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A Study of the Nucleophilic Solvation Based on the Theory of Chemical Equilibrium

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The nucleophilic solvation to a deuterium atom in a methanol-d molecule has been quantitatively studied by using the infrared spectroscopic data of the O–D vibrational band. The position of the O–D band did not change in spite of the variation in the methanol-d concentration in solutions of a single solvent, whereas the area of the O–D peak changed in proportion to the first-order of the methanol-d concentration. From these results, it has been concluded that the area of the O–D band corresponds to the concentration of the methanol-d solvated. In a binary solvent system, which consisted of components with substantial differences in the electron-donating power, two positions of the O–D peak were observed at positions identical to those in the component examined in a single solvent system, and the area of each O–D peak changed with the composition of the system. These results led to the conclusion that the nucleophilic solvation of each component in the binary system took place competitively and individually. From the quantitative treatment of the results on the basis of the theory of chemical equilibrium, the equilibrium constant of the nucleophilic solvation of a solvent to methanol-d was calculated. The following empirical formula was obtained between the electron-donating powers and the nucleophilic equilibrium constants of various solvents:

$$\log K_D = -\frac{3.67}{1 + 8.14 \times 10^{-3} \Delta\nu_D} + 2.16.$$

It is well known, regarding an ionic reaction in solution, that the reaction rate is markedly affected by the kind of solvent, and by the characteristic features of the solvation. Scarcely no quantitative studies of solvation have, however, been reported.

On the other hand, Gordy *et al.* have made a study of the proton-attracting properties of various liquid compounds, using methanol-d as an indicator.[1] In a previous paper[2] the electron-donating power ($\Delta\nu_D$) and the electron-accepting power ($\Delta\nu_A$) of liquid compounds have been measured, and it has been found that the electron donating power of a liquid organic compound is more dominant than the electron-accepting power.

1) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941).

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

The purpose of the present investigation is to study quantitatively the nucleophilic solvation, also making a theoretical treatment of the data on the position and the area of the O–D band of methanol-d in solution.

Experimental

Materials. Tetrahydrofuran, benzene, nitroethane, ethyl propionate, phenetole, triethylamine, pyridine, and methanol-d were obtained commercially. All but methanol-d were purified by the usual methods.

Apparatus and Method. A typical infrared spectroscopic experiment was carried out as follows. A small quantity (0.4 mol/*l*) of methanol-d was added to 1.0 m*l* of the solvent, which consisted of one or two components, in a weighing bottle (2.0 m*l*). After the bottle had then been shaken for 10 min at room temperature (18±3°C), the infrared spectra of the O–D absorption band of methanol-d in the mixture were determined with a Hitachi EPI-2 infrared spectrophotometer (resolving power: 3 cm^{-1} at 10 μ, slit width: 0.03 mm at 10μ) equipped with a sodium chloride prism. The thickness of the cell used in this experiment was 0.010 cm.

Evaluation of the Integrated Intensity of the O-D Absorption Band. The O–D vibrational curve ought theoretically to be symmetrical. In most of the compounds in which the O–D vibrational band shifted to a lower frequency, symmetrical absorption bands were observed (Fig. 1(a)). On the other hand, asymmetrical O–D absorption bands were observed in some compounds which had small shifts (Fig. 1(b)). It may be considered that the phenomenon is caused by the overlapping of the unassociated and associated bands (2400—2500 cm^{-1}). Similarly, two O–D absorption bands in the binary solvent system were observed as asymmetrical bands by the overlapping of two unassociated absorption bands due to each solvent (Fig. 1(c)). Therefore, we estimated the integrated intensity of the unassociated O–D absorption band using the method of the half-value-width. For example, the integrated intensity of a symmetrical band (a) was evaluated as a triangular area (△ABC). In an asymmetrical band (b) or (c), each integrated intensity was separately determined, using each shoulder without an overlapping (*i. e.*, 2△DEF, 2△GIK and 2△HJL). We then took the average values of several measurements (maximum experimental errors: ±1.5%).

