

사염화탄소에서 디메틸설폭시드의 삼투계수와 활동도계수

金永吉 · 辛永國†

충북대학교 자연과학대학 화학과

(1991. 5. 15 접수)

Osmotic and Activity Coefficients of Dimethylsulfoxide
 in Carbon Tetrachloride

Young-Gil Kim and Young-Kook Shin†

Department of Chemistry, College of Natural Science, Chungbuk National University,
 Cheongju 360-763, Korea

(Received May 15, 1991)

Some experiments on the behavior of dimethylsulfoxide (DMSO)¹ in carbon tetrachloride by infrared and light scattering spectroscopy^{2,3} gave evidences for association of DMSO in the solvent. Particularly, Szmant² reported that the association of DMSO in CCl₄ in the low concentration range (0.01~0.3M) was limited to the formation of dimers. The dimerization constant was estimated to be 0.9 mol/l at about 27°C. However, higher DMSO aggregation than dimerization is not obvious, because his procedure was justified as long as the equilibrium was limited to the formation of dimers. In connection with the above studies, we have felt that it is necessary to give more quantitative interpretation on the DMSO behavior in CCl₄. Therefore, in this note we have determined practical osmotic coefficient (ϕ) of DMSO in CCl₄ at 30°C using a Knauer vapor pressure osmometer Model 18533 in combination with a digital meter and a chart recorder. The principle and practice of the vapor pressure osmometry were well described elsewhere^{4,5}. The relation between osmotic coefficient to osmotic activity coefficient (γ) was also described elsewhere^{6,7}. Osmotic coefficients and calculated values of activity coefficients are listed in Table 1.

Studies at low concentration and positive deviation from Raoult's law ($\phi < 1$) as shown in Table 1 made it possible to presume that the osmotic

nonideality of DMSO in CCl₄ could be attributed to the self association of DMSO in the organic medium. 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 (1)⁸

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

where $K_2 = m_2/(m_1)^2$, $K_3 = m_3/(m_1)^3$, ..., and m_1 , m_2 , and m_3 ... are molal concentration of the free mo-

Table 1. Osmotic coefficients, activity coefficients, and association constants of DMSO in carbon tetrachloride at 30°C

m_1^a	ϕ	γ	K_2 m^{-1}	K_3 m^{-2}	K_2^*	K_d	K_p
0.01	0.985	0.971			1.54	1.59	1.55
0.02	0.973	0.945			1.54	1.51	1.43
0.03	0.960	0.920			1.58	1.58	1.45
0.04	0.951	0.901			1.52	1.51	1.36
0.05	0.941	0.881	1.50	1.22	1.53	1.52	1.33
0.07	0.923	0.846			1.54	1.54	1.29
0.10	0.899	0.800			1.56	1.59	1.25
0.12	0.885	0.773			1.58	1.62	1.22
0.16	0.860	0.728			1.60	1.69	1.18
0.20	0.840	0.688			1.65	1.73	1.13

^aInterpolated values from experimental concentrations.

monomer, dimer, and trimer, respectively. Fitting higher than quadratic terms is meaningless, because it gives a scatter in the data. The constants obtained by means of the least square method are listed in Table 1. They indicated that DMSO molecules become associated in CCl_4 to some extent although the values are relatively small. To examine the results, an assumption was made again. If DMSO molecules were presented as an equilibrium mixture of monomer and dimer only, dimer restricted association constant, K_2^* can be obtained by using only the first term on the right side of the equation (1)⁴. The values of K_2^* are expected to be somewhat larger than that of K_2 , because the quadratic term was neglected. The values of K_2^* listed in Table 1 are somewhat larger than that of K_2 as expected. To check the values more closely, another dimerization model⁶ was used, and the dimerization constant, K_d was calculated by equation (2).

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

where m_s is the total stoichiometric concentration. Independence of K_d over the range of concentration as shown in Table 1 also indicated that the value of K_d is reasonable and significant. To understand the osmotic nonideality of DMSO in CCl_4 intently, a multiplization model⁹ which is characterized by the same degree of association in every association step was used. The single polymerization constants, K_p can be calculated by equation (3).

$$K_p = (1 - \phi) / (m_s \phi^2) \quad (3)$$

The calculated K_p values in Table 1 are far from constant. Thus the multiplization model could not be selected as a model describing the DMSO behavior in CCl_4 well.

In conclusion, association of DMSO in CCl_4 can be said to be substantial at the concentration range (0.01~0.2 m), and the dimerization constant obtained by vapor pressure osmometry is close to that by infrared spectroscopy. Further investigation must be executed to make higher aggregation of DMSO in CCl_4 unequivocal.

REFERENCES

1. I. D. Brown, *J. Solution Chem.*, **16**, 205 (1987).
2. H. H. Szmant in "Dimethyl Sulfoxide", S. W. Jacob, E. E. Rosenbaum, and D. C. Wood, Eds., Marcel Dekker, New York, pp. 1-98. 1977.
3. J. B. Kisinger, M. M. Tannahill, M. S. Greenberg, and A. I. Popov, *J. Phys. Chem.*, **77**, 2444 (1973).
4. J. F. Coetzee and R. Lok, *J. Phys. Chem.*, **69**, 2690 (1965).
5. K. L. Stellner, E. E. Tucker, and S. D. Christian, *J. Solution Chem.*, **12**, 307 (1983).
6. M. T. Cung, M. Marrand, and J. Neel, *Biopolymers*, **17**, 1149 (1978).
7. D. Attwood, N. A. Dickinson, V. Mosquera, and V. Perz Villar, *J. Phys. Chem.*, **91**, 4203 (1987).
8. M. Mager and R. Steiner, *Biochem. Biophys. Acta.*, **224**, 80 (1970).
9. N. Sugawara, E. Stevens, G. Bonora, and C. Tonialo, *J. Am. Chem. Soc.*, **102**, 7044 (1980).