

물아닌 용액에서의 용질의 행동에 관한 연구 (제 3 보).
디메틸설폭시드에서의 요소의 회합상수

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The Behavior of Solutes in Nonaqueous Solutions (III).
Association Constant of Urea in Dimethyl Sulfoxide

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All the physico-chemical data in our previous works seem to indicate that self-association of urea in dimethyl sulfoxide (DMSO) is very significant^{1,2}. Particularly, the IR data showed that self-association of urea molecule in the solvent may be predominant not only through N-H...N-H but also through C=O...N-H.³ Here we felt that this present note was necessary in order to give more quantitative interpretations of osmotic behavior of urea in DMSO reported in the previous work². Studies at low concentrations made it possible to presume that the osmotic nonideality of urea could be attributed to only self-association of urea in DMSO. Any other effects leading to nonideality are assumed to be less important. The osmotic activity coefficients (solute), γ , is related to the osmotic coefficients (solvent), ϕ , by equation (1)⁴.

$$\ln \gamma = (\phi - 1) + \int_0^{m_2} (\phi - 1) / m_2 dm_2 \quad (1)$$

γ can be expressed by the form

$$\gamma = m_1 / m_2$$

where m_2 is the total stoichiometric concentra-

tion and m_1 is the molal concentration of the free monomer.

In an attempt to explain the concentration dependence of osmotic properties of urea, consecutive self-association of the monomeric solutes was assumed to proceed to some degree⁵. Since activity coefficient is the ratio of the free monomer to the stoichiometric concentration, a series expansion can be used to obtain the association constants (expansion coefficients) by using equation (2)⁶⁻⁸ where $K_2 = m_2 / (m_1)^2$

$$1/\gamma - 1 = 2K_2 m_1 + 3K_3 (m_1)^2 + \dots \quad (2)$$

$K_3 = m_3 / (m_1)^3$, ..., and m_2 is the molal concentration of the dimer and m_3 is that of the trimer. Fitting higher than quadratic is not meaningful, because it gives the scatter in the data. The constants obtained through the least square method are shown in Table 1. Even though values of the association constants (K_2 and K_3) are relatively small, they indicate that urea molecules become actually associated in DMSO to some extent^{3,13}. To check these results, an assumption was made again. If solute is present as an equilibrium mixture of

monomer and dimer only, dimer-restricted association constant (K_2^*) can be calculated by using only the first term on the right side of the equation (2). Values of K_2^* are expected to be some what larger than K_2 , because the quadratic term was neglected. Values of K_2^* listed in Table 1 showed larger ones than K_2 as expected. To check these values, another dimerization model was used and dimerization constant K_d , was calculated by equation (3)^{3,9,10}.

$$K_d = (1-\phi) / m_2(2\phi-1)^2 \quad (3)$$

Values of K_d also listed in Table 1 showed concentration independence and only less than 10 % difference from the values of K_2^* . These results indicate that value of K_2 is reasonable and significant.

To understand osmotic nonideality of urea more closely, a multiplication model which is characterized by the same degree of association all over the association steps was used. The single polymerization constants all over the concentration, K_p , can be calculated by equation(4)¹¹.

$$K_p = (1-\phi) / (m_2\phi^2) \quad (4)$$

Values of K_p shown in Table 1 decreased with increasing of concentration, and they are far from constant¹². Thus this model can not be selected as describing the system better. This result also indicates that urea in DMSO becomes associated with different degree of association, and that the first successive association model explains the system better¹³⁻¹⁵.

Therefore, osmotic nonideality of urea in DMSO could be understood in terms of successive association to be dimer and trimer with different degree of association.

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Table 1. Association constants obtained from various models.

m	ϕ^*	r^*	K_2 m^{-1}	K_2 m^{-2}	K_2^*	K_d	K_p
0.010	0.986	0.975			1.33	1.48	1.49
0.020	0.973	0.949			1.42	1.50	1.50
0.030	0.963	0.929			1.36	1.44	1.32
0.040	0.950	0.905			1.45	1.54	1.39
0.050	0.938	0.885	1.15	3.21	1.47	1.64	1.41
0.070	0.921	0.847			1.52	1.59	1.34
0.100	0.906	0.822			1.32	1.42	1.15
0.120	0.895	0.789			1.40	1.48	1.09
0.160	0.875	0.750			1.39	1.39	1.03

*Data from reference 2.