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An Infrared Spectroscopic Study of Hydrogen Bonds. The Liquid-Liquid Interaction of Solvents with Trimethylsilanol

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An infrared spectroscopic study of the hydrogen-bonding interaction of binary solvents (S_1–S_2) with trimethylsilanol has been made, where CCl_4 is used as S_1 and the aromatic hydrocarbons and the O- and N-containing solvents, as S_2. On the basis of the findings on the O–H frequency shifts ($\Delta\nu_{OH}$) of trimethylsilanol, the equilibrium constants (K) and the preferential coordination constants (α_{1-2}) of hydrogen-bond formation, the difference in the O–H$\cdots\pi$ and the O–H$\cdots n$ hydrogen-bonding interactions has been discussed. The free-energy changes ($-\Delta G$) were found to be better related to the apparent half-widths ($\Delta\nu_{1/2}$) of the O–H bands than the $\Delta\nu_{OH}$. The $\Delta\nu_{OH}$ of trimethylsilanol caused by the interaction with the solvent was in good correlation with the donor number defined as the heat of mixing of the solvent with antimony(V) chloride. From the linear relationship between the $\Delta\nu_{OH}$ of trimethylsilanol and the $\Delta\nu^{S}_{OH}$ of the surface silanol caused by the gas-phase adsorption on silica gel, it was also found that the proton-donating power of the surface silanol was considerably larger than that of trimethylsilanol and was nearly equal to that of *p*-nitrophenol. There existed a linear relationship through the point of origin between the α_{1-2} and the separation factors (α^{S}_{1-2}) in the liquid-phase adsorption on the silica gel surface.

Many interesting studies of the intramolecular and the intermolecular hydrogen bonds have been made by using such analytical instruments as IR, NMR, and Raman spectrometers.[1] Especially, the O–H$\cdots\pi$ hydrogen-bonding interactions between the proton donors and the solvents containing π-electrons have been systematically studied with the IR technique.[2–4] On the other hand, the spectroscopic studies of the O–H$\cdots n$ interactions of the proton donors with the solvents containing hetero atoms have been mainly focussed on the O–H frequency shifts, the equilibrium constants, and the enthalpy changes of hydrogen-bond formations.[5–10] Many investigations of the hydrogen bond have, in any case, been made in very dilute solutions of such inert solvents as CCl_4. Little attention has been paid to the quantitative difference or to the correlation between the O–H$\cdots\pi$ and the O–H$\cdots n$ interactions.[1] Moreover, few systematic studies of hydrogen-bonding interactions in correlation with the gas-phase and/or the liquid-phase adsorption phenomena on a solid surface have been reported, except for the gas-phase adsorption on silica gel.[11,12] On the other hand, despite the vastness of the literature on intermolecular interactions in solution, the correlation between the nucleophilic coordinations of solvents to the Brönsted acids and the Lewis acids has never been discussed because of the different types of interactions

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involved.[13]

In this paper, the hydrogen-bonding interaction has been studied by means of the IR technique between various proton-acceptor solvents (S_2) in carbon tetrachloride (S_1) solutions and trimethylsilanol, which has a partial structure (SiO–H bond) analogous to the silanol group on the silica gel surface.[14] The objectives of the present work are; (1) to discuss the different types of hydrogen bonds, *i.e.*, the O–H···π and the O–H···*n* interactions; (2) to compare the hydrogen-bonding interaction with trimethylsilanol with the nucleophilic coordination to antimony(V) chloride as a Lewis acid, and (3) to ascertain the relationship between the liquid-liquid interaction with trimethylsilanol and the gas-phase adsorption (solid-gas interaction) or the liquid-phase adsorption (solid-liquid interaction) on silica gel.