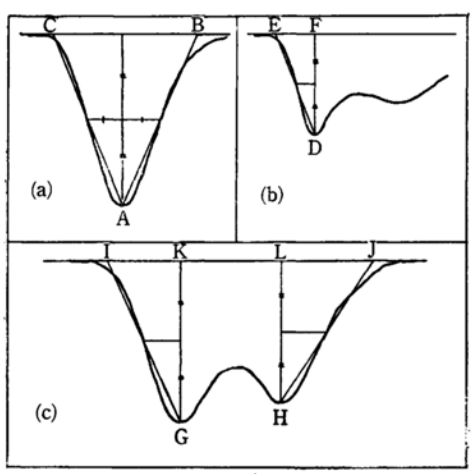

Fig. 1. Evaluation method of the integrated intensity of O–D absorption band.
(a) Single-solvent system; a symmetrical band
(b) Single-solvent system; an asymmetrical band
(c) Binary-solvent system

Results and Discussion

In a Single-solvent System. Since it was observed that the solvent which shifted the O–D band to a lower frequency had the stronger integrated intensity (area) of the O–D band, the

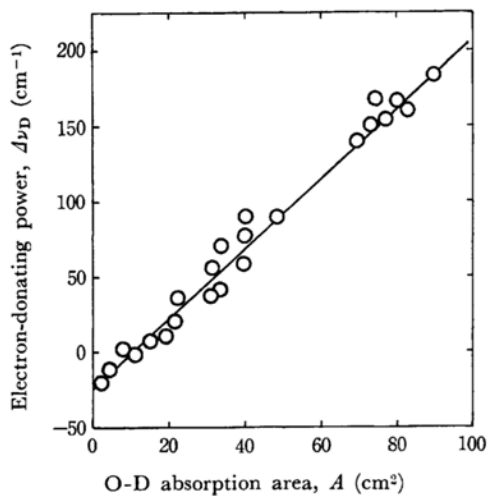

Fig. 2. Relation between the electron-donating powers ($\Delta\nu_D$) and the areas of O–D absorption bands (A).

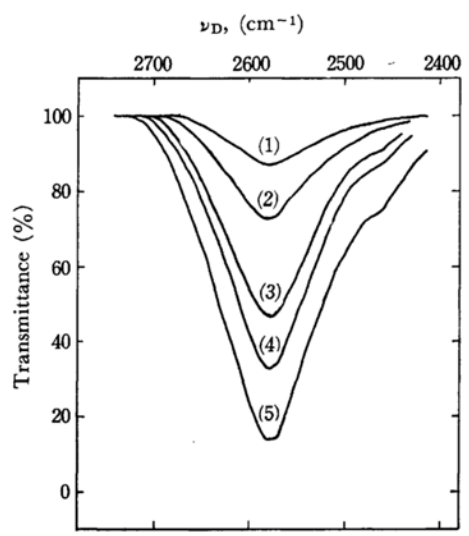

Fig. 3. Infrared spectra of O–D absorption bands in tetrahydrofuran systems.
CH_3OD concentration: (1) 0.085, (2) 0.18, (3) 0.40, (4) 0.58, (5) 0.97 (mol/*l*)

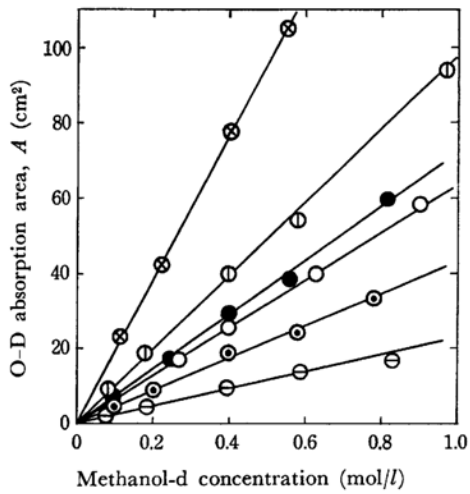

Fig. 4. Relation between the areas of O-D absorption bands and the concentration of CH_3OD in single solvent systems.
⊖ Benzene, ⊙ Nitroethane, ○ Phenetole,
● Ethyl propionate, ⓘ Tetrahydrofuran,
⊗ Triethylamine

positions of the O–D band in various solvents were plotted against the total area (*cf.* Fig. 2). A linear relation was found to exist between the position and the area of the O–D band at the same concentration (0.40 mol/*l*) of methanol-d; that is, the electron-donating power ($\Delta\nu_D$) proposed by us[2] increased as the area (A) increased.

