

디메틸설폭시드와 물 및 알칸올과의 분자 상호작용 : 증기압 삼투법에 의한 연구

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Molecular Interaction of Dimethylsulfoxide with Water and Alkanols : A Vapor Pressure Osmometry Study

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요 약. 디메틸설폭시드와 물 및 몇가지 알칸올간의 분자 상호작용에 관한 연구를 증기압 삼투법으로 40°C에서 수행하였다. 디메틸설폭시드는 물, 메탄올, 에탄올, 1-프로판올, 2-프로판올과 2-메틸-1-프로판올에서는 라울의 법칙에서 부의 벗어남을 나타내었으며, 1-부탄올과 1-펜탄올에서는 라울의 법칙에서 정의 벗어남을 나타내었다. 이 결과를 이중분자간의 상호작용과 DMSO 분자의 자체회합으로 각각 해석하였다. 측정된 물과 알칸올과의 히드록실 양성자의 화학적 이동도 이 결과를 뒷받침하였다.

ABSTRACT. Studies on the molecular interactions of dimethylsulfoxide (DMSO) with water and/or some alkanols were carried out by vapor pressure osmometry at 40°C. Negative deviation from Raoult's law was observed for the DMSO-water, methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-1-propanol systems, whereas positive deviation from Raoult's law was observed for the DMSO-1-butanol and 1-pentanol systems. The results were interpreted in terms of molecular interactions between unlike molecules, and of self-association of DMSO molecules, respectively. Measured chemical shift of hydroxyl proton of the solvents also supported the results.

INTRODUCTION

The behaviors of dimethylsulfoxide in various solvents have been arisen from its distinctive three functional groups¹. The oxygen atom acts as a hard Lewis base and the sulfur acts as a soft Lewis base while the methyl hydrogens act as very weak Lewis acids. Self-association of DMSO in nonpolar CCl₄ has been known to be substantial. The dimerization constant obtained by vapor pressure osmometry² was close to that obtained by infrared spectroscopy³. However, studies on the mixture of DMSO-pyridine by Brillouin scattering, infrared spectroscopy, and other physical data

(density, molar refractivity, and refractive index) showed an association of DMSO even in the 5 mol% DMSO solution⁴. Pyridine is a relatively polar solvent with dipole moment of 2.2 D. Therefore, it is rather perplexing that DMSO molecules show self-association in both polar and nonpolar solvents. It would be of interest to study the molecular interaction of DMSO with water and/or alkanols to compare it with the above systems. In particular, the molecular interactions between hydroxyl proton of water and/or alkanols and hard basic oxygen atom of DMSO molecules would be interesting.

EXPERIMENTAL

DMSO (GPR, Baubury) was purified as described elsewhere⁵ and stored over molecular sieve 4A (Linde type) in a vacuum desiccator with P₂O₅. Water and alkanols were either purified as described elsewhere⁵ and some spectroscopic pure alkanols (methanol and ethanol) were used without further purification. The PMR spectra were recorded at 60 MHz on a Varian EM-360L at ambient temperature. TMS was used as an internal reference. The vapor pressure osmotic coefficient (ϕ) of DMSO in the water and alkanols have been obtained with a Knauer Vapor Pressure Osmometer Model 18533 at 40°C. The principle and practice of the vapor pressure osmometry are well described elsewhere⁸. The relation between osmotic coefficient (ϕ) and osmotic activity coefficient (γ) is also described elsewhere⁷.

RESULTS AND DISCUSSIONS

Although the effect on the proton chemical shift of hydrogen-bonded hydroxyl proton needs a complicated explanation, the induced downfield chemical shift ($\Delta\delta_{\text{OH}}$) of the hydroxyl proton of water may be taken as a measure of the hydrogen bond interaction of DMSO and hydroxyl proton of the water molecule.

$\Delta\delta_{\text{OH}}$ of the water was the largest in this work as shown in Table 1. It seems to be natural that the largest $\Delta\delta_{\text{OH}}$ could be attributed to the very strong dipole-dipole hydrogen bond interaction. The result is in good agreement with the observation that a partly ionic solvate was formed in DMSO-water mixtures^{8,9}.

Hydrogen bond interaction between a hard basic oxygen atom of DMSO and a acidic hydroxyl proton of alkanols was expected to become weaker as the length or branching of alkyl increases, and $\Delta\delta_{\text{OH}}$ was expected to become smaller as the length or branching of the alkyl chains increases¹⁰. $\Delta\delta_{\text{OH}}$ of the alkanols were smaller than that of water as expected. The results suggested that the hydrogen bond interaction of the DMSO with the alkanols is weaker than that of DMSO with water.

Table 1. Induced hydroxyl proton chemical shift ($\Delta\delta_{\text{OH}}$) and dipole moments (μ) of the solvents

Solvents	$\Delta\delta_{\text{OH}}^a$	μ^b
Water (HOH)	30	1.82
Methanol	20	1.70
Ethanol	21	1.70
1-propanol	25	1.67
2-propanol	22	1.70
2-methyl-1-propanol	26	1.79
1-butanol	14	1.66
1-pentanol	16	1.80

^aDownfield chemical shift in Hz at $\chi_{\text{DMSO}}=0.2$, $\Delta\delta_{\text{OH}} = \delta_{\text{OH}}(\text{mixture}) - \delta_{\text{OH}}(\text{solvent})$, ^bIn Debye unit.