Experimental

Materials. All the solvents were obtained commercially and were purified by the usual methods. The trimethylsilanol was synthesized by the method of Sommer.[15]

Spectra Measurements. The composition of the binary mixture of carbon tetrachloride (S_1) and the second solvent (S_2) was cautiously determined by weighing and was varied over quite a wide concentration range. A small quantity of trimethylsilanol was added to a weighing bottle containing the binary mixture to make a solution of 0.004—0.015 mol/*l*. The KBr cell, with an optical thickness of 0.20 cm and filled with the solution, was placed in the irradiation path of infrared light, controlled at 28±3°C, and then allowed to equilibrate before scanning. All the spectral measurements were made by using a Japan Spectroscopic Co., Ltd., Model DS-403G infrared spectrophotometer. The spectral slit width was 1.7 cm^{-1} in the O–H fundamental regions (3400—3700 cm^{-1}).

Analysis of Spectra. The O–H frequency shifts ($\Delta\nu_{OH}$) of trimethylsilanol caused by the S_2 were expressed as the difference from the free O–H absorption frequency in CCl_4 ($\nu_{OH}(CCl_4)=3702$ cm^{-1});

$$\Delta\nu_{OH} = \nu_{OH}(CCl_4) - \nu_{OH}(S_2) \tag{1}$$

In the following equilibrium reaction;

$$SiOH\cdots S_1 + S_2 \rightleftarrows SiO\text{-}H\cdots S_2 + S_1 \tag{2}$$

the concentration ($[SiOH\cdots S_1]$ or $[SiO\text{-}H\cdots S_2]$) of trimethylsilanol solvated by S_1 or S_2 in the binary mixture was estimated from the calibration curve of the trimethylsilanol concentration in each solvent against the absorbance, which had been drawn in advance. However, the O–H absorption band of trimethylsilanol in the polar solvent differed considerably in frequency, in intensity, and in shape from that caused by the solvent in the binary mixture. The concentration $[SiO\text{-}H\cdots S_2]$ of trimethylsilanol solvated by such solvents as ethyl acetate (EA), acetonitrile (AN), dioxane (DOX), and tetrahydrofuran (THF) was replaced by $[SiOH]_0-[SiOH\cdots S_1]$, where $[SiOH]_0$ was the initial concentration. Moreover, in order to evaluate the apparent molar absorption coefficients (κ_2) of hydrogen-bonded complexes with the hetero atoms, the check for the Lambert-Beer rule was made in such dilute solutions of CCl_4 that the free O–H band disappeared, that is, in solutions with volume ratios of CCl_4 : EA=1 : 1, CCl_4 : AN=1 : 1, CC_4 : DOX=2 : 1, and CCl_4 : THF=2 : 1. The concentration $[SiO\text{-}H\cdots S_2]$ estimated by using the apparent molar absorption coefficients agreed, within the limits of experimental error (3—5%), with $[SiOH]_0-[SiOH\cdots S_1]$. The equilibrium constant (α_{1-2}) in Eq. (2), which we called the preferential coordination constant, was calculated by the use of Eq. (3);

$$\alpha_{1-2} = \frac{[SiO\text{-}H\cdots S_2]([S_1]_0 - [SiOH\cdots S_1])}{[SiOH\cdots S_1]([S_2] - [SiO\text{-}H\cdots S_2])} \tag{3}$$

The equilibrium constant (K) of hydrogen-bond formation in very dilute solutions of CCl_4 was estimated from the α_{1-2}.

Results and Discussion

Figures 1 and 2 show typical examples of O–H···π and O–H···*n* spectra observed in CCl_4-benzene and CCl_4-tetrahydrofuran solutions respectively. The

