

인용문헌

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Dimethylsulfoxide와 몇 가지 유기분자와의 상호작용

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Interactions between Dimethylsulfoxide and Some Organic Molecules

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초록: 열가지 유기물질, 즉 니트로벤젠, *m*-디니트로벤젠, *o*-디니트로벤젠, 1,3,5-트리니트로벤젠, *m*-크실렌, 메시틸렌, 비벤질, 비페닐, *o*-페난트린, 및 나프탈린등과 dimethylsulfoxide 사이의 상호작용을 검토했다. 이 유기분자들은 모두 라울의 법칙에서 음의 편차를 나타내며, 전하전이 착물을 형성한다고 생각된다. 그 착물의 안정도상수를 분광광도법으로 측정하고, 몇가지 열역학함수를 계산했으며 결합에너지가 대개 $-1\sim-4$ kcal/몰임을 알았다. 한편 용매의 영향을 검토하여 착물의 안정도가 용매의 극성은 물론 염기도에도 크게 의존함을 알았다.

Abstract The interaction between dimethylsulfoxide molecules and some organic molecules, *i. e.* nitrobenzene, *m*-dinitrobenzene, *o*-dinitrobenzene, 1,3,5-trinitrobenzene, *m*-xylene, mesitylene, bibenzyl, biphenyl, *o*-phenanthrene, naphthalene, has been studied. The organic molecules exhibit negative deviation from Raoult's law due to the formation of the charge transfer complexes with dimethylsulfoxide. The stability constants of the complexes were determined spectrophotometrically, and also some thermodynamic functions were calculated. The binding energies of the complexes appear in the range of $-1\sim-4$ kcal/mole. The stability depends on the polarity and basicity of the solvent used.

Introduction

Solute-solvent interactions of alkaline halides and some organic molecules in dimethylsulfoxide have been reported,¹ in which the

solute molecules exhibited the positive deviation from Raoult's Law.

In this work, the interaction between some organic molecules having benzene ring and dimethylsulfoxide is studied by the measurement of the depression of the freezing point and of

their optical spectra.

The results are interpreted in terms of the formation of charge transfer(C-T) complex between organic molecule(electron acceptor) and dimethylsulfoxide(electron donor).

The stability constants of the C-T complexes are determined by ultraviolet absorption spectroscopy, and the effect of temperature and solvent character on the stability constants are discussed for the C-T complexes formed by several organic molecules. Heat of reaction, change of free energy, and change of entropy are also calculated.

Experimental

Dimethylsulfoxide was purified in the previously reported manner¹. Dinitrobenzenes, trinitrobenzene, bibenzyl, biphenyl, *o*-phenanthrene and naphthalene were recrystallized from ethanol, dried at 30-40°C in vacuum oven and kept over phosphorus pentoxide. Extra-pure grade reagents of nitrobenzene, *m*-xylene, and mesitylene were used without further purification. Spectrograde solvents were used.

The cryoscopic method and the equipment were the same as the manner described previously¹. The melting point determination of all solutions were repeated at least twice and were reproducible to $\pm 0.002^\circ$.

All absorption spectra were recorded on Shimadzu Ratiorecording Spectrophotometer, Type RM. Stoppered quartz cell(1 cm) were kept in a thermostatted cell holder in which the sides and base of the cells were contacted with a thermostatted water bath. Since reference and sample solutions contained the same concentrations of the acceptor in the various solvents, it was necessary to calibrate the absorbancy as mentioned in the following sections.

Treatment of Data

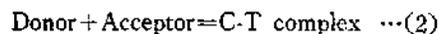
In dilute solution, the osmotic coefficients are calculated by

$$\phi = \Delta T / \lambda m \dots\dots\dots(1)$$

where ϕ is osmotic coefficient, ΔT , lowering of the freezing point, λ , molal freezing point constant ($4.40 \pm 0.01^\circ\text{C/molal}$), and m , molality of the organic substance.

The stability constants of C-T complexes in an organic solvent can be calculated by Rose-Drago equation, in the case that the both concentrations of organic molecule and DMSO are nearly equal and the both absorption spectra of complexes and the organic molecule are overlapped. However, in the case that the concentration of DMSO is over hundred times of that of organic molecule, Benesi-Hildebrand equation has been recommended. Since the situation in this work is not only the same as the latter one, but the absorption spectra of C-T complex and the organic molecules are overlapped, modification of Benesi-Hildebrand equation is made to fit for this work.