In this work, however, reverse correlation between $\Delta\delta_{\text{OH}}$ and chain length or branching of the alkanols was not observed. The observation could be resulted from the fact that the mixing of DMSO could possibly lead to not only simple hydrogen bond interaction but also other kinds of molecular interactions influenced by polarity and magnetic anisotropy of solvents, and differently preferred orientation by molecular interactions between the solute and solvents^{10,11}. However, in 1-butanol and 1-pentanol systems, steric effect by relatively large alkyl groups definitely inhibit hydrogen bond interaction and consequently results in smaller $\Delta\delta_{\text{OH}}$ than those of other alkanols studied. In other words, hydrogen bond interaction in these two solvent systems is so weak that molecular interaction between like molecules is predominant. The result was supported by the measurement of vapor pressure osmotic coefficients of DMSO in the solvents. All the systems except DMSO-1-butanol and DMSO-1-pentanol systems showed negative deviations from Raoult's law ($\phi > 1$) as shown in Fig. 1. The results support the fact that molecular interaction between unlike molecules, solute-solvent interaction, is predominant in these systems. However, DMSO in 1-butanol and 1-pentanol showed positive deviation from Raoult's law ($\phi < 1$). The results indicated that molecular interaction between like molecules is predominant in these two systems. Therefore, it would be reasonable to assume that the positive nonideality

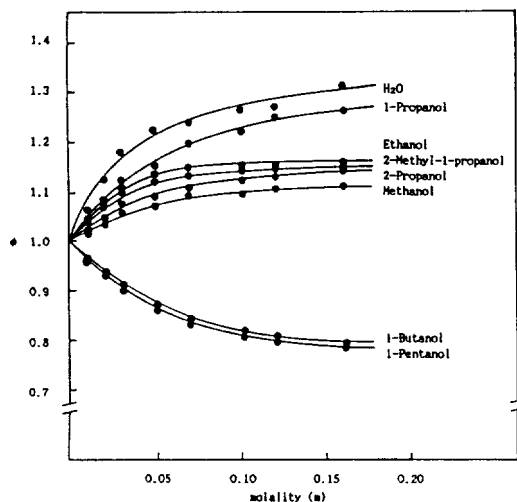


Fig. 1. Osmotic coefficient of DMSO in various alcohols and water at 40°C.

of DMSO could be attributed to the self-association of DMSO molecules in the two alkanol systems.

Since osmotic activity coefficient (γ) is the ratio of the free monomer to the stoichiometric concentration (m_s), dimerization constant, K_2 (m^{-1}) and trimerization constant K_3 (m^{-2}) can be obtained by a series expansion⁸. The calculated K_2 and K_3 are listed in Table 2 and 3, respectively. The results showed that association of DMSO in 1-butanol and 1-pentanol is substantial at the concentration range (0.01~0.16 m). Dimer restricted association constant (K_2^*) and another dimerization constant [$K_d = (1 - \phi)/m_s(2\phi - 1)^2$] using a different dimerization model¹² were also calculated to examine the results. The calculation also indicated that the values of dimerization constants were reasonable and significant. To understand the osmotic nonideality of DMSO in 1-butanol and 1-pentanol more closely, simple polymerization constants¹³ characterized by the same degree of association in every association step [$K_p = (1 - \phi)/(m_s\phi^2)$] were calculated and also listed in Table 2 and 3. The K_p values are far from constant. Thus, multiplication model could not be accepted to describe properly the DMSO behaviors in 1-butanol and 1-pentanol.

In conclusion, the degree of association of

Table 2. Osmotic coefficients (ϕ), activity coefficients (γ) and association constants (K) of DMSO in 1-butanol at 40°C

m_s^a	ϕ	γ	K_2 (m^{-1})	K_3 (m^{-2})	K_2^*	K_d	K_p
0.01	0.966	0.934			3.90	4.05	3.76
0.02	0.934	0.883			3.80	3.90	3.78
0.03	0.914	0.838			3.85	4.18	3.43
0.05	0.873	0.762	3.80	5.21	3.90	4.06	3.33
0.07	0.845	0.707			3.80	4.05	3.10
0.10	0.824	0.653			3.90	4.19	2.59
0.12	0.816	0.627			3.95	3.84	2.30
0.16	0.799	0.583			3.84	4.18	1.97

^aInterpolated values from experimental molal concentrations.

Table 3. Osmotic coefficients (ϕ), activity coefficients (γ) and association constants (K) of DMSO in 1-pentanol at 40°C

m_s^a	ϕ	γ	K_2 (m^{-1})	K_3 (m^{-2})	K_2^*	K_d	K_p
0.01	0.965	0.932			4.20	4.30	3.76
0.02	0.931	0.870			4.30	4.64	3.81
0.03	0.904	0.820			4.46	4.60	3.92
0.05	0.864	0.743	4.47	3.30	4.64	4.70	3.64
0.07	0.837	0.688			4.71	4.80	3.32
0.10	0.819	0.635			4.53	4.50	2.70
0.12	0.805	0.605			4.50	4.40	2.60
0.16	0.790	0.562			4.40	4.30	2.10

^aInterpolated values from experimental molal concentrations.

DMSO in the 1-butanol and 1-pentanol was found to be significant. However, DMSO showed predominant solute-solvent interaction in the other alkanols studied. Further investigation by other physical methods and on the higher aggregation of DMSO in the 1-butanol and 1-pentanol will be executed.

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