Static Relative Permittivities of Water + Acetone and Water + Dimethyl Sulfoxide under Pressures up to 300 MPa at 298.15 K

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Liquid phase static relative permittivities ϵ_r of water + acetone and water + dimethyl sulfoxide have been measured over the whole mole-fraction range under pressures up to 300 MPa at 298.15 K. The pressure P dependence of ϵ_r values for each mixture was well fitted to the Tait-type equation, and the Tait-type parameters, A and B, were determined. For each aqueous mixture, the composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ values at 0.1 MPa evaluated from the static relative permittivity at 0.1 MPa, $\epsilon_r(0.1)$, and the Tait-type parameters was compared with that of the isothermal compressibility κ_T at 0.1 MPa. Values of $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ at 0.1 MPa as a function of composition were also compared for both aqueous mixtures. For pure acetone, $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ values at 0.1 MPa were correlated with temperature by a combination of the present values and the ones evaluated from the literature ϵ_r data.

Introduction

Acetone and dimethyl sulfoxide are versatile polar aprotic solvents, and each compound has the following chemical formula $(CH_3)_2X{=}O$; X = C for acetone and X = S for dimethyl sulfoxide. The static relative permittivity, well-known as the dielectric constant, at 0.1 MPa and 298.15 K, $\epsilon_r(0.1)$, for acetone is less than half of that for dimethyl sulfoxide, and there is a large difference in the dipole moment μ between these compounds (Riddick *et al.*, 1986). Hence it is considered that the $>S{=}O$ group in a dimethyl sulfoxide molecule is more polarizable than the $>C{=}O$ group in an acetone molecule. As a result, there are some possibilities of difference in intermolecular interactions of dimethyl sulfoxide or acetone with water. Many studies on the thermodynamic properties have been done so far to get some insight into the interactions in these aqueous systems.

In a previous paper (Uosaki *et al.*, 1996), we reported the pressure dependence of the static relative permittivities ϵ_r of water + 1-methyl-2-pyrrolidinone and water + 1,3-dimethyl-2-imidazolidinone in the liquid phase over the whole mole-fraction range under pressures up to 300 MPa at 298.15 K and evaluated $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ at 0.1 MPa as a function of composition for each mixture.

We have so far reported the preliminary static permittivity results for water + acetone (Moriyoshi and Uosaki, 1984). In this work, we report not only the liquid phase static relative permittivities of water + dimethyl sulfoxide over the entire mole-fraction range under pressures up to 300 MPa at 298.15 K but also the newly-determined static relative permittivities for water + acetone under the same conditions. In addition, we correlate ϵ_r values with pressure P by use of the Tait-type equation and we evaluate $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ values at 0.1 MPa, which are important for analyzing the thermodynamic properties of electrolyte solutions; some limiting partial molar volumes of electrolytes in water + acetone mixtures (Kawaizumi *et al.*, 1988) and in water + dimethyl sulfoxide mixtures (Garcia-Paneda *et al.*, 1996) have been reported.

Experimental Section

Acetone (Wako Pure Chemical Industries Ltd, >99%) was purified by the standard method (Riddick *et al.*, 1986). Under a N_2 stream at reduced pressure, dimethyl sulfoxide (Tokyo Kasei Kogyo Co. Ltd., >99%) was refluxed over CaH_2 for several hours and then distilled. Water was purified by the method described earlier (Uosaki *et al.*, 1996). Their purities were checked by comparing the measured refractive indices n_D at 298.15 K with those reported in the literature (Riddick *et al.*, 1986). All the mixtures were prepared by mass with a precision of 0.0001 g. The mole-fraction error is estimated to be less than 2×10^{-5}. The procedure and apparatus for measuring ϵ_r have been described in detail previously (Moriyoshi *et al.*, 1990). Temperature was controlled to ±0.01 K, and pressure was measured by a Bourdon gauge with an accuracy of 0.35 MPa. The uncertainty in ϵ_r is estimated to be within ±0.1%.

