

물아닌 용매에서의 용질의 행동에 관한 연구(제1보).  
요소, 1, 3-디메틸요소 및 1, 1, 3, 3-테트라메틸  
요소의 겉보기 몰랄부피

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The Behavior of Solutes in Non-Aqueous Solvents(I).  
The Apparent Molal Volumes of Urea, 1, 3-  
Dimethylurea and 1, 1, 3, 3-tetramethylurea

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**요 약.** 요소, 1, 3-디메틸요소(DMU) 및 1, 1, 3, 3-테트라메틸요소(TMU)의 25°C에서의 겉보기 몰랄부피를 dimethylsulfoxide와 메탄올용액에서 밀도측정으로 얻었다. Dimethylsulfoxide에서 요소는 특히 묽은 용액에서 자체회합성을 보이고, DMU와 TMU는 용질-용매상호작용을 함을 알았다. 한편, 양성자성 용매인 메탄올에서 위의 3가지 용질분자는 모두 용질-용매상호작용을 우세하게 일으키고 있음을 알았다.

**ABSTRACT.** Apparent molal volumes of urea, 1, 3-dimethylurea(DMU), and 1, 1, 3, 3-tetramethylurea(TMU) in dimethylsulfoxide(DMSO) and in methanol have been measured at low concentration by the density measurements at 25°C.

It is confirmed that urea molecules in the dilute DMSO solution self-associate to a greater extent than in the concentrated solution, while DMU and TMU molecules in DMSO solutions interact with the solvent molecules. In addition, the molecules of the three solutes also interact predominately with methanol molecules.

INTRODUCTION

Urea is soluble in water as well as in dipolar aprotic solvents. Although the physicochemical properties of urea-water system have been ex-

tensively studied,<sup>1-6</sup> relatively little is known about the behavior of urea in nonaqueous solvents.

In an attempt to explain the concentration dependence of thermodynamic properties of urea in water, Stokes<sup>7</sup> employed an association model of the form,

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$$\begin{aligned} U+U &= U_2 \\ U_2+U &= U_3 \end{aligned} \quad (1)$$

and derived thermodynamic parameters governing the above equilibria by the Flory-Huggins (volume-fraction) statistics.

The results would tend to indicate that the activity variations of urea and heats of solutions were satisfactorily explained by urea-urea association in urea solution.

Frank and Franks<sup>8</sup> have also explained the thermodynamic properties of aqueous urea solutions by a different model in which urea is assumed to mix ideally with a postulated "dense" (nonhydrogen-bonded) species of water. On the basis of this formalism, their calculations show that urea would cause structure breaking by lowering the chemical potential of the dense species and therefore by shifting the equilibrium.

Recently a NMR study,<sup>9</sup> as a non-thermodynamic method, has been made in a study of aqueous urea solutions. From the results, it has been concluded that there is no evidence for the existence of long-lived dimers or higher aggregates of urea in the solution.

With the above considerations, the decision which model does, in fact, describe the real situation is not an easy one. It, therefore, is desirable to investigate the behavior of urea in solution in detail.

In the present work it has been tried to elucidate the behavior of urea in non-aqueous solvents by studying the concentration dependence of the apparent molal volumes of urea. The apparent molal volumes of the solutes are appropriate to study solute-solute and solute-solvent interaction, since volume properties are easy to visualize geometrically. This report covers only the initial results which have been obtained for urea- and methyl-substituted urea-dimethylsulfoxide and methanol systems.

## EXPERIMENTAL

**Materials.** Dimethylsulfoxide(E. P. Grade from E. Merck) was purified by vacuum distillation, and was treated with molecular sieves 4A(Linde type from M. C. & B.) before use. Absolute methanol (G. R. grade from E. Merck) was used without further purification. Urea and 1,3-dimethylurea (E. P. grade from E. Merck) were recrystallized in methanol-chloroform mixed solvent. 1,1,3,3-tetramethylurea was twice distilled.

**Methods.** Density of the solutions were measured with a densitometer modified in this laboratory after Sinker method (sketched in Fig. 1),<sup>10</sup> equipped with a circulating thermostat.

Temperature was maintained at  $25.0 \pm 0.1^\circ\text{C}$  during the measurements. Reported values are the average of three of five measurements for each solution and have a precision of 0.1~0.3%. The infrared spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer Model 521.

