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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

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Static relative permittivities ϵ_r of water + 1-methyl-2-pyrrolidinone and water + 1,3-dimethyl-2-imidazolidinone mixtures have been measured over the whole mole-fraction range under pressures up to 300 MPa at 298.15 K. The experimental results as a function of pressure P for each mixture were fitted to the Tait-type equation, and the Tait-type parameters, A and B, were determined. Values of $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2} (\partial \epsilon_r/\partial P)_T$ at 0.1 MPa for both binary aqueous mixtures were evaluated from the static relative permittivity at 0.1 MPa, $\epsilon_r(0.1)$, and the Tait-type parameters and compared with each other. For the water + 1-methyl-2-pyrrolidinone mixture, values of $(\partial \ln \epsilon_r/\partial P)_T$ and the isothermal compressibility κ_T at 0.1 MPa as a function of composition were also compared.

Introduction

1-Methyl-2-pyrrolidinone and 1,3-dimethyl-2-imidazolidinone are, respectively, an N-alkylated cyclic amide and an N,N'-dialkylated cyclic urea. We find only one review on solvent properties for some ureas (Barker *et al.*, 1979). Urea is considered to be one of the amides because it has an amide group in the molecule. Hence both cyclic compounds are grouped into cyclic amides. These cyclic amides are not only versatile dipolar aprotic solvents but also ideal substitute solvents for the carcinogenic hexamethylphosphoric triamide. However, there are not many studies on the physical properties of the cyclic amides and their aqueous mixtures (Sears *et al.*, 1966; Virtanen, 1967; Korpela and Virtanen, 1967; Rosenfarb *et al.*, 1976; Langan and Saimon, 1987; Uosaki *et al.*, 1990, 1991).

These cyclic amides are completely miscible with water. In the previous paper (Uosaki *et al.*, 1990), we reported excess molar volumes V_m^E of binary aqueous mixtures of cyclic amides over the whole mole-fraction range at 298.15 K and 308.15 K at atmospheric pressure; V_m^E values for both binary aqueous mixtures are negative over the whole composition range, and each V_m^E minimum occurs around the amide mole fraction of 0.4. We also found that V_m^E values for the aqueous 1,3-dimethyl-2-imidazolidinone mixture were larger in magnitude than those for the aqueous 1-methyl-2-pyrrolidinone mixture at both temperatures. In this paper we report the static relative permittivities ϵ_r of both binary aqueous mixtures of cyclic amide over the whole mole-fraction range under pressures up to 300 MPa at 298.15 K. From the pressure P dependence of ϵ_r values, 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 properties of electrolyte solutions.

Table 1. Static Relative Permittivities ϵ_r for Water + Cyclic Amide Mixtures as a Function of Pressure at 298.15 K

	P/MPa								
x_2	0.1	25	50	75	100	150	200	250	300
	Water (1) + 1-Methyl-2-pyrrolidinone (2)								
0.200	60.33		61.66		62.82	63.85	64.81	65.67	66.49
0.400	48.84		50.00		51.01	51.89	52.70	53.41	54.07
0.600	41.28		42.39		43.35	44.17	44.91	45.56	46.18
0.800	35.94		37.03		37.95	38.76	39.48	40.13	40.72
1	32.16		33.22		34.11	34.87	35.56	36.19	
	32.0[a]								
	32.23[b]								
	Water (1) + 1,3-Dimethyl-2-imidazolidinone (2)								
0.200	58.90		60.12		61.21	62.15	63.02	63.80	64.54
0.400	48.84		49.86		50.71	51.44	52.08	52.65	53.15
0.600	43.52		44.57		45.42	46.13	46.76	47.30	
0.800	39.92		41.06		41.96	42.69			
1	37.47	38.08	38.61	39.11	39.55				
	37.60[c]								

[a] Sears *et al.*, 1966. [b] Langan and Saimon, 1987. [c] Rosenfarb *et al.*, 1976.

