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Static Relative Permittivities of Polyhydric Alcohols under Pressures up to 300 MPa at 298.15 K

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Static relative permittivities ϵ_r of seven polyhydric alcohols, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,5-pentanediol, 3-methyl-1,3-butanediol, 2-methyl-2,4-pentanediol, and 1,2,3-propanetriol, were measured under pressures up to 300 MPa at 298.15 K. Pressure P dependence of ϵ_r of each polyhydric alcohol was fitted to a Tait-type equation, and the Tait-type parameters, A and B, were determined. Correlation equations for estimating $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values at 0.1 MPa for monohydric and polyhydric alcohols are provided.

Introduction

The static relative permittivity, previously termed as the dielectric constant, is one of the basic physical properties and also provides useful information on the intermolecular interactions in liquids from the Kirkwood correlation factor. Furthermore, its pressure coefficient, $(\partial \epsilon_r/\partial P)_T$, is a necessary quantity to evaluate solutions involving charged species. However, few ϵ_r measurements of liquids under high pressure have been made, and sufficient $(\partial\epsilon_r/\partial P)_T$ data have not been reported around 298.15 K.

In previous papers,[1−3] we have reported the static relative permittivities, ϵ_r, of some monohydric alcohols as a function of pressure up to 300 MPa at 298.15 K and analyzed the pressure dependence of ϵ_r values by making use of a Tait-type equation. Furthermore, the pressure dependence of ϵ_r values of 1,2-butanediol, 1,3-butanediol, and 1,4-butanediol and their aqueous mixtures has been studied up to 300 MPa at 298.15 K.[4] By use of the values of the Tait-type parameters and the static relative permittivity at 0.1 MPa, $\epsilon_r(0.1)$, we evaluated the dielectric parameters, $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$, of three aqueous butanediol mixtures over the whole composition range and discussed the composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values from the relative position of the OH groups in butanediols. Since polyhydric alcohols have more than two OH groups, it is expected that the polyhydric alcohols have more complicated structures through inter- and intramolecular hydrogen bonding than monohydric alcohols.

In continuation of our work on the static relative permittivity measurements for alcohols under high pressure, we measured ϵ_r values for some polyhydric alcohols under high pressure up to 300 MPa at 298.15 K; Danforth[5] has reported ϵ_r values for 1,2,3-propanetriol up to 1216 MPa at 273.15 K and 303.15 K. The ϵ_r values as a function of pressure at 298.15 K obtained in this work were fitted with the Tait-type equation. A comparison between the present data and the literature values under high pressure is made for 1,2,3-propanetriol. Additionally, we provide correlation equations for the dielectric parameters, $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$, at 0.1 MPa.

Table 1. Refractive Indices, n_D, and Static Relative Permittivities, $\epsilon_r(0.1)$, for Polyhydric Alcohols at 0.1 MPa and 298.15 K

	n_D		$\epsilon_r(0.1)$	
alcohol	this work	lit	this work	lit
1,2-ethanediol	1.4304	1.4306[a]	40.70	37.7,[a] 40.61,[b] 40.68,[c] 40.8,[d] 40.97[e]
1,2-propanediol	1.4313	1.4314[a]	28.67	28.76,[f] 28.9[g]
1,3-propanediol	1.4384	1.4386[a]	34.69	34.1, [g] 34.9[h]
1,5-pentanediol	1.4480	1.4484[a]	26.90	26.9[h]
3-methyl-1,3-butanediol	1.4401		24.56	
2-methyl-2,4-pentanediol	1.4258	1.4257[a]	25.17	25.08,[i] 25.1[j]
1,2,3-propanetriol	1.4722	1.4730[a]	42.49	42.5[a]

[a] Riddick et al.[6] [b] Douhéret and Pal.[7] [c] Calculated from an empirical equation given by Koizumi and Hanafusa.[8] [d] Morenas and Douhéret.[9] [e] Corradini et al.[10] [f] Tombari et al.[11] [g] This value is calculated from the ϵ_r values at the temperatures from 243 to 423 K reported by Zhuravlev,[12] assuming that the relation $\epsilon_r = a + b/T$ is valid, where T is the temperature in K and a and b are the coefficients. [h] Wang et al.[13] [i] Calculated from an empirical equation given by Ikada.[14] [j] Grineva et al.[15]