The influence of the methanol-d concentration on the position and the area of O–D peak was also studied. The infrared spectra of tetrahydrofuran systems with various concentrations of methanol-d are shown in Fig. 3. It is evident that the position of the O–D absorption band does not change, regardless of the variation in its concentration, whereas its area increases with the concentration of methanol-d. Such features were also observed in other solvent systems. As shown in Fig. 4, this linear relation between the area of the O–D band and the methanol-d concentration was found to exist in various solvents. Therefore, the following equation was obtained:

$$A = \alpha(CH_3OD)_0 \qquad (1)$$

where $(CH_3OD)_0$ is the concentration of methanol-d in a pure solvent, and α is a constant, its exact nature depending on the kind of solvent. The area of the band depending only on the kind of solvent increases with the concentration of methanol-d. This fact suggests that the area of the O–D band corresponds to the concentration of the methanol-d solvated. This led to the following relation:

$$A = \frac{1}{\beta}(CH_3O\text{–}D\cdots nS) \qquad (2)$$

where $(CH_3O\text{–}D\cdots nS)$ is the concentration of methanol-d solvated by n molecules of the solvent, and β is a proportional constant.

On the basis of the above considerations, the nucleophilic solvation of a solvent to methanol-d may be quantitatively studied on the basis of the theory of chemical equilibrium; that is, the solvent, methanol-d, and solvated methanol-d are considered to be in equilibrium:

$$CH_3OD + nS \overset{K_D}{\rightleftharpoons} CH_3O\text{–}D\cdots nS \qquad (3)$$

K_D is the equilibrium constant. The concentration of methanol-d solvated in the equilibrium state is expressed by Eq. (4):

$$(CH_3O\text{–}D\cdots nS) = \frac{K_D(S)^n(CH_3OD)_0}{1 + K_D(S)^n} \qquad (4)$$

The parentheses indicate the concentration of each component in equilibrium. Using Eqs. (2) and (4), Eq. (5) is given as follows:

$$A = \frac{K_D(S)^n(CH_3OD)_0}{\beta(1 + K_D(S)^n)} \qquad (5)$$

Consequently, it is found that the constant (α) in Eq. (1) corresponds to $K_D(S)^n/\beta(1+K_D(S)^n)$ in Eq. (5).

In a Binary-solvent System. As a sample of a binary solvent system consisting of components with large differences in the electron-donating power, the infrared spectra in the tetrahydrofuran-nitroethane system are shown in Fig. 5. It is evident from Fig. 5 that the positions of the two O–D bands do not change in spite of the variation in the composition of the system, while the areas of the two bands do markedly vary with the composition. Moreover, the position of each

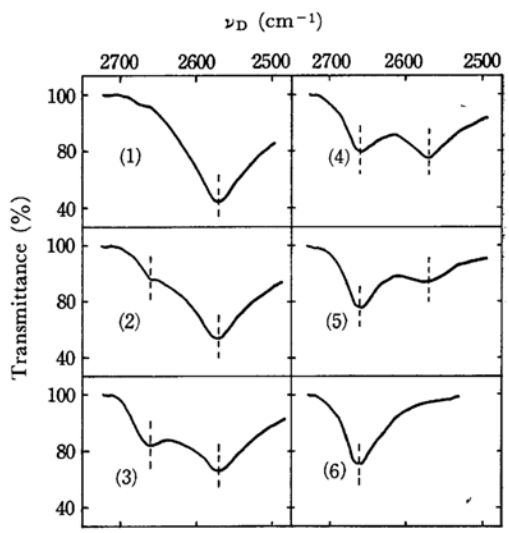

Fig. 5. Infrared spectra of the O–D absorption bands in tetrahydrofuran-nitroethane systems.
Tetrahydrofuran : Nitroethane (volume ratio)
(1) 1 : 0, (2) 3 : 1, (3) 1 : 1, (4) 1 : 3,
(5) 1 : 19, (6) 0 : 1

of the two peaks is identical with that due to tetrahydrofuran or nitroethane in a single-solvent system. Similar features were observed in other binary systems. If both components, S_1 and S_2, simultaneously solvate to one molecule of methanol-d, the position of the O-D band might be different from the position of each O-D peak appearing in the single solvent (S_1 or S_2) and might be observed between them. The experimental results, however, did not agree with this prediction. This fact leads to the conclusion that each component in a binary-solvent system solvates to each molecule of methanol-d individually and competitively.

