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Liquid-phase Adsorption from Binary Solutions on Silica Gel. Separation Factors and Orientation of Adsorbed Components on the Surface

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The preferential adsorption equilibria of various binary solutions of cyclohexane-aromatic compounds and cyclohexane-cyclic ethers on chromatographic silica gel have been studied at 30°C. On the basis of the assumption that the adsorption is of the Langmuir-type, the separation factors (α) and the numbers of moles in the adsorbed-phase per unit mass of silica gel (n^σ/m) have been calculated. The values of log α correlate well not only with the electron-donating properties of the preferentially-adsorbed components, but also with the powers of the gas-phase adsorption on silica gel and of the liquid-liquid interaction with liquid trimethylsilanol. Moreover, on the basis of the information on n^σ/m, the orientation angles of the adsorbed components on the surface have been evaluated. The adsorption of the aromatic hydrocarbons was nearly flat to the surface, and that of the cyclic ethers, perpendicular.

Theoretical and experimental studies of the gas-phase adsorption on the solid surface have been actively made since the latter half of the 1910's.[1] The chemical structures of the surface have also been made clearer by means of analytical instruments.[2] The liquid-phase adsorption on the solid surface has been mainly studied from the standpoint of the industrial purifications of the organic solvents, the lubricating oils, and so on.[3-6] Little attention has, however, been paid to quantitative discussions of the power of adsorption from solutions on the solid surface and of the orientation of the adsorbed components on the surface, although they have been some qualitative studies.[7-9]

In this investigation, the adsorption equilibria of various binary solutions of cyclohexane-aromatic compounds and cyclohexane-cyclic ethers on chromatographic silica gel have been studied at 30°C. The objectives of the present work are: (1) to discuss the separation factors in connection with the electronic properties of the adsorbed components, (2) to compare the liquid-phase adsorption on silica gel (solid-liquid interaction) with the gas-phase adsorption on silica gel (solid-gas hydrogen bond) and with the liquid-phase coordination to trimethylsilanol (liquid-liquid hydrogen bond), and (3) to evaluate the orientation angles of the components adsorbed on the surface.

Experimental

Materials. Spectro-grade cyclohexane, benzene, toluene, *p*-xylene, chlorobenzene, anisole, dioxolane, 1,4-dioxane, and tetrahydrofuran were used as the adsorbates. These adsorbates were dried with silica gel and were then used without further purification. The adsorbent was silica gel (100–200 mesh) for thin-layer chromatography. The silica gel (dried at 160°C) had the following characteristics; B.E.T.(N_2) area = 383 m^2/g, and pH of aqueous suspension =7.0.

Adsorption Equilibria. Portions of about 4 g of accurately-weighed silica gel, dried at 160°C, were placed in glass ampoules and degassed for about 6 hr. The ampoules were then filled with about 10 m*l* of a binary solution of the cyclohexane-second solvent of a known composition. The sealed ampoules were placed in a constant-temperature bath controlled at 30 ± 0.2°C and then allowed to equilibrate while being stirred frequently. The analysis of the equilibrium mixture was made with a Shimadzu gas chromatograph, GC-4AIT.

Results and Discussion

In order to discuss quantitatively the adsorption equilibrium of the mixture of the cyclohexane (S_1)-second solvent (S_2) on the silica gel, we must first determine the form of the adsorption isotherm. The selective adsorbed capacity (a_2) of the preferentially-adsorbed component, which is S_2 in each binary solution, can be approximately calculated by the following equation:[8]

$$a_2 = \frac{V_{M2}\cdot n^0}{m}\,\frac{x_2^0 - x_2^l}{1 - x_2^l} \tag{1}$$

where V_{M2} is the molar volume of S_2 (m*l*/mol); *m*, the weight of silica gel (g); n^0, the total number of moles of the original mixture (mol), and x_2^0 and x_2^l, the mole fractions of S_2 in the original liquid and the non-adsorbed liquid at equilibrium respectively. It can be said that Eq. (1) holds over a wide concentration range ($0<x_2^l<1$) when the adsorption power of S_2 is so large in comparison with that of S_1 that the surface

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[1] S. Brunauer, "The Adsorption of Gases and Vapors," Vol. 1, Oxford Univ. Press, Oxford (1945).

[2] M. L. Hair, "Infrared Spectroscopy in Surface Chemistry," Marcel Dekker, INC., New York (1967).

[3] B.J. Mair and A.F. Forziati, *J. Res. Nat. Bur. Stand.*, **32**, 151, 165 (1944).

[4] A. E. Hirschler and T. S. Mertes, *Ind. Eng. Chem.*, **47**, 193 (1955).