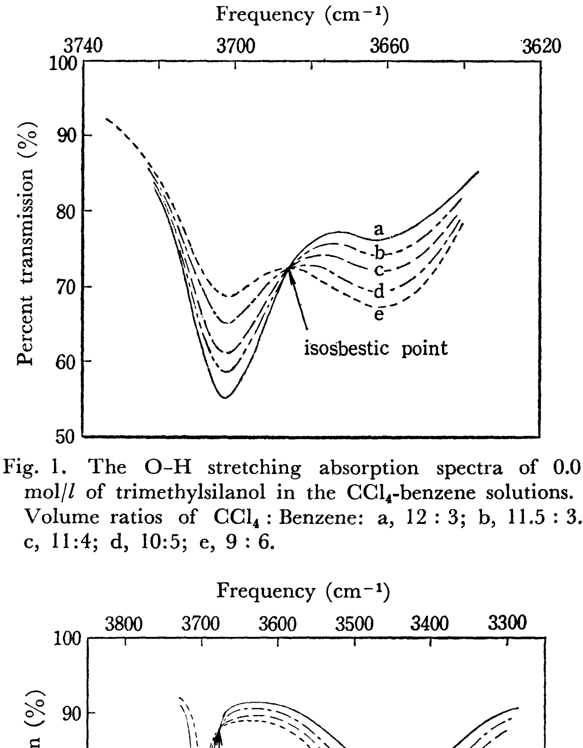

Fig. 1. The O–H stretching absorption spectra of 0.012 mol/*l* of trimethylsilanol in the CCl_4-benzene solutions. Volume ratios of CCl_4 : Benzene: a, 12 : 3; b, 11.5 : 3.5; c, 11:4; d, 10:5; e, 9 : 6.

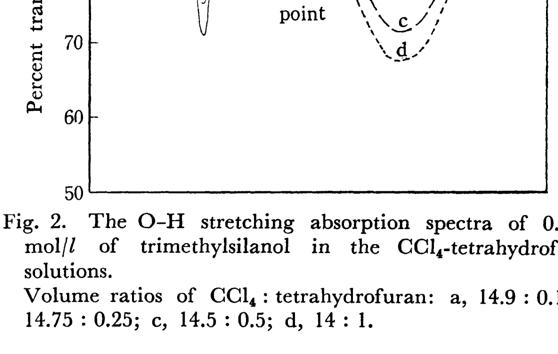

Fig. 2. The O–H stretching absorption spectra of 0.0063 mol/*l* of trimethylsilanol in the CCl_4-tetrahydrofuran solutions.
Volume ratios of CCl_4 : tetrahydrofuran: a, 14.9 : 0.1; b, 14.75 : 0.25; c, 14.5 : 0.5; d, 14 : 1.

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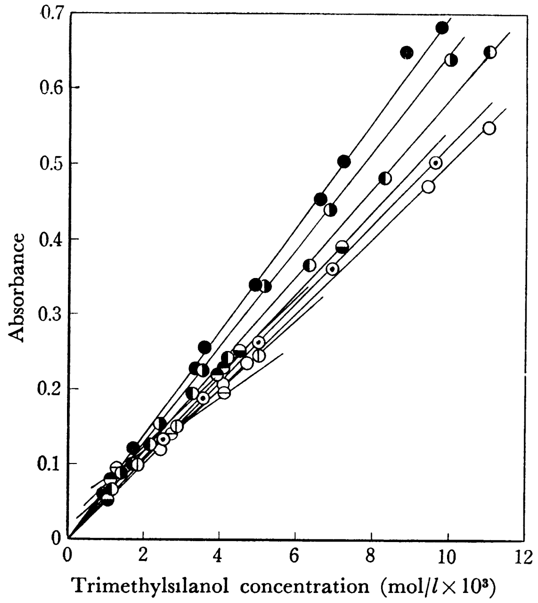

Fig. 3. The Lambert-Beer rule between the concentrations of trimethylsilanol solvated by solvents and the absorbances at the maximum points of O-H stretching absorption bands.

●, Carbon tetrachloride; ○, Benzene; ⊙, Chlorobenzene; ◐, Toluene; ◑, *p*-Xylene; ◓, Ethyl acetate (in 50 volume % CCl_4 solution); ◒, Acetonitrile (in 50% CCl_4); ⦶, Dioxane (in 67% CCl_4); ⦶, Tetrahydrofuran (in 67% CCl_4).