Results and Discussion

The ϵ_r measurements were made more than twice for each solution, and the values were reproducible to within ±0.1%. The averaged experimental values for water + acetone and water + dimethyl sulfoxide in the liquid phase at 298.15 K are listed in Table 1 as functions of P and the mole fraction of the organic component, x_2. Some literature values of the static relative permittivities at 0.1 MPa and 298.15 K, $\epsilon_r(0.1)$, for pure organic compounds are also included in Table 1 for comparison.

Figures 1 and 2 show the $\epsilon_r(0.1)$ values at 298.15 K for water + acetone and water + dimethyl sulfoxide as a function of composition, respectively. The literature $\epsilon_r(0.1)$ values for each aqueous mixture are also plotted for comparison. The present $\epsilon_r(0.1)$ values for water + acetone agree with the literature (Albright, 1937; Schiavo *et al.*, 1979) within ±0.8% over the whole mole-fraction range. For water + dimethyl sulfoxide, the literature values (Lindberg and Kenttämaa, 1960; Douheret and Morenas, 1967; Tommila and Pajunen, 1968; Schiavo *et al.*, 1979) are also in agreement with ours within ±0.8%.

Figures 3 and 4 show the pressure dependence of the experimental ϵ_r results for each solution. With increasing

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Table 1. Static Relative Permittivities ϵ_r for Water + Acetone and Water + Dimethyl Sulfoxide as a Function of Pressure at 298.15 K

	P/MPa											
x_2	0.1	10	20	30	40	50	100	125	150	200	250	300
						Water (1) + Acetone (2)						
0.200	53.56					55.15	56.54		57.76	58.87	59.88	60.81
0.400	38.76					40.39	41.69		42.79	43.75	44.61	45.39
0.600	30.07					31.59	32.76		33.71	34.53	35.26	35.91
0.800	24.63					26.05	27.10		27.94	28.66	29.30	29.87
1	20.74 20.74[a] 20.56[b]					22.06	23.00		23.77	24.40	24.96	25.45
						Water (1) + Dimethyl Sulfoxide (2)						
0.200	74.33					75.85	77.22		78.44	79.57	80.60	81.57
0.400	67.78					69.13	70.30		71.34	72.27	73.12	73.90
0.600	60.08					61.21	62.13		62.93	63.63	64.23	64.78
0.800	52.94					53.79	54.48	54.77	55.05			
1	46.41 46.60[b] 46.35[c] 46.45[d]	46.54	46.67	46.80	46.91	47.02						

[a] Albright, 1937. [b] Schiavo *et al.*, 1979. [c] Douheret and Morenas, 1967. [d] Casteel and Sears, 1974.

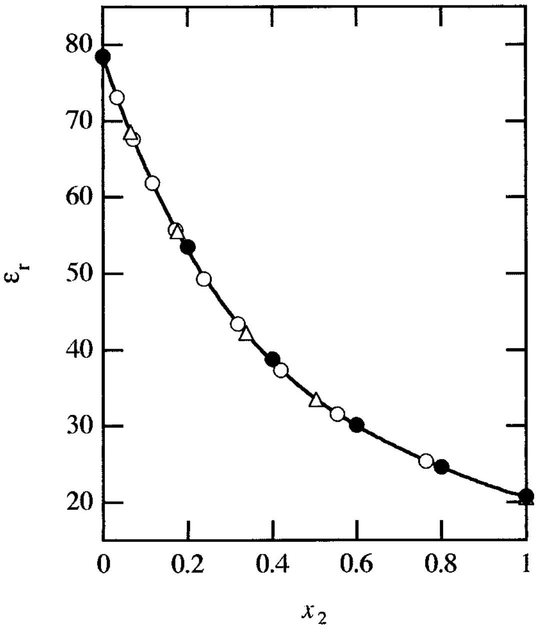

Figure 1. Static relative permittivities at 0.1 MPa and 298.15 K, $\epsilon_r(0.1)$, against mole fraction, x_2, for water (1) + acetone (2) (●, this work; ○, Albright, 1937; △, Schiavo *et al.*, 1979).