On the basis of these findings, the solvation may be considered to consist of the following equilibrium reactions:

$$CH_3OD + nS_1 \overset{K_{D1}}{\rightleftharpoons} CH_3O\text{-}D\cdots nS_1 \qquad (6)$$

$$CH_3OD + mS_2 \overset{K_{D2}}{\rightleftharpoons} CH_3O\text{-}D\cdots mS_2 \qquad (7)$$

where n or m is the number of solvent molecules coordinating to a deuterium atom of methanol-d, and K_{D1} or K_{D2} is the equilibrium constant of each reaction. $CH_3O\text{-}D\cdots nS_1$ and $CH_3O\text{-}D\cdots mS_2$ indicate the state of methanol-d solvated by n molecules of the component S_1 and by m molecules of the component S_2 respectively. From the reactions (6) and (7), Eqs. (8) and (9) are obtained as follows:

$$(CH_3O\text{-}D\cdots nS_1) = \frac{K_{D1}(S_1)^n(CH_3OD)_0}{1 + K_{D1}(S_1)^n + K_{D2}(S_2)^m} \qquad (8)$$

$$(CH_3O\text{-}D\cdots mS_2) = \frac{K_{D2}(S_2)^m(CH_3OD)_0}{1 + K_{D1}(S_1)^n + K_{D2}(S_2)^m} \qquad (9)$$

As has been described previously, the concentration of the solvated methanol-d can be evaluated as the area of the O-D absorption band; that is $(CH_3O\text{-}D\cdots nS_1)$ may be expressed by $\beta_1 A_1$. A_1 is the area due to the component S_1. By substituting the relation described above into Eqs. (8) and (9), and by taking the ratio of Eq. (8) to Eq. (9), Eq. (10) is given:

$$\frac{(CH_3O\text{-}D\cdots nS_1)}{(CH_3O\text{-}D\cdots mS_2)} = \frac{\beta_1 A_1}{\beta_2 A_2} = \frac{K_{D1}(S_1)^n}{K_{D2}(S_2)^m} \qquad (10)$$

Equation (10) shows that a straight line exists between $\beta_1 A_1/\beta_2 A_2$ and $(S_1)^n/(S_2)^m$.

Since the interaction force that we are considering is a kind of hydrogen bonding, it seems reasonable to consider that the solvation number of methanol-d is unity in all systems, *i. e.*, that $n=m=1$. Moreover, in order to simplify Eq. (10), it is assumed that β is a constant independent of the kind of solvent. Using the above considerations, Eq. (10) is expressed as Eq. (11):

$$\frac{A_1}{A_2} = \frac{K_{D1}(S_1)}{K_{D2}(S_2)} \qquad (11)$$

As shown in Fig. 6, we tried to plot A_1/A_2 against $(S_1)/(S_2)$ in all binary systems. In view of this fact, it may be concluded that the solvation number is unity and that β is a constant which is independent of the kind of solvent used. A straight-line slope indicates the relative ratio of the equilibrium constant of the solvent for a standard solvent. The ratios of the equilibrium constants of various solvents against tetrahydrofuran as a standard solvent are listed in Table 1.

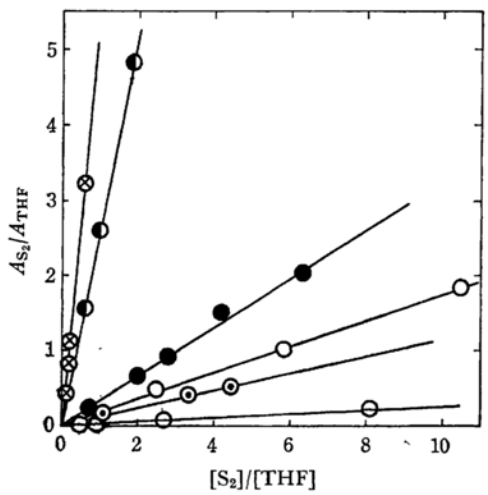

Fig. 6. Relation between the area ratios of O-D bands and the mol ratios of solvents S_2 in tetrahydrofuran-solvent S_2 systems.
Solvent S_2: ⊖ Benzene, ⊙ Nitroethane, ○ Phenetole, ● Ethyl propionate, ◐ Pyridine, ⊗ Triethylamine

Using Eqs. (8) and (11), we can obtain an equation by which the equilibrium constant can be calculated. When we substitute Eq. (11) into the reciprocal of Eq. (8), Eq. (12) is given as:

$$(S_1)\left(1 + \frac{A_2}{A_1}\right) = \frac{(CH_3OD)_0}{\beta}\,\frac{(S_1)}{A_1} - \frac{1}{K_{D1}} \qquad (12)$$