Lambert-Beer rule held fairly well over a wide concentration range of trimethylsilanol in CCl_4 and in the aromatic hydrocarbons, but not in solvents containing oxygen and nitrogen atoms diluted by CCl_4, as has been described in the experimental section (Fig. 3). This may be due to the large polarity of the hydrogen-bonded complex with the hetero atom. As is shown in Figs. 1 and 2, the isosbestic points were observed in every binary solution studied in the present work except the CCl_4-acetonitrile solution.[16] This fact leads to the conclusion that all hydrogen-bonded complexes have compositions of 1 : 1.[4c] Moreover, the fact that the preferential coordination constants, calculated on the basis of the 1 : 1 complex, are reasonably constant over the wide concentration range of the S_2 provides indirect support for the 1 : 1 assumption.

In Table 1, the apparent molar absorption coefficients (κ_2) and the apparent half-widths ($\Delta\nu_{1/2}$) of the O-H bands bonded by the solvents, the equilibrium constants (K) of the hydrogen-bond formation in very dilute CCl_4 solutions, and the preferential coordination constants (α_{1-2}) of the binary mixtures are summarized, together with the O-H frequency shifts ($\Delta\nu_{OH}$) of trimethylsilanol caused by the S_2. The error limits in Table 1 are believed to be within about 5%.[4c]

Difference in the O-H···π and O-H···n Hydrogen Bonds. It should be noted in Table 1 that the apparent molar absorption coefficients which are characteristic of the hydrogen-bonded complexes are nearly equal within 230—300 l/mol·cm, even though the O-H···π and O-H···*n* hydrogen bonds are of different types.[17] On the other hand, the half-widths, expressing the relaxation phenomenon of the complexes, changed markedly with different forms of hydrogen-bonding interaction, *i.e.*, ~50 cm^{-1} for O-H···π and 120—160 cm^{-1} for O-H···*n* complexes.[18] Moreover, the $\Delta\nu_{OH}$, α_{1-2}, and K values of solvents containing the oxygen and nitrogen atoms are large in comparison with those of the aromatic hydrocarbons. These results suggest the stronger nucleophilic coordination of the lone-pair-electrons of the hetero atom to trimethylsilanol than that of the π-electrons of the benzene nuclei. A major difference in the two types of hydrogen-bonding interactions is considered to appear more conspicuously in the entropy effect than in the enthalpy effect.

In order to confirm this theory, the free-energy changes ($-\Delta G$) of hydrogen-bond formation were plotted against the $\Delta\nu_{OH}$ values, which were propor-

TABLE 1. SPECTRAL PROPERTIES, EQUILIBRIUM CONSTANTS AND PREFERENTIAL COORDINATION CONSTANTS OF HYDROGEN BOND BETWEEN TRIMETHYLSILANOL AND PROTON ACCEPTOR SOLVENTS (S_2) IN CCl_4 SOLUTIONS

Solvent (S_2)	Mole fraction of S_2 in CCl_4-S_2	κ_2[a] (l/mol·cm)	$\Delta\nu_{1/2}$[a] (cm^{-1})	$\Delta\nu_{OH}$ (cm^{-1})	α_{1-2}	K (l/mol)	$-\Delta G$ (kcal/mol)
Chlorobenzene	0.24—0.45	264	43±1	29±1	1.97±0.21	0.19±0.02	−0.98±0.07
Benzene	0.21—0.45	252	52±3	40±1	2.25±0.07	0.22±0.01	−0.90±0.03
Toluene	0.18—0.78	293	50±2	59±1	2.36±0.21	0.23±0.02	−0.87±0.07
p-Xylene	0.15—0.75	326	35±1	63±1	2.59±0.18	0.25±0.02	−0.82±0.05
Ethyl acetate	0.03—0.50	258	131±6	146±3	15.5 ±0.3	1.50±0.03	0.24±0.02
Acetonitrile	0.02—0.65	275	128±8	140—175[b]	18.1 ±3.8	1.76±0.37	0.34±0.14
Dioxane	0.01—0.23	229	145±9	220±6	30.6 ±7.6	2.97±0.74	0.65±0.17
Tetrahydrofuran	0.01—0.08	—	150±9	265±3	35.6 ±4.1	3.46±0.39	0.74±0.07