Experimental Section

1,2-Ethanediol (>99%), 3-methyl-1,3-butanediol (>99%), and 2-methyl-2,4-pentanediol (>99%) were purchased from Wako Pure Chemical Industries, Ltd. 1,2-Propanediol (>99%) and 1,2,3-propanetriol (>99%) were obtained from Kanto Chemical Co., Inc. 1,3-Propanediol (98%) and 1,5-pentanediol (>97%) were, respectively, supplied from Aldlich Chemical Co., Inc., and Tokyo Chemical Industry Co., Ltd. Under a dry N_2 stream, each reagent was refluxed over CaH_2 at reduced pressure for several hours and then distilled. The same treatment was repeated more than twice. 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, along with those reported in the literature.[6−15] Uncertainty in n_D is less than 0.0001. Our n_D values for 1,2-ethanediol, 1,2-

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Table 2. Static Relative Permittivities, ϵ_r, for Polyhydric Alcohols as a Function of Pressure at 298.15 K

	ϵ_r						
alcohol	0.1 MPa	50 MPa	100 MPa	150 MPa	200 MPa	250 MPa	300 MPa
1,2-ethanediol	40.70	41.80	42.83	43.77	44.65	45.48	46.27
1,2-propanediol	28.67	29.67	30.56	31.34	32.08	32.76	33.40
1,3-propanediol	34.69	35.42	36.11	36.72	37.30	37.83	38.34
1,5-pentanediol	26.90	27.53	28.08	28.60	29.06	29.49	29.90
3-methyl-1,3-butanediol	24.56	25.22	25.81	26.33	26.79	27.23	27.64
2-methyl-2,4-pentanediol	25.17	25.88	26.44	26.89	27.28	27.63	27.96
1,2,3-propanetriol	42.49	43.39	44.24	45.04	45.80	46.54	47.25

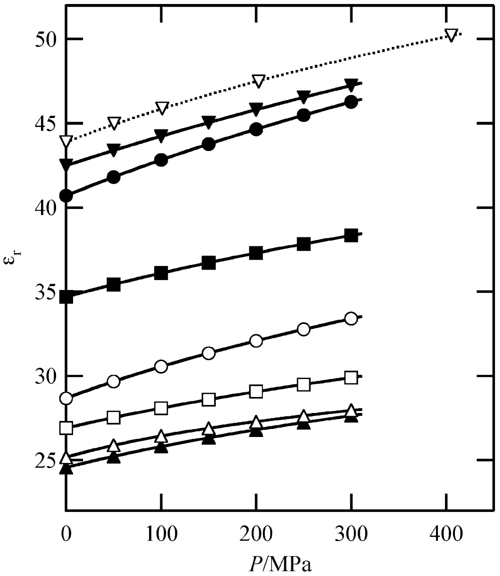

Figure 1. Pressure dependence of the static relative permittivities, ϵ_r, for polyhydric alcohols at 298.15 K: ●, 1,2-ethanediol; ○, 1,2-propanediol; ■, 1,3-propanediol; □, 1,5-pentanediol; ▲, 3-methyl-1,3-butanediol; △, 2-methyl-2,4-pentanediol; ▼, 1,2,3-propanetriol; ▽ 1,2,3-propanetriol by Danforth.[5] The smoothed full or broken curves are based on the values of $\epsilon_r(0.1)$ and A and B given in Table 3.

propanediol, 1,3-propanediol, and 2-methyl-2,4-pentanediol agree with the reported ones within 0.0002. Those for 1,5-pentanediol and 1,2,3-propanetriol are, however, in poor agreement with the literature values. The present $\epsilon_r(0.1)$ value for 1,2-ethanediol coincides with literature values within ±0.7%, except for the value 37.7.[6] The $\epsilon_r(0.1)$ values for 1,2-propanediol, 1,5-pentanediol, 2-methyl-2,4-pentanediol, and 1,2,3-propanetriol agree within ±0.6% with those reported in the literature. To the best of the authors' knowledge, n_D and $\epsilon_r(0.1)$ values for 3-methyl-1,3-butanediol at 298.15 K have not been measured.

The procedure and apparatus for the capacitance measurements have been described in detail earlier.[16] A high-pressure vessel equipped with a three-terminal capacitor was immersed in a water bath of which temperature was controlled to ±0.01 K. Pressure was measured with a Bourdon gauge and accurate to ±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 thrice for each polyhydric alcohol, and the ϵ_r values thus obtained were reproduced to within ±0.08%.

Results and Discussion

The experimentally obtained ϵ_r values for each polyhydric alcohol at 298.15 K are summarized as a function of pressure in Table 2. Figure 1 shows plots of ϵ_r values for polyhydric alcohols against pressure. The ϵ_r values up to around 400 MPa for 1,2,3-propanediol interpolated from the measured values at 273.15 K and 303.15 K[5] are also included in Figure 1. The interpolated values for 1,2,3-propanetriol are larger than ours at each pressure, and its deviation becomes larger with an increase in pressure: 1.39 at 0.1 MPa and 1.74 at 300 MPa.