Experimental Section

Guaranteed-reagent grade 1-methyl-2-pyrrolidinone and 1,3-dimethyl-2-imidazolidinone were obtained from Wako Pure Chemical Industries Ltd. and Tokyo Kasei Kogyo Co., Ltd., respectively. According to the suppliers, the purity of the materials was better than 99%. Under a N_2 stream at reduced pressure, each compound was refluxed over CaH_2 for several hours and then distilled at least twice. Water was distilled from an alkaline solution of $KMnO_4$ and then distilled. 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; Uosaki *et al.*, 1990). All the mixtures were prepared by mass. The mole-fraction error is estimated to be less than 2×10^{-5}.

The measurements of ϵ_r were carried out by means of a transformer ratio-arm bridge with a three-terminal dielectric cell for frequencies in the range of 10 to 50 kHz. Details of the apparatus and experimental procedure for the measurements were described earlier (Moriyoshi *et al.*, 1990). The uncertainty in ϵ_r is estimated to be within ±0.1%.

Results and Discussion

The experimental ϵ_r values of binary aqueous mixtures of cyclic amides in the liquid phase under high pressures at 298.15 K are listed in Table 1, in which x_2 represents the mole fraction of organic components. Literature values

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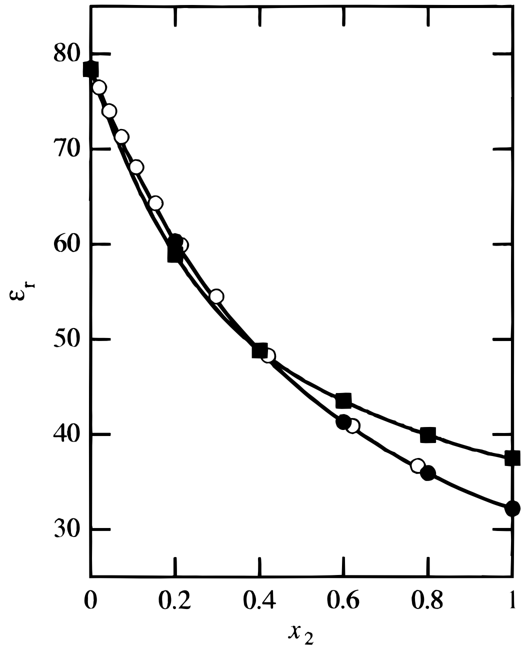

Figure 1. Static relative permittivities at 0.1 MPa, $\epsilon_r(0.1)$, against mole fraction, x_2, for water (1) + 1-methyl-2-pyrrolidinone (2) (●, this work; ○, Virtanen, 1967) and + 1,3-dimethyl-2-imidazolidinone (2) (■, this work) at 298.15 K.

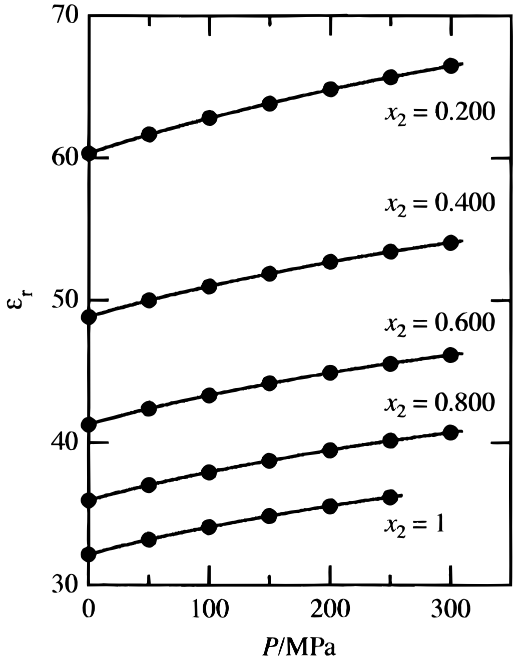

Figure 2. Pressure dependence of the static relative permittivities, ϵ_r, for water (1) + 1-methyl-2-pyrrolidinone (2) under high pressures at 298.15 K. The smoothed curves are based on the parameters *A* and *B* in Table 2.

of the static relative permittivities at 0.1 MPa and 298.15 K, $\epsilon_r(0.1)$, for pure cyclic amides are also given in Table 1 for comparison.