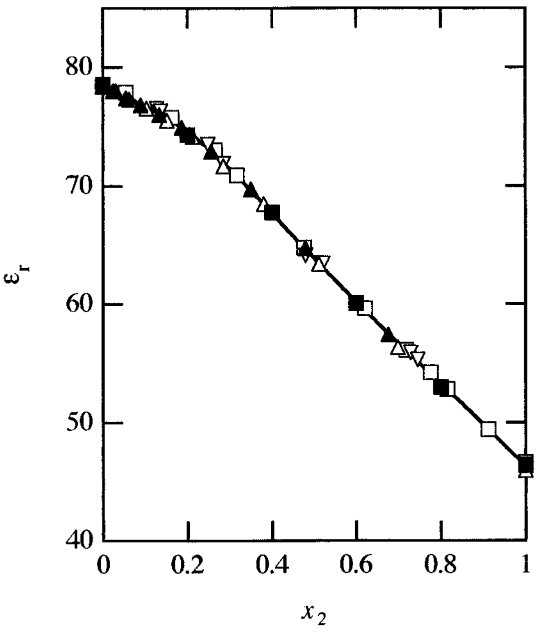

Figure 2. Static relative permittivities at 0.1 MPa and 298.15 K, $\epsilon_r(0.1)$, against mole fraction, x_2, for water (1) + dimethyl sulfoxide (2) (■, this work; □, Lindberg and Kenttämaa, 1960; ▲, Douheret and Morenas, 1967; △, Tommila and Pajunen, 1968; ▽, Schiavo *et al.*, 1979).

pressure, ϵ_r increases and $(\partial\epsilon_r/\partial P)_T$ becomes smaller. Some dimethyl sulfoxide solutions froze at high pressures. It is considered that the ϵ_r datum for pure dimethyl sulfoxide at 50 MPa and 298.15 K is the value under the superpressed state. After the capacitance measurements at 50 MPa were finished, the pressure was increased at the rate of about 3 MPa/min. Near 60 MPa, a sudden drop of the pressure to about 32 MPa was found because of the freezing of dimethyl sulfoxide. Compared with the estimated freezing pressure P_f, 40.9 MPa, at 298.15 K from the Simon equation (Fuchs *et al.*, 1980), the present value is relatively low. The pressure difference is mainly caused by the freezing of dimethyl sulfoxide that occurred in an endothermic process, so the temperature of dimethyl sulfoxide in a dielectric cell should be slightly lower than the temperature of 298.15 K; an estimated temperature of dimethyl sulfoxide at that pressure from the Simon equation is about 296.8 K, which is about 1.4 K lower than a water-bath temperature. In an aqueous dimethyl sulfoxide mixture of the composition $x_2 = 0.800$, the pressure drop from 170 MPa to 160 MPa was also found.

To correlate the pressure dependence of the ϵ_r data for each solution, we used the Tait-type equation of the form

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

where $\epsilon_r(P)$ is the static relative permittivity at the pressure P. The Tait-type parameters, A and B, for each solution, which were determined from the nonweighted least-squares method, are summarized in Table 2, along with the standard deviations $\sigma(\epsilon_r)$ of the fit. Furthermore, Table 2 includes the results for pure water (Moriyoshi *et al.*, 1990). In any solution the $\sigma(\epsilon_r)$ values in the present work are less than 0.01, which is within the experimental uncertainty and the reproducibility. Hence, the $\epsilon_r(P)$ value