In any alcohol, $(\partial \epsilon_r/\partial P)_T$ becomes smaller with an increase in pressure. As reported in previous papers,[17,18] such a $\epsilon_r - P$ behavior is always observed if solutions are not solidified. The dependence of ϵ_r values on pressure for each polyhydric alcohol is correlated with the following Tait-type equation

$$1 - \frac{\epsilon_r(0.1)}{\epsilon_r(P)} = A \ln\left(\frac{B + P}{B + 0.1}\right) \qquad (1)$$

where $\epsilon_r(P)$ is the static relative permittivity at the pressure P in MPa. The Tait-type parameters, A and B, for each alcohol were determined from the nonweighted least-squares method. The Tait-type parameters thus determined, together with the standard deviations $\sigma(\epsilon_r)$ of the fit, are listed in Table 3, where the parameters for butanediols previously reported are also tabulated. Since the $\sigma(\epsilon_r)$ values in this work are less than 0.01, $\epsilon_r$values at any pressure up to the maximum pressure P_{max} can be evaluated from the Tait-type equation by use of $\epsilon_r(0.1)$ and A and B values.

The $(\partial \epsilon_r/\partial P)_T$, $(\partial \ln \epsilon_r/\partial P)_T$, and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values are required not only to evaluate electrolyte solution data at atmospheric pressure but to estimate a contribution of the electrostriction to the partial molar volume of an individual ion using the Born equation. These values at 0.1 MPa can be evaluated from $\epsilon_r(0.1)$ and the Tait-type parameters as follows

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

$$\left(\frac{\partial \ln\epsilon_r}{\partial P}\right)_T = \frac{A}{B + 0.1} \qquad (3)$$

$$\epsilon_r^{-2}\left(\frac{\partial \epsilon_r}{\partial P}\right)_T = \frac{A}{\epsilon_r(0.1)(B + 0.1)} \qquad (4)$$

We used ϵ_r for $\epsilon_r(P)$ in these equations for simplicity. The $(\partial \ln \epsilon_r/\partial P)_T$ values at 0.1 MPa are also listed in Table 3.

It is of great importance to estimate dielectric properties such as $(\partial \epsilon_r/\partial P)_T$ at 0.1 MPa from easily available or measurable physical properties. The relations between $(\partial \ln \epsilon_r/\partial P)_T$ at 0.1 MPa and the isothermal compressibility at 0.1 MPa, κ_T, so far have been proposed[19,20]

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_T \approx \kappa_T \qquad (5)$$

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_T = (1.057 \pm 0.031)\left\{\frac{\epsilon_r(0.1) - 1}{\epsilon_r(0.1)}\right\}\kappa_T \qquad (6)$$

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 Polyhydric Alcohols, Standard Deviations of Fit of Equation 1, $\sigma(\epsilon_r)$, and $(\partial \ln \epsilon_r/\partial P)_T$ at 0.1 MPa

alcohol	$\epsilon_r(0.1)$	A	B/MPa	$\sigma(\epsilon_r)$	$P_{\max}$[a]/MPa	$(\partial \ln \epsilon_r/\partial P)_T$/TPa	ref
1,2-ethanediol	40.70	0.1790	312.6	0.01	300.0	572.4	this work
1,2-propanediol	28.67	0.1650	220.8	0.01	300.0	746.9	this work
1,3-propanediol	34.69	0.1436	318.7	0.01	300.0	450.4	this work
1,2-butanediol	22.40	0.1623	187.1	0.00	300.0	867.0	*b*
1,3-butanediol	28.68	0.1221	221.7	0.01	300.0	550.5	*b*
1,4-butanediol	30.99	0.1110	221.6	0.00	40.0	500.7	*b*
1,5-pentanediol	26.90	0.1345	270.8	0.01	300.0	496.5	this work
3-methyl-1,3-butanediol	24.56	0.1317	225.7	0.01	300.0	583.3	this work
2-methyl-2,4-pentanediol	25.17	0.0812	124.8	0.02	300.0	650.1	this work
1,2,3-propanetriol	42.49	0.1992	456.0	0.01	300.0	436.7	this work
	43.88[c]	0.1403[c]	271.8[c]	0.06[c]	405.3	516.0	*d*

[a] Maximum pressure applicable to calculate $\epsilon_r(P)$ values from the values of $\epsilon_r(0.1)$, A, and B by the Tait-type equation. [b] Reference 4. [c] These values are based on the interpolated ϵ_r values from the reported ϵ_r values at 273.15 K and 303.15 K,[5] assuming that the relation $\epsilon_r = a + b/T$ is valid at each pressure, where T is the temperature in K and a and b are the coefficients. [d] Danforth.[5]