Assuming only 1 : 1 C-T complex is formed, the stability constant can be formulated by equation 3.



$$K = \frac{(\text{Complex})}{(\text{Donor})(\text{Acceptor})} \dots\dots\dots(3)$$

When the initial concentrations of acceptor, donor, and the complex are designated as C_A , C_D , and C_C , respectively, and the condition is $C_D \gg C_C$, equation 3 is rewritten as,

$$K = \frac{C_c}{(C_A - C_c)C_D} \dots\dots\dots(4)$$

$$\frac{1}{C_D} = \left(\frac{C_A}{C_c}\right)K - K \dots\dots\dots(5)$$

The absorbancy measured, A_c , should be calibrated mainly because of the following two facts: (1) the absorption spectra of acceptor and complex are overlapped, and (2) the reference and sample solutions have the same concentrations of the organic substances. To obtain the actual absorbancy of the complex, the absorbancy which corresponds to the concentration of acceptor consumed to form complex must be added to the absorbancy measured.

$$\varepsilon_c C_c = A_c + \varepsilon_A C_c \text{ or } C_c = A_c / (\varepsilon_c - \varepsilon_A) \dots\dots(6)$$

where ε_c and ε_A are molar extinction coeffi-

icients of the complex and acceptor, respectively. From equation 5 and 6, the equation 7 is obtained.

$$\frac{1}{C_D} = \left(\frac{(\varepsilon_c - \varepsilon_A)C_A}{A_c}\right)K - K \dots\dots\dots(7)$$

When the absorbances of the complexes are measured by keeping constant C_A and by changing C_D , and $1/C_D$ are plotted against C_A/A_c , then K and ε_c can be obtained from Fig. 3).

The thermodynamic functions were calculated by equation 8.

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots(8)$$

Result and Discussion

The osmotic coefficients and the negative deviation from Raoult's law: As shown in Fig. 1, the observed osmotic coefficients of the organic molecules exhibit the followings: (1) for the molecules containing nitro group, the

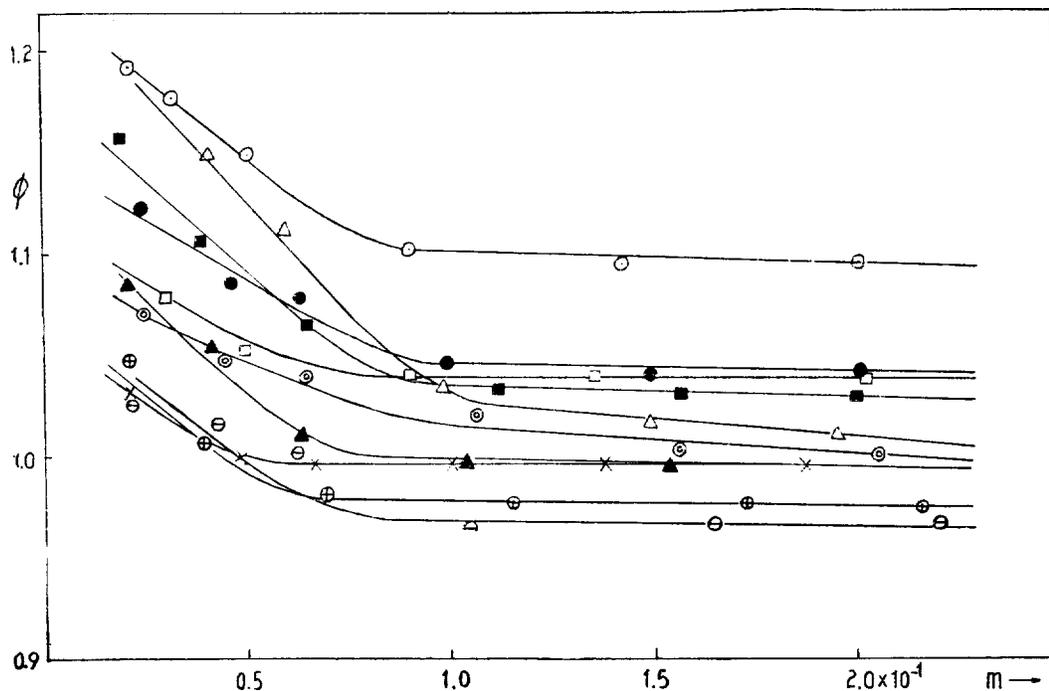


Fig. 1. The osmotic coefficients of some organic molecules in dimethylsulfoxide
 ⊙ 1, 3, 5-trinitrobenzene, ● *m*-dinitrobenzene, □ *o*-dinitrobenzene, ■ *o*-phenanthrene, △ bibenzyl,
 ⊕ biphenyl, ▲ naphthalene, × nitrobenzene, ⊕ *m*-xylene, ⊖ mesitylene