a) As for the free O-H absorption band in CCl_4, κ_1=356 l/mol·cm and $\Delta\nu_{1/2}$=18±1 cm^{-1}.
b) The $\Delta\nu_{OH}$ increases with the increase in the acetonitrile concentration in the binary mixture.[16]

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[17] The κ_2 and $\Delta\nu_{1/2}$ values of the O-H absorption band in *p*-xylene were 326±5 l/mol·cm and 35±1 cm^{-1} respectively. This may be caused by the asymmetric O-H band in *p*-xylene, which differs from the symmetric bands in other aromatic hydrocarbons.

[18] The $\Delta\nu_{1/2}$ values of O-H···*n* complexes decreased slightly with an increase in the concentration of trimethylsilanol.

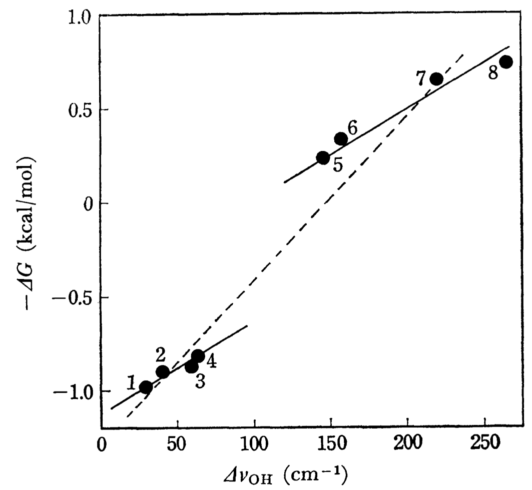

Fig. 4. Relationship between the free energy changes ($-\Delta G$) of hydrogen bond formation and the O-H frequency shifts ($\Delta\nu_{OH}$).
1, Chlorobenzene; 2, Benzene; 3, Toluene; 4, *p*-Xylene; 5, Ethyl acetate; 6, Acetonitrile; 7, Dioxane; 8, Tetrahydrofuran.

tional to the enthalpy changes of hydrogen-bond formation, as had been pointed out in the earlier papers.[1,8] As is shown in Fig. 4, a linear relationship is apparently obtained between them. However, further observation indicates different straight lines for the aromatic hydrocarbons and the solvents containing the hetero atoms, whose slopes are nearly equal to each other. This can be explained as resulting from the remarkable difference in the entropy effects of π- and n-hydrogen bonds. A similar result had been reported for the phenol adducts with π-electron and lone-electron donors.[4b,c]

On the other hand, the $\Delta\nu_{1/2}$ value should be an overall value expressing the molecular movement of the O-H group in solutions, including the enthalpy and the entropy changes. Therefore, the ΔG value may be expected to have a better correlation with the $\Delta\nu_{1/2}$ value than with the $\Delta\nu_{OH}$. As is confirmed in Fig. 5, the ΔG *vs.* $\Delta\nu_{1/2}$ relationship is satisfied in various binary solutions, regardless of the form of the hydrogen bond.