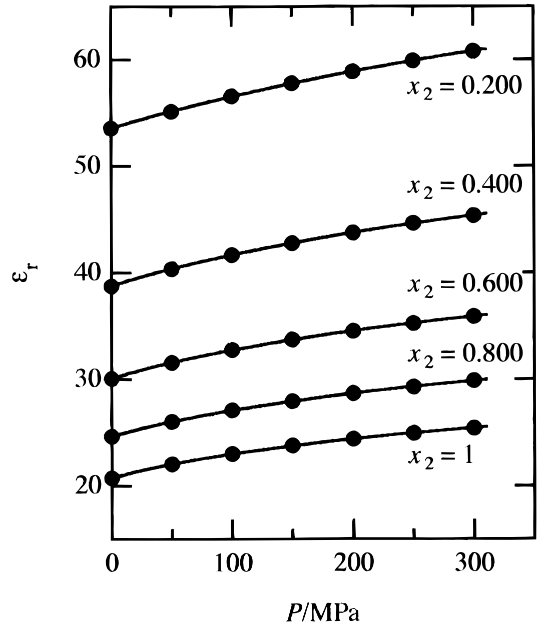

Figure 3. Pressure dependence of the static relative permittivities, ϵ_r, for water (1) + acetone (2) at 298.15 K. The smoothed curves are based on the parameters *A* and *B* in Table 2.

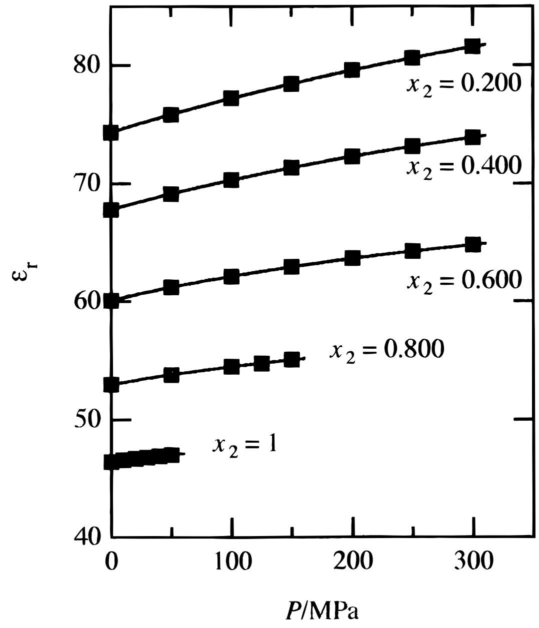

Figure 4. Pressure dependence of the static relative permittivities, ϵ_r, for water (1) + dimethyl sulfoxide (2) at 298.15 K. The smoothed curves are based on the parameters *A* and *B* in Table 2.

at any pressure up to the maximum pressure P_{max} can be evaluated very precisely from the Tait-type equation. Since Hartmann *et al.* (1965a) reported ϵ_r values of acetone up to 182.4 MPa at three temperatures, 293.15 K, 308.15 K, and 323.15 K, we also included the Tait-type parameters in Table 2, which were determined from their results; they applied some equations to analyze their ϵ_r data and reported some parameters similar to the Tait-type parameters (Hartmann *et al.*, 1965b).

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, $\sigma(\epsilon_r)$

x_2	T/K	$\epsilon_r(0.1)$	*A*	*B*	$\sigma(\epsilon_r)$	P_{max}[a]/MPa
		Water (1) + Acetone (2)				
0[b]	298.15	78.41	0.2185	463.6	0.02	300.0
0.200	298.15	53.56	0.1311	202.0	0.00	300.0
0.400	298.15	38.76	0.1182	122.9	0.00	300.0
0.600	298.15	30.07	0.1143	95.1	0.00	300.0
0.800	298.15	24.63	0.1131	80.7	0.01	300.0
1	293.15[c]	21.24	0.1043	68.4	0.01	182.4
	298.15	20.74	0.1115	70.3	0.01	300.0
	308.15[c]	19.75	0.1085	62.1	0.01	182.4
	323.15[c]	18.34	0.1047	49.0	0.01	182.4
		Water (1) + Dimethyl Sulfoxide (2)				
0.200	298.15	74.33	0.1194	271.8	0.01	300.0
0.400	298.15	67.78	0.09842	227.1	0.00	300.0
0.600	298.15	60.08	0.07063	166.8	0.01	300.0
0.800	298.15	52.94	0.05617	153.1	0.00	150.0
1	298.15	46.41	0.04750	158.4	0.01	50.0

[a] 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. [b] The data at this composition are cited from the literature (Moriyoshi *et al.*, 1990). [c] At these temperatures the $\epsilon_r(0.1)$, *A*, and *B* values are based on the ϵ_r data (Hartmann *et al.*, 1965a).