osmotic coefficients decrease in the order of 1, 3, 5-trinitrobenzene > *m*-dinitrobenzene > *o*-dinitrobenzene > nitrobenzene, (2) for the molecules having condensed aromatic ring, the decreasing order is *o*-phenanthrene > bibenzyl > biphenyl > naphthalene, and (3) in the case where the organic molecule contains methyl group, the coefficients decrease in the order of *m*-xylene > mesitylene.

In dilute solution, all of the organic molecules studied display the negative deviation from Raoult's law. These phenomena, in general, were observed in the case of enhancing the structure of solvent by solute molecules,⁴ solvation through hydrogen bonding or dipole-dipole interaction, or solvation by forming the C-T complex.⁵ In this work, the negative deviation from Raoult's law can be explained by postulating that C-T complex may be formed between DMSO molecule and organic molecule due to the high basicity of DMSO molecule.

Absorption spectra of charge transfer complexes: The organic molecules in carbon tetrachloride show absorption in the region of 260 $m\mu$ to 327 $m\mu$. However, the absorption of DMSO does not appear in the wavelength above 270 $m\mu$. On the other hand, C-T bands in carbon tetrachloride appear in the wavelength of 270 $m\mu$ to 320 $m\mu$, with the reference cell containing the same concentration of the organic substance as the sample solution (Fig. 2).

Since the reference cell contains the same concentration of the organic substances as the sample solution and many C-T bands in another systems^{6,7,8} showed the absorption spectra in the region of 270 $m\mu$ to 320 $m\mu$, it is clear that the spectra obtained correspond to C-T band. And it is also a reasonable postulation that one to one C-T complexes are formed, by knowing the facts that the plots of $1/C_D$ versus C_A/A_C give the

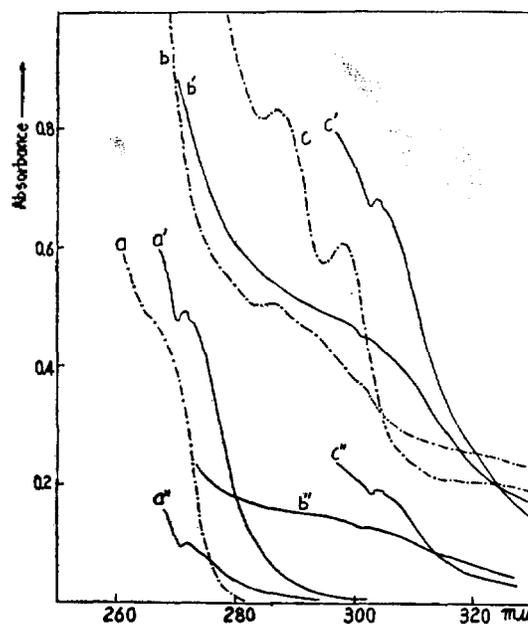


Fig. 2. The absorption spectra of charge-transfer complexes of some organic molecules and dimethylsulfoxide in carbon tetrachloride.

- a: bibenzyl ($6.8 \times 10^{-4}M$) only
 a': bibenzyl ($2.08 \times 10^{-3}M$) + DMSO ($2.50 \times 10^{-1}M$)
 a'': bibenzyl ($2.08 \times 10^{-3}M$) + DMSO ($4.66 \times 10^{-2}M$)
 b: 1, 3, 5-trinitrobenzene ($8.40 \times 10^{-4}M$) only
 b': 1, 3, 5-trinitrobenzene ($1.26 \times 10^{-3}M$) + DMSO ($9.61 \times 10^{-2}M$)
 b'': 1, 3, 5-trinitrobenzene ($1.26 \times 10^{-3}M$) + DMSO ($1.60 \times 10^{-2}M$)
 c: *m*-dinitrobenzene ($7.63 \times 10^{-4}M$)
 c': *m*-dinitrobenzene ($2.14 \times 10^{-3}M$) + DMSO ($3.53 \times 10^{-1}M$)
 c'': *m*-dinitrobenzene ($2.14 \times 10^{-3}M$) + DMSO ($5.88 \times 10^{-2}M$)

straight line as shown in Fig. 3 and the molar extinction coefficients of the complexes do not change at different concentrations of DMSO.

