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A Definition of Selectivity of Nucleophilic Solvation in a Binary Solution

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This is the third paper of a series in which the behavior of nucleophilic solvation is investigated by a measurement of the position and the area of the O-D vibrational band of methanol-d. In a binary solution which consisted of two components remarkably different in electron-donating power, the relation between the mol fraction (n_1) of the S_1 component and the area fraction (N_1) of S_1 was not a straight line, but a concave or convex curve. This fact suggests that a component co-ordinates selectively to a deuterium atom in a methanol-d molecule. The following definition of the selectivity of nucleophilic solvation to methanol-d as a cation model of the S_2 component to the S_1 component is proposed:

$$(S_{S_1}^{S_2})_D = \sqrt{\left(\frac{dN_2}{dn_2}\right)_{n_2=0} \Big/ \left(\frac{dN_1}{dn_1}\right)_{n_1=0}}$$

The selectivity of the S_2 solvent to the S_1 solvent was considered in detail in connection with the equilibrium constant of the nucleophilic solvation to methanol-d of the solvent; the selectivity was also found to be defined as the ratio of the equilibrium constants of the solvents used. Since there was a correlation between the equilibrium constants and the electron-donating powers, it was concluded that the selectivity of an S_2 solvent to a standard solvent, S_1, could be quantitatively estimated by measuring only the position of the O-D vibrational band of methanol-d in each solvent.

It has previously been reported in connection with ionic copolymerization that the monomer reactivity ratios are significantly affected by the kind of solvent and catalyst used;1,2) the systematic interpretation is difficult even in the simplest cases.3) Recently, Overberger and Kamath have tried to explain this phenomenon on the basis of the preferential solvation of the growing ion pair by the more polar monomer in nonpolar solvents.4) This concept of the preferential solvation makes it possible to explain qualitatively many experimental results.5,6) There have been, however, few quantitative investigations of the preferential solvation.

In the first paper of this series,7) the electron-donating power ($\Delta\nu_D$) and the electron-accepting power ($\Delta\nu_A$) of liquid organic compounds have been defined by using methanol-d and acetophenone as indicators. The second paper8) was undertaken to make clear the characteristic behavior of the nucleophilic solvation in single or binary systems on the basis of the theory of chemical equilibrium.

The main purpose of the present work is to define the selectivity of nucleophilic solvation to the methanol-d of the solvent in a binary solution and to consider it in connection with the equilibrium constant of the nucleophilic solvation to the methanol-d of the solvent. It has been found that the selectivity defined is equal to the ratio of the equilibrium constants of the two components in a binary solution.

Experimental

The experimental technique is the same as that used before8) and so will not be described here.

Results and Discussion

As has been described previously,8) in a binary solvent system consisting of two components remarkably different in electron-donating power, it was observed that the position of neither O-D absorption bands changed in spite of the variation in the composition of the system, while the area

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1) C. G. Overberger, R. J. Ehrig and D. Tanner, *J. Am. Chem. Soc.*, **76**, 772 (1954).

2) A. V. Tobolsky and R. J. Boudreau, *J. Polymer Sci.*, **51**, S53 (1961).

3) B. D. Phillips, T. L. Hanlon and A. V. Tobolsky, *ibid.*, **A2**, 4231 (1964).

4) C. G. Overberger and V. G. Kamath, *J. Am. Chem. Soc.*, **85**, 446 (1963).

5) C. S. Marvel and J. F. Dunphy, *J. Org. Chem.*, **25**, 2209 (1960).

6) S. Okamura, T. Higashimura and K. Takeda, *Kobunshi Kagaku*, **18**, 389 (1961).

7) T. Kagiya, Y. Sumida and T. Inoue, This Bulletin, **41**, 767 (1968).

8) T. Kagiya, Y. Sumida and T. Inoue, *ibid.*, **41**, 773 (1968).

of each band changed remarkably with the composition. It was therefore concluded that the nucleophilic solvation to methanol-d of each component in a binary system took place competitively and individually.