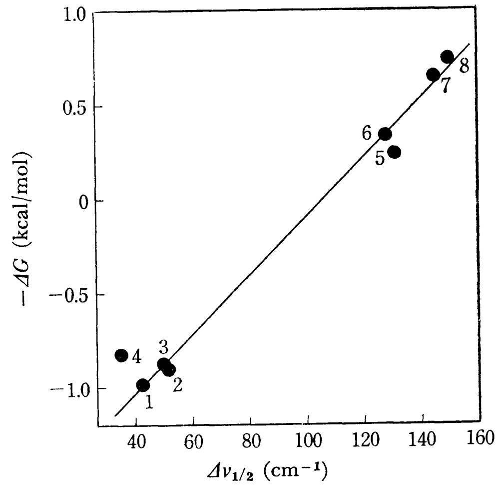

Fig. 5. Relationship between the free energy changes ($-\Delta G$) of hydrogen bond formation and the apparent half-widths ($\Delta\nu_{1/2}$) of O-H bands.
1, Chlorobenzene; 2, Benzene; 3, Toluene; 4, *p*-Xylene; 5, Ethyl acetate; 6, Acetonitrile; 7, Dioxane; 8, Tetrahydrofuran.

Interaction Forces of Solvents toward the Brönsted and Lewis Acids. As has been mentioned in the previous papers,[10a,d] the $\Delta\nu_{OH}$ can be regarded as a measure of the proton-accepting (the electron-donating) properties of S_2 toward the Brönsted acid. On the other hand, Gutmann *et al.* have made quantitative calorimetric measurements of the interactions of a number of solvents containing the hetero atoms with antimony(V) chloride and have proposed a donor number for each of the solvents toward the Lewis acid.[13] A comparison of the electron-donating properties of the solvents toward the different kinds of acids, *e.g.*, the Brönsted and Lewis acids, is shown in Fig. 6, where the $\Delta\nu_{OH}$ values of pyridine, dimethyl sulfoxide, dimethylformamide, and *N,N*-dimethylacetamide have been approximated from the data for deuteromethanol as a proton donor.[10a] The $\Delta\nu_{OH}$ increased linearly with the increase in the donor numbers. It seems that it can be concluded from this fact that there exists a certain physicochemical rule between the intermolecular interactions toward the Brönsted acid and the Lewis acid, despite the different types of interactions.

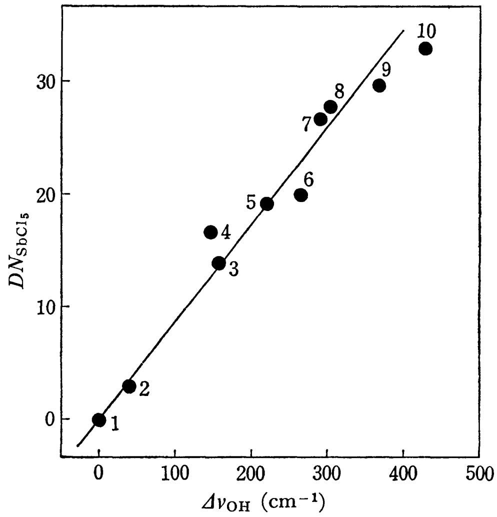

Fig. 6. Relationship between the donor numbers (DN_{SbCl_5}) and the O-H frequency shifts ($\Delta\nu_{OH}$).
1, Carbon tetrachloride; 2, Benzene; 3, Acetonitrile; 4, Ethyl acetate; 5, Dioxane; 6, Tetrahydrofuran; 7, Dimethylformamide; 8, *N,N*-Dimethylacetamide; 9, Dimethyl sulfoxide; 10, Pyridine.
The $\Delta\nu_{OH}$ values of solvents (7—10) were estimated from the data for deuteromethanol.
The DN_{SbCl_5} of CCl_4 was approximated by that of 1,2-dichloroethane.

Liquid-liquid Interaction with Trimethylsilanol and Solid-gas and Solid-liquid Interaction with the Silica Gel Surface. It is well known that the silanol group on the silica gel surface plays an effective role in the catalytic reactions. In order to make clear the intermolecular interactions on the silica gel surface, the liquid-liquid interaction with trimethylsilanol was compared with the gas-phase adsorption (solid-gas interaction) and