Stabilities of charge transfer complexes: The stability constants of the C-T complexes are presented in Table 1.

The stability constants have the same order as that of the osmotic coefficients in the range of 0.1 to 0.2 molality. Thus, the descending

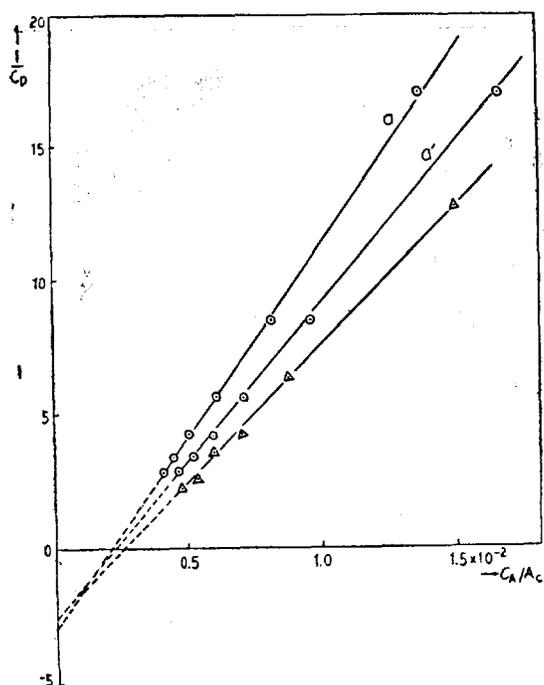


Fig. 3. Plots of $1/C_D$ vs. C_A/A_C in carbon tetrachloride at 25°C

- *m*-dinitrobenzene (a $(2.14 \times 10^{-3} M)$
 a' $(3.00 \times 10^{-3} M)$)
 △ *o*-dinitrobenzene $(3.53 \times 10^{-3} M)$ at 25°C

order of both osmotic coefficients and stability constants show 1, 3, 5-trinitrobenzene > *m*-dinitrobenzene > *o*-dinitrobenzene > nitrobenzene. These facts can be explained in the light of electron density: electron density in benzene ring decreases as the number of nitro group increases, and also *m*-dinitrobenzene has smaller electron density than *o*-dinitrobenzene. It is apparent that the osmotic coefficients and stability constants are in the order of *m*-xylene > mesitylene, since electron density in electron donating group increases. In the compounds with the condensed aromatic ring, it is clear that the stability is in the order of *o*-phenanthrene > bibenzyl > biphenyl > naphthalene, because the aromatic character of the compound decreases as the number of benzene ring increases.

Referring to the magnitude of dipole moment (order: nitrobenzene > *m*-dinitrobenzene > *o*-dinitrobenzene),⁹ it is found that the stability of C-T complex does not show completely favorable relation with polarity of the acceptor molecule.

Thermodynamic functions: The stability constants with varying temperature of the C-T

Table 1. Formation constants for the charge-transfer complexes of some organic molecules and dimethylsulfoxide in carbon tetrachloride (at $25.0 \pm 0.2^\circ C$)

Organic substance	Wavelength* (mμ)	Molar extinction coefficient complex (ϵ_c)	Formation constant K_f (l/mole)	Osmotic coefficient at 0.2m
1, 3, 5-trinitrobenzene	>300	496	9.74	1.10
<i>m</i> -dinitrobenzene	>304	495	2.76	1.04
<i>o</i> -dinitrobenzene	>310	733	2.35	1.04
<i>o</i> -phenanthrene	>310	383	0.76	1.01
Bibenzyl	271	541	0.72	1.01
Biphenyl	280	477	0.60	1.00
Naphthalene	>303	463	0.49	0.998
Nitrobenzene	>305	914	0.80	0.998
<i>o</i> -xylene	>272	516	0.48	0.978
Mesitylene	>217	315	0.25	0.966

*The values used in calculations of molar extinction coefficients. The notation ">" means the range of wavelengths in which the measurements of absorbances are possible for calculation of K_f .

Table 2. Formation constants for charge-transfer complexes of dimethylsulfoxide—nitrobenzenes at various temperature in carbon tetrachloride.