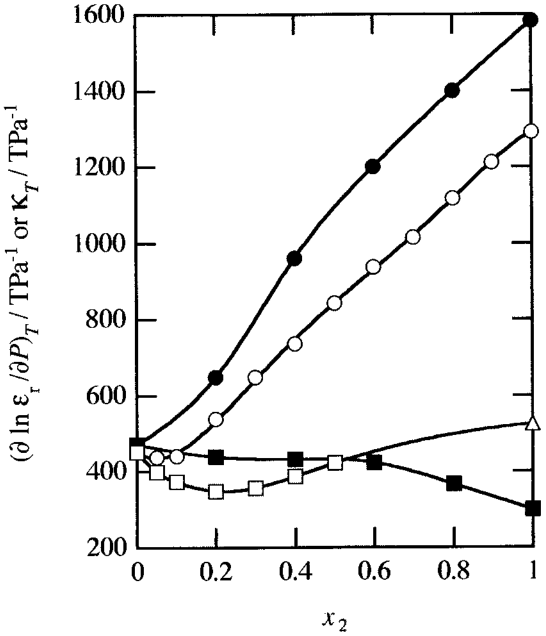

Figure 5. Composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ and κ_T at 0.1 MPa and 298.15 K for water (1) + acetone (2) (●, ○) and water (1) + dimethyl sulfoxide (2) (■, □). Closed and open symbols represent $(\partial \ln \epsilon_r/\partial P)_T$ and κ_T, respectively. The κ_T value for dimethyl sulfoxide at 0.1 MPa and 298.15 K (△) is cited from the literature (Tamura *et al.*, 1994).

The $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ values are respectively needed to obtain the thermodynamic properties such as the partial molar volume of electrolytes at infinite dilution from the apparent partial molar volume and to analyze the contribution of the electrostriction to the partial molar volume of an individual ion. These values at 0.1 MPa can be evaluated from $\epsilon_r(0.1)$ and the Tait-type parameters as follows:

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

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

For brevity we used ϵ_r for $\epsilon_r(P)$ in these equations.

Figure 5 shows the composition dependence of the calculated $(\partial \ln \epsilon_r/\partial P)_T$ values at 0.1 MPa and 298.15 K for each aqueous mixture, together with the isothermal compressibility, $\kappa_T = -(\partial \ln V/\partial P)_T$, at 0.1 MPa and 298.15 K,

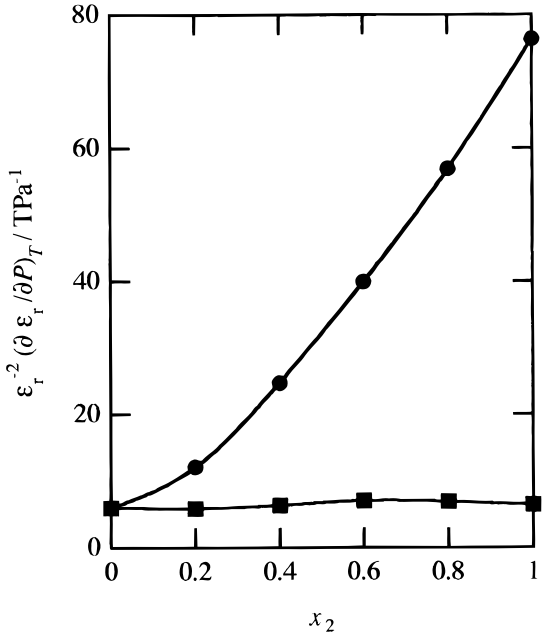

Figure 6. Composition dependence of $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ at 0.1 MPa and 298.15 K for water (1) + acetone (2) (●) and water (1) + dimethyl sulfoxide (2) (■).