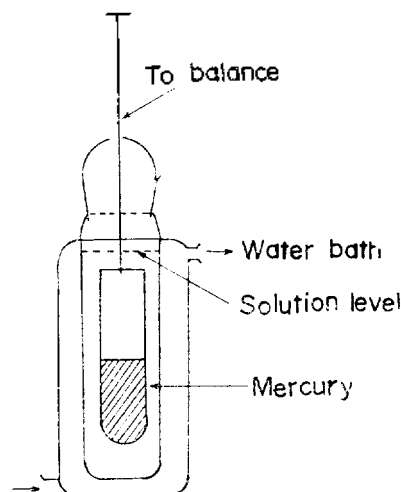


Fig. 1. Float assembly for measurement of densities of solutions.

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**Calculation.** Density,  $d$ , of the solutions was given by

$$d = d_0 + \frac{W_0 - W}{V} \quad (2)$$

where  $d_0$  is the density of pure solvent;  $W_0$  and  $W$  are the weights of the float in pure solvent and in solutions, respectively, and  $V$  is the volume of the float.

In terms of the experimentally measured density,  $d$ , the apparent molal volume  $\phi_v$  is calculated by the expression (3).

$$\phi_v = \frac{1000(d_0 - d)}{md_0d} + \frac{M_2}{d} \quad (3)$$

where  $M_2$  is the molecular weight of solute and  $m$  is the molality of solution.

## RESULTS AND DISCUSSION

The partial molal volume of solute in solution ( $\bar{V}_2$ ) is given by equation (4).

$$\bar{V}_2 = \phi_v + m \left( \frac{\partial \phi_v}{\partial m} \right) \quad (4)$$

Table 1. Apparent molal volumes of urea, 1,3-dimethylurea, and 1,1,3,3-tetramethylurea in dimethylsulfoxide at 25°C.

Urea		Dimethylurea		Tetramethylurea	
molal concn. $\times 10^2$	$\phi_v$	molal concn. $\times 10^2$	$\phi_v$	molal concn. $\times 10^2$	$\phi_v$
1.2	47.7	1.4	84.3	1.7	107.6
2.0	46.7	2.0	84.9	3.4	107.5
2.6	44.6	2.6	85.8	5.2	107.6
2.7	44.4	3.9	85.9	9.9	107.5
3.7	43.0	4.6	86.2	9.2	107.6
4.0	42.9	5.5	86.0	11.4	107.6
5.3	42.5	5.8	86.1	13.4	107.8
8.4	42.1	6.7	86.1	15.0	107.9
10.7	42.2	8.1	86.2	18.6	107.9
12.0	42.1	8.8	86.2	19.2	108.0
13.2	42.0	10.0	86.3	21.5	108.0
14.9	41.8				
16.4	41.6				

where  $\phi_v$  is the apparent molal volume which can be obtained from density data, and  $m$  molality of solute. The slope  $\left( \frac{\partial \phi_v}{\partial m} \right)$  is obtained from the plotting of  $\phi_v$  against  $m$ .

The apparent molal volumes of urea, 1,3-dimethylurea(DMU), and 1,1,3,3-tetramethylurea(TMU) in dimethylsulfoxide(DMSO) and methanol solutions are listed in Table 1 and Table 2.

As seen in Fig. 2, the slope  $\left( \frac{\partial \phi_v}{\partial m} \right)$  for urea in DMSO is negative, while those for DMU and TMU give the very small and positive values. These results indicate that the behavior of urea molecule is quite different from those of DMU and TMU molecules in DMSO solutions. In general, it is well known that the negative slope indicate the solute interaction in solution, and the positive slope is thought to reflect the solute-solvent interaction in solution. In particular, urea solution exhibits the large negative slope in the dilute solution

Table 2. Apparent molal volumes of urea, 1,3-dimethylurea and 1,1,3,3-tetramethylurea in methanol at 25°C

Urea		Dimethylurea		Tetramethylurea	
molal concn. $\times 10^2$	$\phi_v$	molal concn. $\times 10^2$	$\phi_v$	molal concn. $\times 10^2$	$\phi_v$
1.2	26.0	1.3	69.6	2.2	114.1
2.3	27.4	1.9	69.5	4.4	114.4
2.9	28.0	2.4	69.0	6.6	114.5
3.5	28.2	3.5	69.5	8.8	114.5
4.4	28.3	4.5	69.9	10.1	114.2
5.4	28.5	5.2	70.5	12.3	115.2
6.2	28.6	6.3	70.8	14.5	115.2
6.9	28.7	6.9	70.7	16.8	115.4
8.5	29.5	8.1	70.9	19.0	116.1
9.3	29.9	9.0	70.8	21.3	115.9
10.6	30.9	9.7	70.9	24.6	116.2
11.8	31.5	10.9	70.8	25.8	116.2
12.8	32.1	11.9	71.0	28.1	116.3