On the other hand, with such a system, it may also be that a component with a strong electron-donating power preferentially solvates to a deuterium atom in a methanol-d molecule. With the purpose of considering this phenomenon, the area of each O-D band due to one of the two components was measured in tetrahydrofuran (THF$=$S$_1$, $\Delta\nu_D=90$) - solvents (S$_2$) systems by the half-value-width method.[8] Benzene ($\Delta\nu_D=0$), nitroethane (8), phenetole (25), ethyl propionate (32), pyridine (168), and triethylamine (238) were employed as the S$_2$ solvents. From the experimental results obtained, the relation between the mol fractions (n_{THF}) of THF and the area fractions (N_{THF}) of THF was plotted in Fig. 1. The

$$n_{THF} = \frac{(THF)}{(THF) + (S_2)} \qquad (1)$$

$$N_{THF} = \frac{A_{THF}}{A_{THF} + A_2} \qquad (2)$$

parentheses indicate the concentration of the component, and A is the area of an O-D absorption band due to the component.

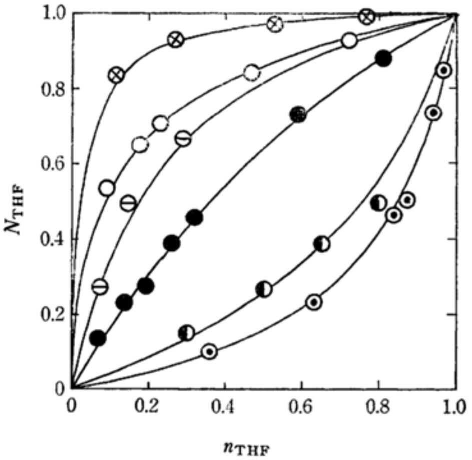

Fig. 1. Relation between the area fractions of O-D bands and the mol fractions of solvents in binary solvent systems containing 0.40 mol/l methanol-d.
Standard solvent: Tetrahydrofuran
Solvent S$_2$: ⊗ Benzene, ○ Nitroethane, ● Ethyl propionate, ⊖ Phenetole, ◐ Pyridine, ⊙ Triethylamine

It is apparent from Fig. 1 that N_{THF} increases with an increase in n_{THF}. The n_{THF}-N_{THF} curves do not give straight lines, but vary convexly or concavely, depending on the kind of S$_2$ solvent; that is, N_{THF} values in the same mol fraction of THF are remarkably dependent on the electron-donating powers of S$_2$. In the case of using an S$_2$ whose electron-donating power is weaker than that of THF, for example, in the tetrahydrofuran-benzene and tetrahydrofuran-nitroethane systems, the N_{THF} value increases precipitously upon the addition of a small amount of tetrahydrofuran to a single S$_2$ solvent. In the contrary case, N_{THF} increases slowly. Similar features were also observed in ethyl propionate-S$_2$ solvents systems (Fig. 2). These facts indicate that one component with a strong electron-donating power solvates to methanol-d selectively.

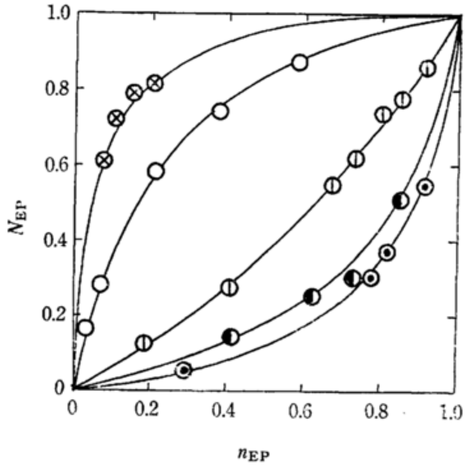

Fig. 2 Relation between the area fractions of O-D bands and the mol fractions of solvents in binary solvent systems containing 0.40 mol/l methanol-d.
Standard solvent: Ethyl propionate
Solvent S$_2$: ⊗ Benzene, ○ Nitroethane, ⦶ Tetrahydrofuran, ◐ Pyridine, ⊙ Triethylamine

In order to investigate quantitatively the behavior of selective solvation, the selectivity $(S_{S_1}^{S_2})_D$ of nucleophilic solvation to methanol-d of an S$_2$ solvent to an S$_1$ solvent is defined as follows:

$$(S_{S_1}^{S_2})_D = \sqrt{\left(\frac{dN_2}{dn_2}\right)_{n_2=0} \Bigg/ \left(\frac{dN_1}{dn_1}\right)_{n_1=0}} \qquad (3)$$

This definition is given graphically in Fig. 3, where the slope of the tangent line at the origin (0, 0) or the spot (1, 1) on the n_1-N_1 co-ordinates corresponds to the square of the denominator or the numerator in Eq. 3.