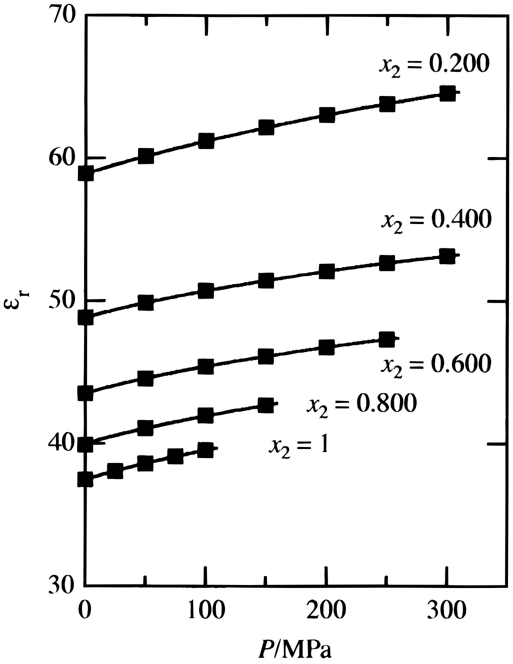

Figure 3. Pressure dependence of the static relative permittivities, ϵ_r, for water (1) + 1,3-dimethyl-2-imidazolidinone (2) under high pressures at 298.15 K. The smoothed curves are based on the parameters *A* and *B* in Table 2.

The composition dependence of $\epsilon_r(0.1)$ values at 298.15 K for water + 1-methyl-2-pyrrolidinone and water + 1,3-dimethyl-2-imidazolidinone mixtures obtained in the present work is shown in Figure 1, in which the literature values for the water + 1-methyl-2-pyrrolidinone mixture estimated from the $\epsilon_r(0.1)$ data measured at three temperatures, 283.15 K, 293.15 K, and 303.15 K, by Virtanen (1967) are also included for comparison. The interpolated $\epsilon_r(0.1)$ values from data by Virtanen are slightly higher than the present values over the whole mole-fraction range. When the composition dependence of $\epsilon_r(0.1)$ values for both aqueous mixtures of cyclic amides is compared, the $\epsilon_r(0.1)$ values for the aqueous 1-methyl-2-pyrrolidinone mixture are larger than those for the aqueous 1,3-dimethyl-2-imidazolidinone mixture in the lower mole-fraction range up to $x_2 = 0.4$ and the reverse is observed at higher mole fractions. The mole fraction at which the composition dependence of $\epsilon_r(0.1)$ values for both aqueous mixtures crosses becomes slightly larger with an increase in pressure.

Figures 2 and 3 show the experimental results for each binary aqueous mixture as a function of pressure. In all cases ϵ_r increases with a rise in pressure and $(\partial\epsilon_r/\partial P)_T$ becomes smaller with pressure. Some solutions froze at high pressures, as shown by a sudden drop of ϵ_r. The freezing pressure at 298.15 K for pure 1-methyl-2-pyrrolidinone is about 280 MPa, while that for pure 1,3-dimethyl-2-imidazolidinone is about 120 MPa. Aqueous 1,3-dimethyl-2-imidazolidinone mixtures of the compositions $x_2 = 0.600$ and $x_2 = 0.800$ froze around 280 MPa and 170 MPa at 298.15 K, respectively. Other aqueous mixtures of 1-methyl-2-pyrrolidinone and of 1,3-dimethyl-2-imidazolidinone show no indication of freezing up to 300 MPa at 298.15 K.