because a rough correlation between $(\partial \ln \epsilon_r/\partial P)_T$ and κ_T values has been suggested without a theoretical basis (Kawaizumi and Zana, 1974). From the compression measurements, the κ_T values for water + acetone over the whole mole-fraction range and those for water + dimethyl sulfoxide in the composition range $x_2 = 0-0.5$ have been obtained (Moriyoshi and Uosaki, 1984). The κ_T value for pure dimethyl sulfoxide was taken from the literature (Tamura *et al.*, 1994). For water + acetone, there is a slight resemblance of the composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ and κ_T values, but $(\partial \ln \epsilon_r/\partial P)_T$ values are larger than κ_T values over the whole composition range; the largest deviation is found at $x_2 = 0.6$, and its value is about 23%. For water + dimethyl sulfoxide, the $(\partial \ln \epsilon_r/\partial P)_T$ values decrease with the composition, while the κ_T values show a minimum at $x_2 = 0.2$; the composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ values is very different from that of κ_T values. Also in this system, a large difference in magnitude between these values is found; the $(\partial \ln \epsilon_r/\partial P)_T$ value for pure dimethyl sulfoxide is 76% less than the κ_T value. From the previous paper (Uosaki *et al.*, 1996) and the present results, it should be noted that the use of κ_T values to estimate the $(\partial \ln \epsilon_r/\partial P)_T$ values gives unreliable results.

The $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ values as a function of x_2 are shown in Figure 6. The values for water + acetone increase from 6.01 at $x_2 = 0$ to 76.36 at $x_2 = 1$, while those for water + dimethyl sulfoxide vary only between about 6 and 7 and show no significant composition dependence.

The static relative permittivities for pure acetone under high pressures have been reported at three temperatures, 293.15 K, 308.15 K, and 323.15 K (Hartmann *et al.*, 1965a). Estimated $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ values at 0.1 MPa from their data are plotted against temperature in Figure 7, together with our results at 298.15 K. The values in the temperature range of 293.15 K to 323.15 K are well represented by the following equation:

$$X/\text{TPa}^{-1} = A_0 + A_1(T/\text{K}) + A_2(T/\text{K})^2 \qquad (4)$$

where X is $(\partial \ln \epsilon_r/\partial P)_T$ or $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$. Table 3 gives the parameters A_j, along with the standard deviation $\sigma(X)$ of the fit. In each case, the $\sigma(X)$ value is small enough to evaluate the values accurately at any temperature between 293.15 K and 323.15 K.

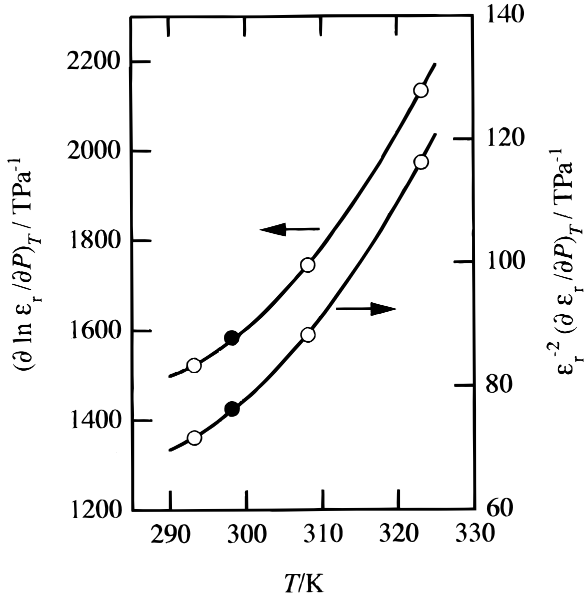

Figure 7. Temperature dependence of $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ at 0.1 MPa for acetone (●, this work; ○, Hartmann *et al.*, 1965a).