From Eq. (12), it may be expected that there is a linear relation between $(S_1)(1+A_2/A_1)$ and $(S_1)/A_1$, that its slope is constant in any kind of solvent at the same concentration of methanol-d, and that the value of the armature gives the reciprocal of the equilibrium constant. In Figs. 7 and 8, the propriety of Eq. (12) is confirmed in two cases, a tetrahydrofuran-solvent S_2 system and an ethyl propionate-solvent S_2 system. It may be seen in the two figures that a linear relationship exists between $(S_1)(1+A_2/A_1)$ and $(S_1)/A_1$. The values of the equilibrium constants of typical compounds are listed in Tables 1 and 2. The results in Table 1 show that the values $(K_{D2}/K_{D,THF})_{Fig.}$ obtained from the slope of the line in Fig. 6 agree well with

TABLE 1. RATIOS OF NUCLEOPHILIC EQUILIBRIUM CONSTANTS OF SOLVENTS AGAINST TETRAHYDROFURAN

Solvent	$\left(\frac{K_{D_2}}{K_{D,THF}}\right)_{Fig.}$	K_D (*l*/mol)	$\left(\frac{K_{D2}}{K_{D,THF}}\right)_{Calc.}$
Benzene	0.030_4	0.036_9	0.035_1
Nitroethane	0.11_0	0.058_5	0.055_7
Phenetole	0.17_5	0.17_8	0.17_0
Ethyl propionate	0.32_5	0.32_0	0.30_4
Tetrahydrofuran	1.00	1.0_5	1.00
Pyridine	2.6_3	2.6_8	2.5_5
Triethylamine	5.5_0	6.1_0	5.8_1

TABLE 2. EQUILIBRIUM CONSTANT OF NUCLEOPHILIC SOLVATION TO METHANOL-D

	Compound	$\Delta\nu_D$ (cm^{-1})	K_D (*l*/mol)	ΔG_D (kcal/mol)
	Aromatic Hydrocarbons			
1	Benzene	0	0.036_9	1.9_1
2	Ethylbenzene	4	0.044_0	1.8_0
3	Styrene	2	0.032_0	1.9_9
4	α-Methylstyrene	4	0.041_2	1.8_5
5	*p*-Methylstyrene	2	0.038_1	1.8_9
	Esters			
6	Ethyl acetate	39	0.31_7	0.66_4
7	Ethyl propionate	32	0.32_0	0.65_9
8	Methyl isobutyrate	32	0.32_2	0.65_5
9	Vinyl acetate	21	0.13_4	1.1_6
10	Ethyl acrylate	33	0.30_0	0.69_6
11	Methyl metacrylate	37	0.33_4	0.63_4
	Lactones			
12	β-Propiolactone	34	0.25_8	0.80_2
13	γ-Butyrolactone	66	0.70_1	0.20_5
14	ε-Caprolactone	82	0.97_4	0.016_0
	Ketones			
15	Methyl ethyl ketone	57	0.51_4	0.38_5
16	Methyl vinyl ketone	89	1.0_2	-0.010_7
	Ethers			
17	Diethyl ether	78	0.72_5	0.18_6
18	Ethyl vinyl ether	31	0.15_8	1.0_7
19	Phenetole	25	0.17_3	0.99_8
20	*p*-Methoxystyrene	28	0.11_4	1.2_6
21	Propylene oxide	59	0.45_5	0.45_5
22	Epichlorohydrin	45	0.35_2	0.60_5
23	Styrene oxide	51	0.41_4	0.51_0
24	3,3-Bischloromethyloxetane	78	0.89_1	0.066_1
25	Tetrahydrofuran	90	1.0_5	-0.028_0
26	1,3-Dioxolane	58	0.54_8	0.34_8
27	4-Methyl-1,3-dioxolane	56	0.53_8	0.35_8
28	Tetrahydropyran	93	1.4_3	-0.20_6
	Amines			
29	Pyridine	168	2.6_8	-0.57_0
30	Triethylamine	238	6.1_0	-1.0_4
	Nitriles			
31	Propionitrile	52	0.29_3	0.71_0
32	Acrylonitrile	37	0.19_2	0.95_5
	Nitro Compounds			
33	Nitroethane	8	0.058_5	1.6_4