For each mixture, we correlated the ϵ_r values as a function of pressure with 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* at 298.15 K. The Tait-type parameters, *A* and *B*, for each mixture were determined from the nonweighted least-squares method and are listed in Table 2, together with the standard deviations $\sigma(\epsilon_r)$ of the fit. In any case the $\sigma(\epsilon_r)$ values are less than 0.01, which is within experimental uncertainty. Therefore it is suggested that the pressure dependence of ϵ_r is represented very precisely by the Tait-type equation.

Table 2. Parameters of the Tait-Type Equation and Standard Deviations $\sigma(\epsilon_r)$ at 298.15 K

x_2	A	B	$\sigma(\epsilon_r)$
Water (1) + 1-Methyl-2-pyrrolidinone (2)			
0.200	0.1161	245.8	0.01
0.400	0.1084	207.7	0.01
0.600	0.1091	182.3	0.01
0.800	0.1183	176.4	0.00
1	0.1213	166.4	0.01
Water (1) + 1,3-Dimethyl-2-imidazolidinone (2)			
0.200	0.1066	236.4	0.01
0.400	0.07987	169.8	0.01
0.600	0.08004	145.5	0.01
0.800	0.09118	149.3	0.01
1	0.1003	144.8	0.01

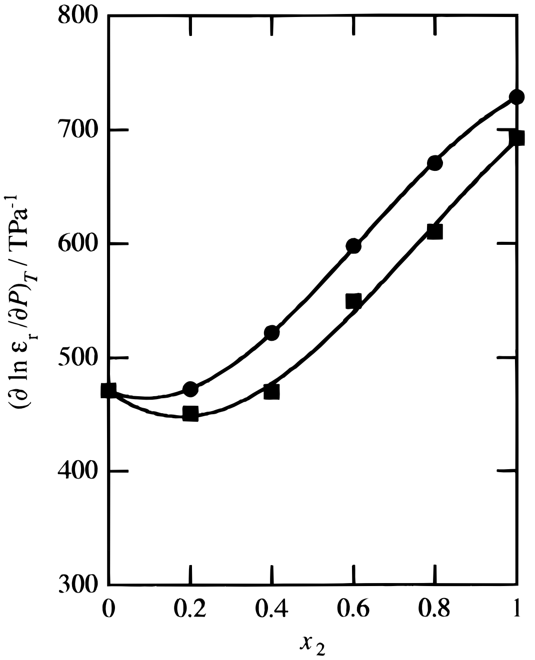

Figure 4. Composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ at 0.1 MPa and 298.15 K for water (1) + 1-methyl-2-pyrrolidinone (2) (●) and +1,3-dimethyl-2-imidazolidinone (2) (■).

The values of $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ are essential quantities to analyze physical properties in electrolyte solutions. We estimate these values at 0.1 MPa from $\epsilon_r(0.1)$ and the Tait-type parameters as follows:

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

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

In these equations we used ϵ_r in place of $\epsilon_r(P)$ for simplicity.

Figures 4 and 5 represent the calculated $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ values at 0.1 MPa and 298.15 K for each binary aqueous mixture as a function of x_2. From Figure 4 we find that there is a shallow minimum at lower x_2 for the water + 1,3-dimethyl-2-imidazolidinone mixture; its composition is about 0.2. On the other hand, the $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ value increases with x_2 for each mixture, as shown in Figure 5. Such a composition dependence of $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ has been observed in the water + ethanol mixture (Moriyoshi *et al.*, 1990).

