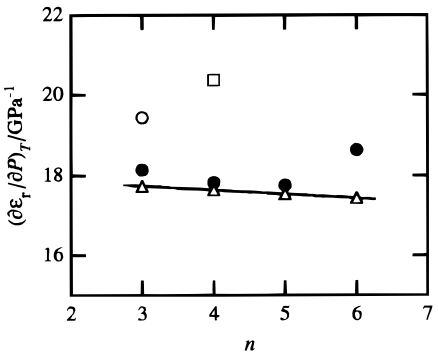

Figure 3. Effect of *n* in $H(CH_2)_{n-2}CH(CH_3)CH_2OH$ on $(\partial\epsilon_r/\partial P)_T$ at 0.1 MPa and 298.15 K (●, this work; △, based on eq 5; ○, Danforth, 1931; □, Bennett et al., 1973).

(Danforth, 1931) and 2-methyl-1-butanol (Bennett et al., 1973) from the parameters given in Table 3. The values from eq 5 decrease linearly with *n*. There is a good agreement between the values from eq 4 and eq 5, except for 2-methyl-1-hexanol ($n = 6$). Its difference for 2-methyl-1-hexanol is about 6%. The calculated $(\partial\epsilon_r/\partial P)_T$ values for 2-methyl-1-propanol ($n = 3$) and 2-methyl-1-butanol ($n = 4$) based on literature ϵ_r values are 7% and 14% larger than ours obtained from eq 4, respectively.

In conclusion, it is found that eqs 2 and 3 give the static relative permittivities, ϵ_r, under high pressure and the dielectric parameter, $(\partial\epsilon_r/\partial P)_T$, at 0.1 MPa and 298.15 K for 2-methyl-1-alkanols, $H(CH_2)_{n-2}CH(CH_3)CH_2OH$ ($n = 3$ to 6), with good accuracy.

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