With the use of tetrahydrofuran or ethyl propionate as a standard solvent S$_1$, the selectivities of various solvents to the standard solvent were calculated by Eq. (3); they are listed in Table 1. It is obvious that the selectivity of benzene or of nitroethane to tetrahydrofuran is about 1/30 or 1/20, whereas that of triethylamine to tetrahydrofuran is about 6.

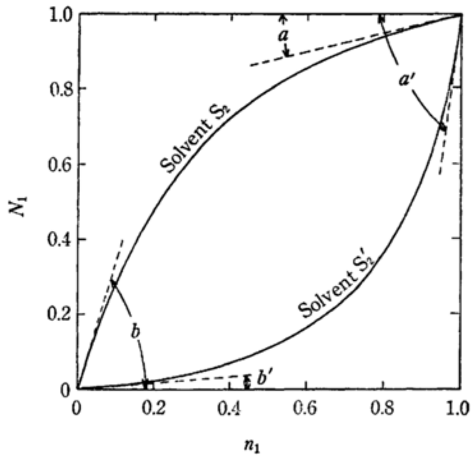

Fig. 3. Graphical evaluation of the selectivity of nucleophilic solvation of solvent S_2 to solvent S_1.

$$(S^{S_2}_{S_1})_D = \sqrt{\left(\frac{dN_2}{dn_2}\right)_{n_2=0} \bigg/ \left(\frac{dN_1}{dn_1}\right)_{n_1=0}} = \sqrt{\frac{a}{b}}\,,\quad \sqrt{\frac{a'}{b'}}$$

Table 1. Selectivities of nucleophilic solvation of solvents S_2 to tetrahydrofuran or ethyl propionate

Solvent S_2	$\Delta\nu_D$ (cm^{-1})	$(S^{S_2}_{\text{THF}})_D$	$(S^{S_2}_{\text{EP}})_D$
Benzene	0	0.034_2	0.11_4
Nitroethane	8	0.054_4	0.18_2
Phenetole	25	0.17_2	—
Ethyl propionate	32	0.32_0	1.00
Tetrahydrofuran	90	1.00	3.1_3
Pyridine	168	2.6_1	7.1_5
Triethylamine	238	5.7_0	$13._5$

It may be also considered from Table 1 that the selectivity is closely correlated to the electron-donating power. On the other hand, it has previously been reported that the electron-donating power ($\Delta\nu_D$) is good relation with the equilibrium constants of solvents.[8] Consequently, a correlation also seems to exist between the selectivities and the equilibrium constants of solvents. Therefore, the selectivity of solvents was considered in detail in connection with the equilibrium constant. The square of the numerator $(dN_2/dn_2)_{n_2=0}$ in Eq. (3) is expressed as the following formula:

$$\left(\frac{dN_2}{dn_2}\right)_{n_2=0} = \lim_{n_2\to 0}\frac{N_2}{n_2} = \lim_{(S_2)\to 0}\frac{1+(S_1)/(S_2)}{1+A_1/A_2} \tag{4}$$

In the second paper,[8] a linear relationship through the point of origin was observed to exist between the area ratio and the concentration ratio of two components, and it was found that the slope corresponded to the ratio of the equilibrium constants of the two solvents:

$$\frac{A_1}{A_2} = \frac{K_{D1}(S_1)}{K_{D2}(S_2)} \tag{5}$$

When we place the relationship of Eq. (5) into Eq. (4), Eq. (4) is simplified as follows:

$$\lim_{(S_2)\to 0}\frac{1+(S_1)/(S_2)}{1+A_1/A_2} = \lim_{(S_2)\to 0}\frac{1+(S_1)/(S_2)}{1+K_{D1}(S_1)/K_{D2}(S_2)} = \frac{K_{D2}}{K_{D1}} \tag{6}$$