to  $m=0.05$ . This means that urea molecules in the dilute solution self-associate to a greater extent than in the more concentrated solution. The similar phenomenon was observed in study on osmotic coefficients of urea in DMSO solution.<sup>12</sup> On the other hand, it is obvious from Fig. 2b and Fig. 2c that DMU molecules interact predominantly with the solvent molecules, and that TMU molecules seem to exhibit little cooperative effect with DMSO molecules as well as with themselves. Fig. 3, showing the plots of  $\phi_v$  vs.  $m$ , reveals the somewhat different effect with DMSO solutions. The behavior of urea in methanol changes into the inverse effect comparing with it in DMSO. The curve shows clearly the positive slope. The positive slopes are interpreted as indicating solute-solvent interaction and then structure-breaking effects,

<sup>13a,b</sup> and is generally observed in aqueous solutions of normal electrolytes. As seen in Fig. 3b and c, DMU and TMU in methanol have the same characteristic behavior in DMSO, although the slopes indicate that the solute-solvent interactions in methanol are greater than in DMSO.

In addition ir spectra have been studied to confirm the self-association of urea molecules in DMSO solution(Fig. 4 and Fig. 5). As seen in Fig. 4d, DMU gives C=O stretching vibration at  $1650\text{cm}^{-1}$  and N-H bending vibration at  $1550\text{cm}^{-1}$ . The two bands are completely separated with increasing concentration of solute and also even in the solution of 0.02 molality(Fig. 4b). For urea, however, the stretching vibration is observed at  $1670\text{cm}^{-1}$  and the bending vibration at  $1620\text{cm}^{-1}$ . From Fig. 5, one observes that these vibration bands are overlapped even

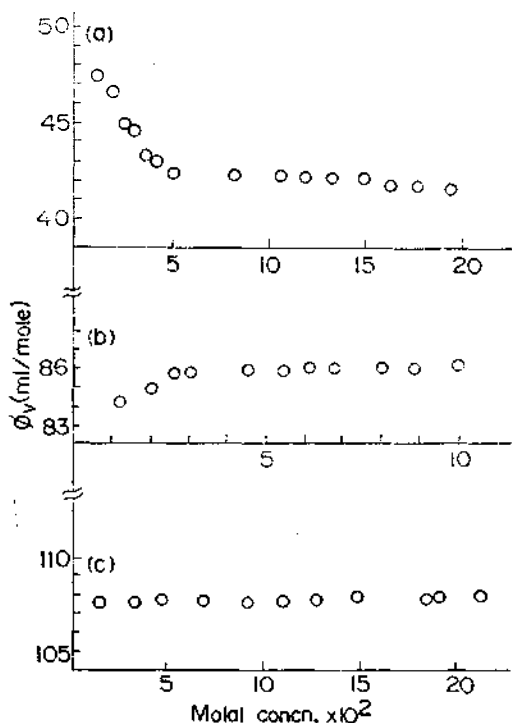


Fig. 2. Apparent molal volumes vs. molal concentration of a) Urea, b) 1,3-dimethylurea, c) 1,1,3,3-tetramethylurea in DMSO at 25°C

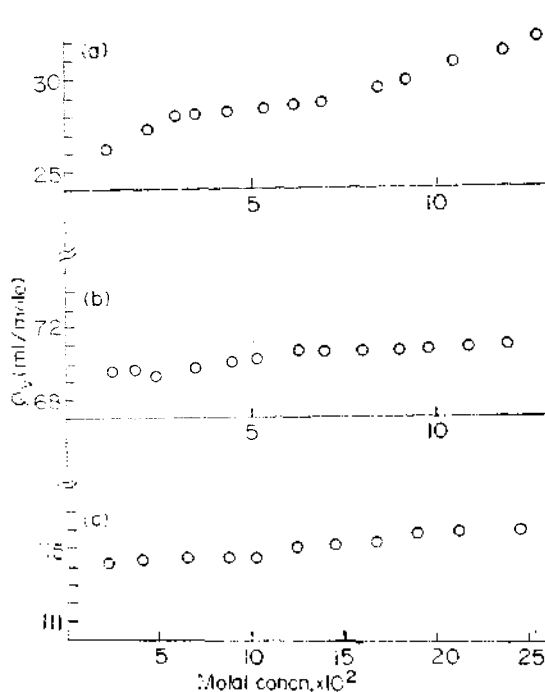


Fig. 3. Apparent molal volumes vs. molal concentration of a) urea, b) 1,3-dimethylurea, c) 1,1,3,3-tetramethylurea in MeOH at 25°C

in the solution 0.5 malality. This indicates the self-association of urea molecules in the solution

may may be predominant not only through  $N-H\cdots N-H$ , but also through  $C=O\cdots H-N$ .