Temp. (°C)	1, 3, 5-trinitrobenzene		<i>m</i> -dinitrobenzene		<i>o</i> -dinitrobenzene	
	Formation constant K_f (l/mole)	Molar extinction coefficient ($\lambda=300m\mu$)	Formation constant K_f (l/mole)	Molar extinction coefficient ($\lambda=304m\mu$)	Formation constant K_f (l/mole)	Molar extinc- tion coefficient ($\lambda=310m\mu$)
5.0	12.2	493	3.08	456	2.68	732
15.0	11.0	496	2.93	459	2.50	733
25.0	9.74	496	2.78	459	2.35	733
35.0	8.84	484	2.59	463	2.19	737

complexes of 1, 3, 5-trinitrobenzene, *m*-dinitrobenzene, and *o*-dinitrobenzene with DMSO are presented in Table 2, and the free energy changes (ΔG), the enthalpy changes (ΔH), and the entropy changes (ΔS) are listed in Table 3. It is seen that the stability constants decrease as temperature increases and that the molar extinction coefficient shows independent of temperature. From the values of free energy changes, the calculated energies of the C-T complexes appear in the binding range of $-1 \sim -4$ kcal/mole, similar to those reported.¹⁰

It is interesting fact that the orders of magnitudes of the enthalpy changes coincide with those of the osmotic coefficients. Particularly, the values of ΔG and ΔH for 1, 3, 5-trinitrobenzene are much greater than those of *m*- and *o*-dinitrobenzene. These phenomena show a strong evidence that the stabilization by symmetrically intramolecular arrangement in the donor molecule may play the important role in characterizing those constants.

It is also understandable that the values of the entropy changes are negative, because the orderliness of donor molecule-acceptor molecule increases by the formation of C-T complexes.

Solvent effect: The stability constants for the C-T complexes of 1, 3, 5-trinitrobenzene in six solvents which have the different dielectric con-

stants are listed in Table 4.

It is seen that the stability constants are decreased and that the absorption bands shift slightly to longer wavelength, as the polarity of the solvent increases. O. D. Bonner interpreted those phenomena in his study of *N*-methylacetamide-*m*-dinitrobenzene system as follow.⁵ "It might be expected that a solvent having a higher dielectric constant would be more effective in the separation of an electron source and electron sink just as it enhances ionization and decreases dipole-dipole interactions. It is also probable that *N*-methylacetamide is solvated to a greater extent by the more polar solvents and that this solvent shell must be removed when complex is formed." In this study, however, order of magnitudes of the stability constants does not agree with the order of dielectric constants.

Table 3. Thermodynamic constants for charge-transfer complexes of dimethylsulfoxide—nitrobenzenes in carbon tetrachloride

Nitrobenzenes	ΔH (kcal/mole)	ΔS (kcal/mole. deg.)	ΔG (kcal/mole)
1, 3, 5-trinitrobenzene	-1.95	-1.90	-1.43
<i>m</i> -dinitrobenzene	-1.06	-1.65	-0.61
<i>o</i> -dinitrobenzene	-1.03	-1.87	-0.52

Table 4. Formation constants for charge-transfer complexes of dimethylsulfoxide and 1, 3, 5-trinitrobenzene in various solvents.

Solvent	Dielectric constant	Wavelength (<i>mμ</i>)	Formation constant (<i>l/mole</i>) (25. 0°C)	Molar extinction coefficient ($\epsilon_{\text{complex}}$)
Dioxane	2. 209 (25°C)	330	0. 20	1370
Carbon tetrachloride	2. 228 (25°C)	300	9. 74	496
Diethyl ether	4. 337 (20°C)	295	1. 84	1569
Chloroform	4. 806 (20°C)	301	0. 44	1146
Dichloromethane	9. 08 (20°C)	305	0. 17	1740
Acetone	20. 70 (25°C)	338	0. 055	1604

Moreover, the stability constant is unexpectedly small value in dioxane, which cannot be explained completely with only Bonner's concept. In order to explain the above fact, one must consider additional factors. For instance, the reason of small stability constant in dioxane, even through its polarity being small enough, should be explained along with the high basicity. It is well known fact that the dioxane molecule has two oxygen atoms which act as the center of nucleophilic properties which affect high basicity. Therefore, it is concluded that the stability of the C-T complex depends on both polarity and basicity of the solvent.

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