Table 2. Selectivities of nucleophilic solvation of solvents S_2 to tetrahydrofuran

Solvent S_2	K_D (l/mol)	$(S^{S_2}_{\text{THF}})_D$	$\dfrac{K_{D2}}{K_{D,\text{THF}}}$	$(S^{S_2}_{\text{EP}})_D(S^{\text{EP}}_{\text{THF}})_D$
Benzene	0.036_9	0.034_2	0.035_1	0.036_5
Nitroethane	0.058_5	0.054_4	0.055_7	0.058_3
Phenetole	0.17_8	0.17_2	0.17_0	—
Ethyl propionate	0.32_0	0.32_0	0.30_5	0.32_0
Tetrahydrofuran	1.0_5	1.00	1.00	1.0_0
Pyridine	2.6_8	2.6_1	2.5_5	2.2_9
Triethylamine	6.1_0	5.7_0	5.8_1	4.3_2

Table 3. Selectivities of nucleophilic solvation of solvents S_2 to ethyl propionate

Solvent S_2	K_D (l/mol)	$(S^{S_2}_{\text{EP}})_D$	$\dfrac{K_{D2}}{K_{D,\text{EP}}}$	$(S^{S_2}_{\text{THF}})_D(S^{\text{THF}}_{\text{EP}})_D$
Benzene	0.036_9	0.11_4	0.11_5	0.10_7
Nitroethane	0.058_5	0.18_2	0.18_3	0.17_0
Ethyl propionate	0.32_0	1.00	1.00	1.0_0
Tetrahydrofuran	1.0_5	3.1_3	3.2_8	3.1_3
Pyridine	2.6_8	7.1_5	8.3_8	8.1_7
Triethylamine	6.1_0	$13._5$	$19._1$	$17._8$

By the same method, the square of the denominator $(\mathrm{d}N_1/\mathrm{d}n_1)_{n_1=0}$ is given by Eq. (7):

$$\left(\frac{\mathrm{d}N_1}{\mathrm{d}n_1}\right)_{n_1=0} = \frac{K_{\mathrm{D1}}}{K_{\mathrm{D2}}} \tag{7}$$

Consequently, the selectivity of an S_2 solvent to an S_1 solvent is defined as the following equation by using Eqs. (3), (6) and (7):

$$(S_{\mathrm{S_1}}^{\mathrm{S_2}})_{\mathrm{D}} = \frac{K_{\mathrm{D2}}}{K_{\mathrm{D1}}} \tag{8}$$

Equation (8) shows that the selectivity so defined can be calculated by using the ratio of the equilibrium constants. In order to confirm the propriety of Eq. (8), the selectivities of the S_2 solvents to tetrahydrofuran calculated by the various methods are listed in Table 2. Column 3 shows the value obtained by Eq. (3), column 4 the ratio of the equilibrium constants of the two solvents, and column 5 the value calculated by the following equation:

$$\text{column } 5 = (S_{\mathrm{EP}}^{\mathrm{S_2}})_{\mathrm{D}} \times (S_{\mathrm{THF}}^{\mathrm{EP}})_{\mathrm{D}} = 0.320(S_{\mathrm{EP}}^{\mathrm{S_2}})_{\mathrm{D}} \tag{9}$$

It is evident from the results shown in Table 2 that the observed values of selectivity are in good accordance with the calculated values.

Similarly, the selectivities of S_2 solvents to ethyl propionate are listed in Table 3. The observed values accord well with the calculated values. This fact indicates that the relationship of multiplication or division plays a part in the selectivity.

On the other hand, it has previously been concluded that the equilibrium constant of the nucleophilic solvation to methanol-d can be used as a measure of the force of the general nucleophilic co-ordination to the electrophilic compounds.[8] It has now also been found that the equilibrium constants are related to the electron-donating powers as follows:

$$\log K_{\mathrm{D}} = -\frac{3.67}{1+8.14\times10^{-3}\,\Delta\nu_{\mathrm{D}}} + 2.16 \tag{10}$$

These facts make reasonable the conclusion that the selectivity of the co-ordination of an S_2 solvent to a standard solvent, S_1, can be estimated by using Formula (10) and Eq. (8).

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