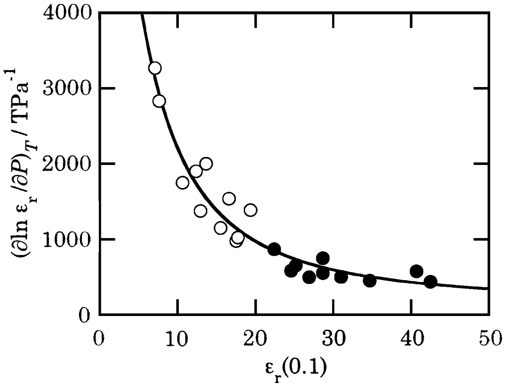

Figure 2. Plots of $(\partial \ln \epsilon_r/\partial P)_T$ at 0.1 MPa against $\epsilon_r(0.1)$ at 298.15 K: ●, polyhydric alcohols; ○, monohydric alcohols. The smoothed curve is based on eq 7.

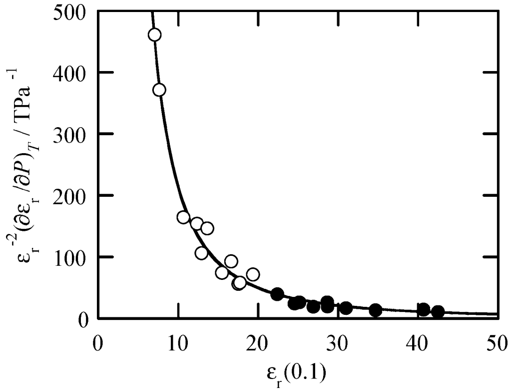

Figure 3. Plots of $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ at 0.1 MPa against $\epsilon_r(0.1)$ at 298.15 K: ●, polyhydric alcohols; ○, monohydric alcohols. The smoothed curve is based on eq 8.

In both equations, κ_T values are needed to get $(\partial \ln \epsilon_r/\partial P)_T$ values at 0.1 MPa. Although κ_T values for many organic compounds are available, those for polyhydric alcohols are unfortunately scarce. Hence it is impossible to confirm whether these two equations are well applied to polyhydric alcohols. As pointed out in the previous work,[3] we have suggested that there is a good correlation between $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ and $\epsilon_r(0.1)$ for some monohydric alcohols. In Figures 2 and 3, $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values at 0.1 MPa are, respectively, plotted against $\epsilon_r(0.1)$ values for monohydric alcohols reported in the previous works and for polyhydric alcohols investigated in this work. As shown in Figures 2 and 3, there is a trend that $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values at 0.1 MPa decrease with increasing $\epsilon_r(0.1)$. So simple regression equations were investigated to reproduce the $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values at 0.1 MPa as well as possible and obtained equations as follows

$$\left(\frac{\partial \ln \epsilon_r}{\partial P}\right)_T/\mathrm{TPa}^{-1} = \frac{5.91 \times 10^5}{\{\epsilon_r(0.1) + 7.02\}^2} + 163 \qquad (7)$$

$$\epsilon_r^{-2}\left(\frac{\partial \epsilon_r}{\partial P}\right)_T/\mathrm{TPa}^{-1} = \frac{1.91 \times 10^4}{\{\epsilon_r(0.1) - 0.58\}^2} - 1.07 \qquad (8)$$

The calculated values using both equations are also plotted in Figures 2 and 3. These two equations use only the $\epsilon_r(0.1)$ value to estimate $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values at 0.1 MPa for monohydric and polyhydric alcohols; the standard deviation for eqs 7 and 8 is, respectively, 202 TPa^{-1} and 13.6 TPa^{-1}. Since Marcus and Hefter[20] have reported that the standard deviation for $(\partial \ln \epsilon_r/\partial P)_T$ at 0.1 MPa was 150 TPa^{-1} when they used eq 6, it seems that eq 7 is not so good as eq 6 to estimate $(\partial \ln \epsilon_r/\partial P)_T$ value at 0.1 MPa. They excluded some values to derive eq 6, while we included all of the data for monohydric and polyhydric alcohols we have so far measured. So our correlation equation for $(\partial \ln \epsilon_r/\partial P)_T$ at 0.1 MPa is more reliable to use. Moreover, the $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values at 0.1 MPa are reproduced with good accuracy from the standard deviation for eq 8. Hence it is concluded that eqs 7 and 8 can be used to estimate the dielectric parameters by making use of only $\epsilon_r(0.1)$ data.

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