Table 3. Coefficients A_j and Standard Deviation $\sigma(X)$ for Least-Squares Representations of $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ for Acetone by Eq 4

X/TPa^{-1}	A_1	A_2	A_3	$\sigma(X)$
$(\partial \ln \epsilon_r/\partial P)T$	30082	−204.16	0.36412	4.7
$\epsilon_r^{-2}(\partial\epsilon_r/\partial P)T$	1986.8	−13.802	0.024797	0.38

Literature Cited

Albright, P. S. Experimental Tests of Recent Theories Descriptive of the Salting-out Effect. *J. Am. Chem. Soc.* **1937**, *59*, 2098−2104.

Casteel, J. F.; Sears, P. G. Dielectric Constants, Viscosities, and Related Physical Properties of 10 Liquid Sulfoxides and Sulfones at Several Temperatures. *J. Chem. Eng. Data* **1974**, *19*, 196−200.

Douheret, G.; Morenas, M. Dielectric Constants of Some Aqueous-organic Mixtures. *C. R. Acad. Sci. Paris, Ser. C* **1967**, *264*, 729−731 (in French).

Fuchs, A. H.; Ghelfenstein, M.; Szwarc, H. Melting Curve and Pressure-Volume-Temperature Data of Liquid Dimethyl Sulfoxide up to 150 MPa. *J. Chem. Eng. Data* **1980**, *25*, 206−208.

Garcia-Paneda, E.; Yanes, C.; Munoz de Miguel, E.; Maestre, A. Limiting Partial Molar Volumes of Tetra-*n*-alkylammonium Bromides in Dimethyl Sulfoxide + Water Mixtures at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1149−1151.

Hartmann, H.; Neumann, A.; Rinck, G. Pressure Dependence of the Dielectric Constants of Some Organic Liquids. *Z. Phys. Chem. N. F.* **1965a**, *44*, 204−217 (in German).

Hartmann, H.; Neumann, A.; Rinck, G. Analytic Description of the Pressure Dependence of the Dielectric Constants of Liquids. *Z. Phys. Chem. N. F.* **1965b**, *44*, 218−226 (in German).

Kawaizumi, F.; Zana, R. Partial Molal Volumes of Ions in Organic Solvents from Ultrasonic Vibration Potentials and Density Measurements. II. Ethanol and Dimethylformamide. *J. Phys. Chem.* **1974**, *78*, 1099−1105.

Kawaizumi, F.; Nakao, F.; Nomura, H. Partial Molar Volumes and Compressibilities of 1-1 Type Chlorides, Bromides, [Ph$_4$P]Cl, and [Ph$_4$B] in Water-Acetone Mixtures. *J. Chem. Eng. Data* **1988**, *33*, 204−211.

Lindberg, J. J.; Kenttämaa, J. Some Considerations of the Structure of Dimethyl Sulfoxide-Water Mixtures in the Light of Thermodynamic and Dielectric Behavior. *Suom. Kemist.* **1960**, *B33*, 104−107.

Moriyoshi, T.; Uosaki, Y. Compressive and Dielectric Properties of Aqueous Non-Electrolyte Mixtures. *J. Soc. Mater. Sci. Jpn.* **1984**, *33*, 127−133 (in Japanese).

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.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

Schiavo, S.; Fuoss, R. M.; Marrosu, G.; Guida, G. Ion Pairing of Quaternary Salts in Solvent Mixtures. *J. Solution Chem.* **1979**, *8*, 557−571.

Tommila, E.; Pajunen, A. The Dielectric Constants and Surface Tensions of Dimethyl Sulphoxide-Water Mixtures. *Suom. Kemist.* **1968**, *B41*, 172−176.

Tamura, K.; Murakami, S.; Akagi, Y.; Fukumori, M.; Kawasaki, Y. Thermodynamic Properties of Binary Mixtures: Hexamethylphosphoric Triamide + a Polar Liquid at 25 °C. *J. Solution Chem.* **1994**, *23*, 263−273.

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.

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