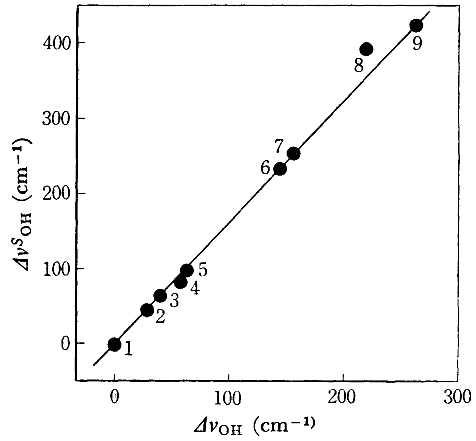

Fig. 7. Relationship between the O-H frequency shifts ($\Delta\nu^S_{OH}$) of silica gel surface silanol by gas-phase adsorption and the O-H frequency shifts ($\Delta\nu_{OH}$) of trimethylsilanol.

1, Carbon tetrachloride; 2, Chlorobenzene; 3, Benzene; 4, Toluene; 5, *p*-Xylene; 6, Ethyl acetate; 7, Acetonitrile; 8, Dioxane; 9, Tetrahydrofuran.

the liquid-phase adsorption (solid-liquid interaction) on silica gel.

The $\Delta\nu_{OH}$ values of trimethylsilanol were plotted against the $\Delta\nu^S_{OH}$ values, which were the O–H frequency shifts of the surface silanol caused by the monolayer adsorption of gases on silica gel,[12,19] where the O–H absorption frequency by CCl_4 vapor was taken to be 3704 cm^{-1}. As is shown in Fig. 7, a good linear relationship, with a slope of 1.60 was obtained between them. The value of this slope indicates that the O–H group of the surface silanol is more acidic than that of trimethylsilanol; that is, the ionic dissociation energy of the surface O–H bond is smaller than that of the trimethylsilanol O–H bond.[10d] This may correspond to the fact that the O–H fundamental frequency of silica gel is 3749 cm^{-1} in the gas-phase,[12] considerably larger than that (*ca.* 3710 cm^{-1}) of trimethylsilanol.[10d] In a previous paper,[10d] we defined the proton-donating power (Φ_D) of the donor, independent of the kind of proton acceptor, as the ratio of the O–H frequency shift of the proton donor in a certain acceptor to that of methanol as a standard proton donor;

$$\Phi_D = \frac{\Delta\nu_{RO-H}(\text{proton acceptor})}{\Delta\nu_{MeO-H}(\text{proton acceptor})} \tag{4}$$

This definition rests on the fact that there exists a linear relationship, through the point of origin, between $\Delta\nu_{RO-H}$ and $\Delta\nu_{MeO-H}$ in the same proton acceptor.[8d,10d] According to our definition, the Φ_D of the trimethylsilanol and the silica gel surface silanol were determined to be 1.65 and 2.65 respectively. The value of

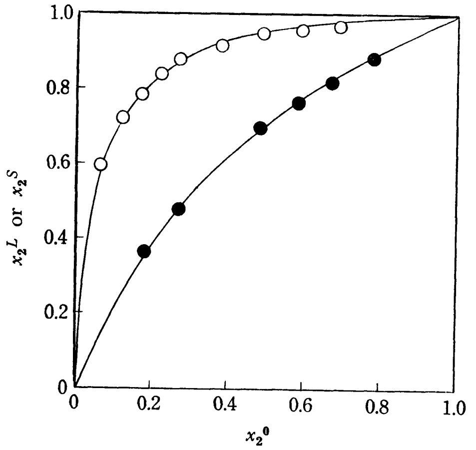

Fig. 8. Plots of the mole fractions (x_2^L) of trimethylsilanol bonded by S_2 or the mole fractions (x_2^S) of S_2 adsorbed on silica gel against the mole fractions (x_2^0) of non-bonded S_2.

●; Carbon tetrachloride-Toluene (Trimethylsilanol), $\alpha_{1-2}=2.36$

○; Cyclohexane-Toluene (Silica gel), $\alpha^S_{1-2}=18.6$.