Some studies on the temperature dependence of ϵ_r have been reported for binary aqueous mixtures, but studies on the pressure dependence of ϵ_r are limited and hence there are few $(\partial \ln \epsilon_r/\partial P)_T$ and $\epsilon_r^{-2}(\partial\epsilon_r/\partial P)_T$ values for specified solutions. An estimation method of $(\partial \ln \epsilon_r/\partial P)_T$ has been suggested (Kawaizumi and Zana, 1974). In this method, the following relation was used, with an accuracy of about 10%:

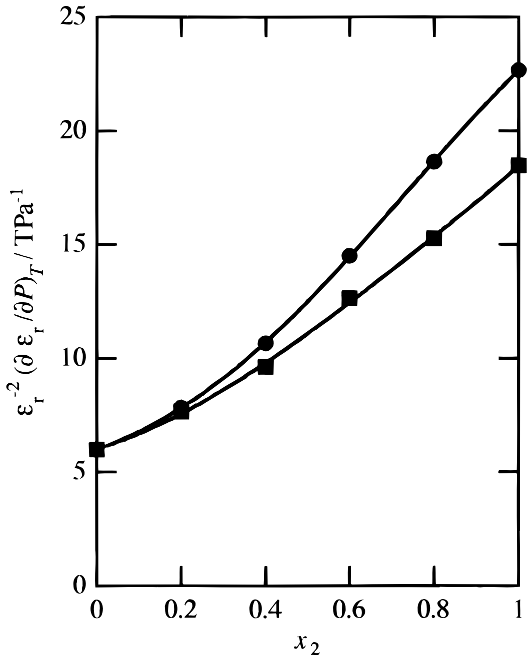

Figure 5. Composition dependence of $\epsilon_r^{-2}(\partial \epsilon_r/\partial P)_T$ at 0.1 MPa and 298.15 K for water (1) + 1-methyl-2-pyrrolidinone (2) (●) and +1,3-dimethyl-2-imidazolidinone (2) (■).

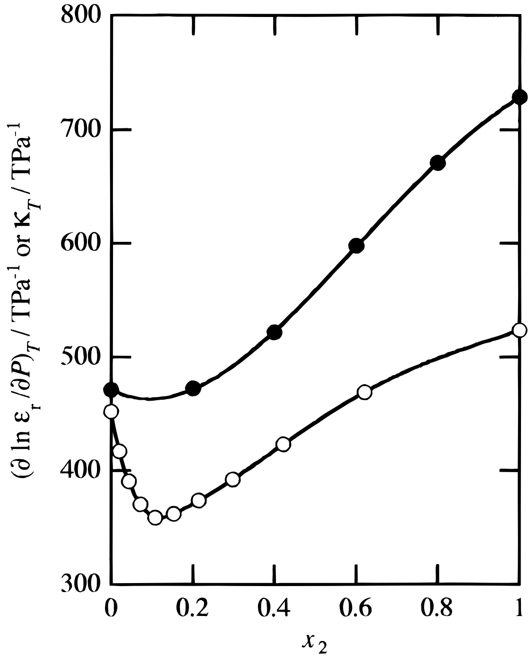

Figure 6. Composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ (●) and κ_T (○) at 0.1 MPa and 298.15 K for water (1) + 1-methyl-2-pyrrolidinone (2).

$$\left(\frac{\partial \ln \epsilon_r}{\partial p}\right)_T \approx \kappa_T \tag{4}$$

In this equation κ_T is the isothermal compressibility as $\kappa_T = -(\partial \ln V/\partial P)_T$. Although there is no theoretical basis, it was reported that there was a good agreement between both values, especially for water. To ascertain whether the above approximate relation holds or not, $(\partial \ln \epsilon_r/\partial P)_T$ and κ_T values for the water + 1-methyl-2-pyrrolidinone mixture are plotted as a function of x_2 in Figure 6, because no κ_T values for the water + 1,3-dimethyl-2-imidazolidinone mixture are available in the literature. A slightly similar composition dependence of $(\partial \ln \epsilon_r/\partial P)_T$ and κ_T is found in Figure 6, but a fair disagreement between these values is observed, except for water; there is an approximately 4% difference for water, but approximately 40% for 1-methyl-2-pyrrolidinone. These results suggest the use of eq 4 to obtain $(\partial \ln \epsilon_r/\partial P)_T$ leads to poor values.

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