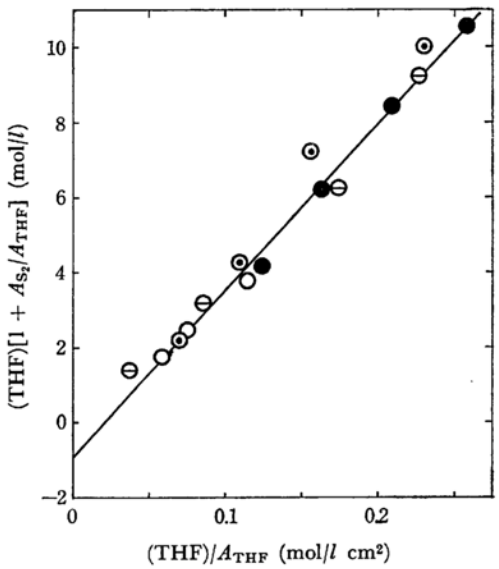

Fig. 7. Calculation method of nucleophilic equilibrium constant of tetrahydrofuran to CH_3OD.
Solvent S_2: ⊖ Benzene, ⊙ Nitroethane,
○ Phenetole, ● Ethyl propionate

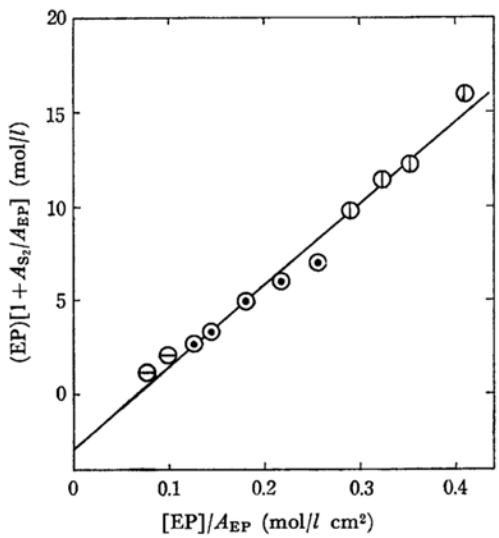

Fig. 8. Calculation method of nucleophilic equilibrium constant of ethyl propionate to CH_3OD.
Solvent S_2: ⊖ Benzene, ⊙ Nitroethane,
⓪ Tetrahydrofuran.

the values $(K_{D2}/K_{D,THF})_{Calc.}$ calculated by means of the K_D values, so we can approximately estimate the unknown K_D value by measuring the $K_{D2}/K_{D,THF}$ value.

It may also be seen in Table 2 that the equilibrium constant increases with the electron-donating power of the solvent. With the purpose of considering this relation, we plotted the equilibrium constants against the electron-donating powers; we thus obtained the following empirical formula:

$$\log K_D = -\frac{3.67}{1 + 8.14 \times 10^{-3} \Delta\nu_D} + 2.16 \quad (13)$$

This empirical formula shows that the equilibrium constant of nucleophilic solvation to methanol-d can be quantitatively estimated by measuring the shift of the O–D vibrational band of methanol-d.

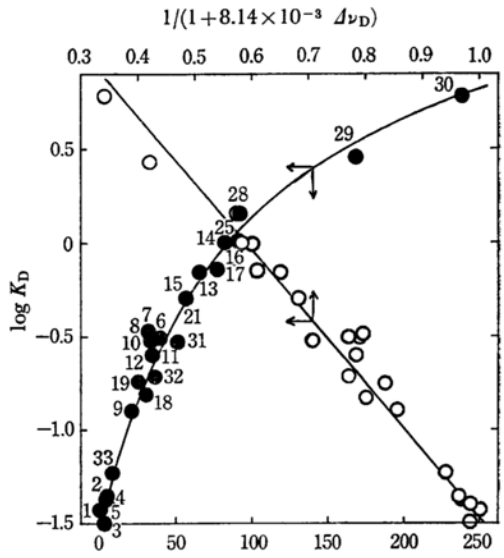

Fig. 9. Relation between the nucleophilic equilibrium constants of solvents and the electron-donating powers.
The number of a point represents the number in Table 2.

On the other hand, as has been reported previously, the shift of the O–D band is linearly related to the co-ordination power to diethyl zinc as an electrophilic compound. On the basis of these facts, it may be concluded that the equilibrium constant of the solvation to methanol-d can be used as a measure of the force of the general nucleophilic co-ordination to electrophilic compounds.