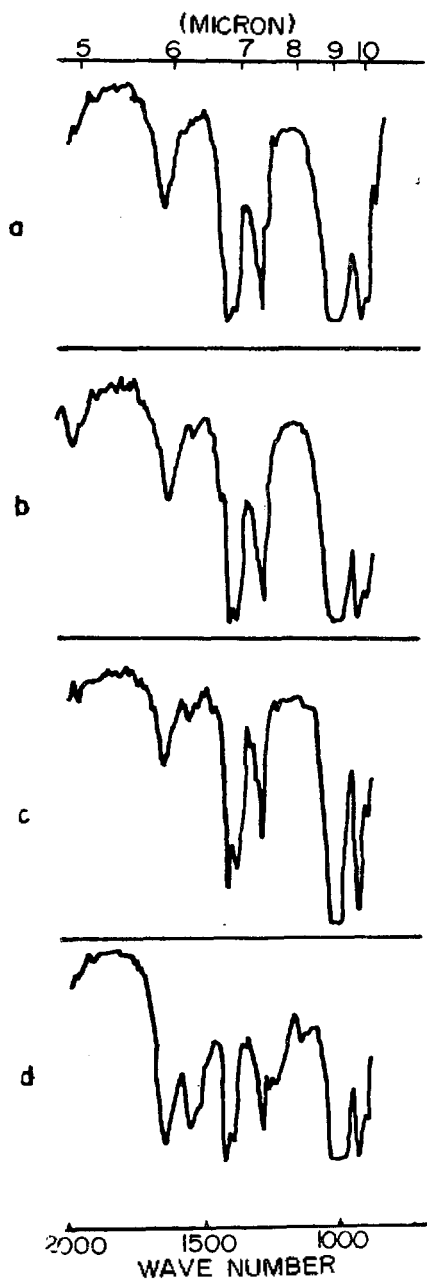


Fig. 4. IR spectra of dimethylurea-DMSO solution a) 0.02mole/l, b) 0.04mole/l, c) 0.1mole/l, d) 0.5 mole/l.

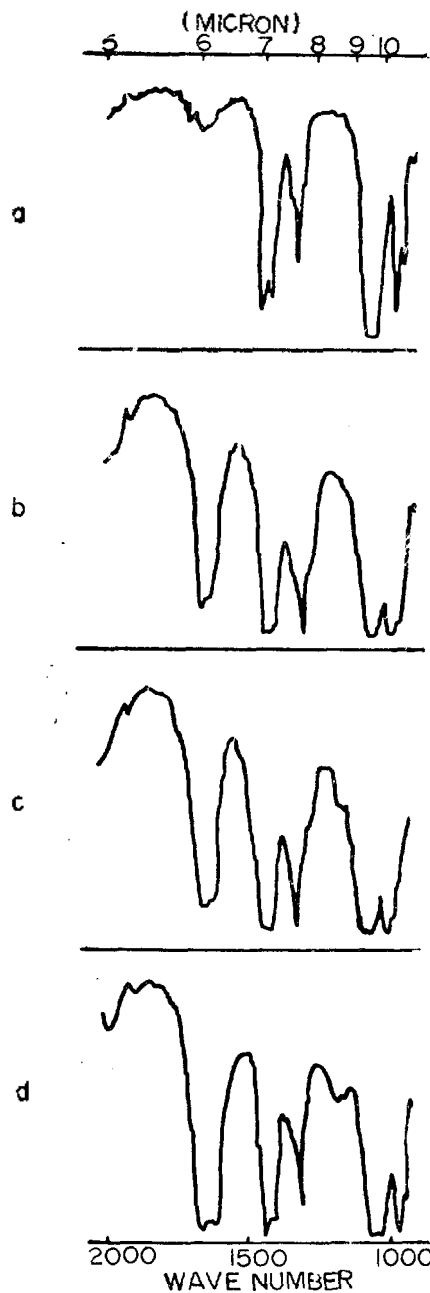


Fig. 5. IR spectra of urea-DMSO Solution a) pure DMSO, b) 0.02mole/l, c) 0.1 mole/l, d) 0.5mole/l.

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