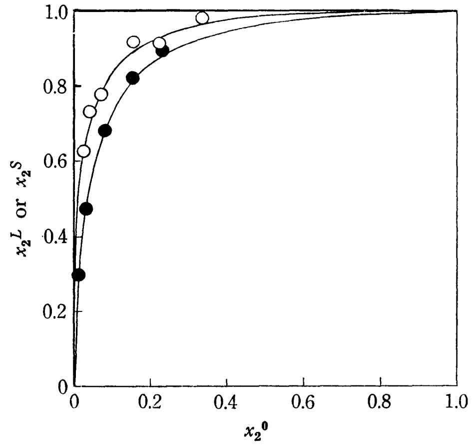

Fig. 9. Plots of the mole fractions (x_2^L) of trimethylsilanol bonded by S_2 or the mole fractions (x_2^S) of S_2 adsorbed on silica gel against the mole fractions (x_2^0) of non-bonded S_2.

●; Carbon tetrachloride-Dioxane (Trimethylsilanol), $\alpha_{1-2}=30.6$

○; Cyclohexane-dioxane (silica gel), $\alpha^S_{1-2}=63.3$.

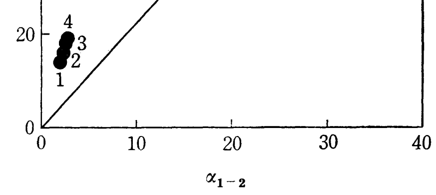

Fig. 10. Relationship between the preferential coordination constants (α_{1-2}) of trimethylsilanol and the separation factors (α^S_{1-2}) of silica gel.

1, Chlorobenzene; 2, Benzene; 3, Toluene; 4, *p*-Xylene; 5, Ethyl acetate; 6, Dioxane; 7, Tetrahydrodrofuran.

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19) The silanol O-H frequency shifts on the silica gel surface depend slightly on the surface coverage; they grow considerably with the surface coverage up to a monolayer, while on further adsorption they change very slowly.

20) For such a homologous series of adsorbates as the aromatic hydrocarbons, the $\Delta\nu_{OH}$ increases as the differential heat of adsorption becomes larger.

surface silanol is nearly equal to that (2.92) of *p*-nitrophenol. On the other hand, the $\Delta\nu_{OH}$ is not related to the differential heat of adsorption, expressing the total energy of the complicated interaction with the surface at a given coverage.[20] However, from a comparison of the homogeneous and heterogeneous hydrogen-bonding interactions, it can be concluded that there is a difference in the Φ_D, namely, the sensitivity to proton acceptors, but no essential difference in the nucleophilic coordination phenomena.

In order to compare the liquid-liquid interaction with trimethylsilanol with the solid-liquid interaction with the silica gel surface, we examined the relationship between the preferential coordination constants (α_{1-2}) to trimethylsilanol and those ($\alpha^S{}_{1-2}$) on silica gel, that is, the separation factors. The latter was obtained from the data on the preferential adsorption from the binary solution of cyclohexane(S_1)-second solvent(S_2) on silica gel.[11] In Fig. 8 and 9, the mole fractions ($x_2{}^L$) of trimethylsilanol bonded by the S_2 or those ($x_2{}^S$) of the S_2 adsorbed on the silica gel are plotted against the mole fractions ($x_2{}^0$) of the nonbonded S_2 in the equilibrium solution. It should be noted in Figs. 8 and 9 that the binary mixtures are better separated on the silica gel surface than in trimethylsilanol. The separation power of silica gel or trimethylsilanol is characterized by the $\alpha^S{}_{1-2}$ or the α_{1-2}. A quantitative relationship between the α_{1-2} and the $\alpha^S{}_{1-2}$ is illustrated in Fig. 10. A straight line, though not good, is drawn with a slope of 2.2 through the point of origin. This may correspond to the fact that the Φ_D of surface silanol is larger than that (1.65) of trimethylsilanol.[10d] It can be said from the above considerations that the separation powers of proton donors in the same binary mixture become larger as the Φ_D values of the donors increase.