[5] a) E. Funakubo, *Sekiyu Kagaku Zasshi*, **6**, 759 (1963); b) H. Takisawa, E. Funakubo, and I. Moritani, *Brennstoff-Chem.*, **43**, 7 (1962); c) E. Funakubo, I. Moritani, N. Toshima, and T. Nagai, *Kogyo Kagaku Zasshi* ,**66**, 237 (1963).

[6] a) T. Yagi, K. Uchimoto, K. Shimizu, and M. Hirahama, *ibid.*, **68**, 326 (1965); b) T. Yagi, K. Shimizu, and K. Uchimoto, *ibid.*, **68**, 331 (1965); c) T. Yagi, K. Shimizu, K. Uchimoto, and S. Maeda, *ibid.*, **68**, 335 (1965).

[7] J. L. Olsen, U. S. Patent 2564717 (Sun Oil Co., 1951); R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornel Univ. Press, Ithaca, New York (1955), p. 150.

[8] S. Eagle and J. W. Scott, *Ind. Eng. Chem.*, **42**, 1287 (1950).

[9] D. Hadzi, "Hydrogen Bonding," Pergamon Press, New York (1959), p. 449.

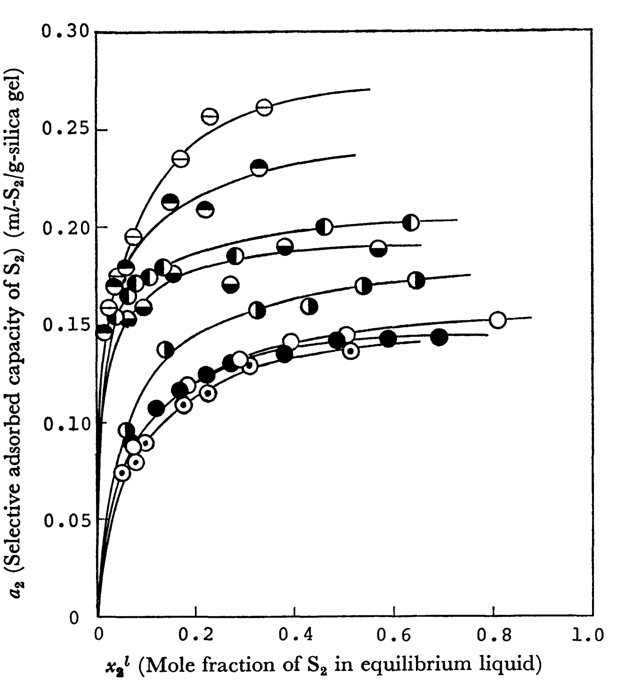

Fig. 1. Adsorption isotherms for cyclohexane (S_1) - second solvent (S_2) mixtures on silica gel.
S_2: ⊙, Chlorobenzene; ○, Benzene; ●, Toluene; ◑ *p*-Xylene; ◐, Anisole; ⊖, Dioxolane; ◓, 1,4-Dioxane; ◒, Tetrahydrofuran.

can be almost entirely covered by S_2, even in a low concentration range of S_2. The above condition was assumed to be satisfied for the present binary solutions.

The adsorption isotherms of a_2 *versus* x_2^l are shown in Fig. 1. In the high concentration range of S_2, it is so difficult to evaluate accurately the very small difference between the x_2^0 and the x_2^l that the experimental error in the a_2 becomes larger. However, there are good linear relationships between x_2^l/a_2 and x_2^l, as is shown in Fig. 2. From these results, we assumed that the adsorption from the mixtures used in this experiment was of the Langmuir-type.[10]

On the other hand, according to Everett,[11] the behavior of a perfect solution in contact with a Langmuir-type adsorbing surface can be discussed on the basis of the following equation:

$$\frac{x_1^l\cdot x_2^l}{n^0\cdot\Delta x_2^l/m}=\frac{m}{n^\sigma}\left(x_2^l+\frac{1}{\alpha-1}\right) \tag{2}$$

where n^σ is the number of moles in the adsorbed-phase; Δx_2^l, the change in the mole fraction of S_2 due to the adsorption, and α, the separation factor for the equilibrium reaction:

$$(S_1)^\sigma+(S_2)^l \rightleftarrows (S_1)^l+(S_2)^\sigma \tag{3}$$

The above equation (2) rests on the assumptions that; (i) the adsorption is of the Langmuir-type; (ii) α remains constant over the entire concentration range; (iii) the ratio of the activity coefficients ($\gamma_1^l\gamma_2^\sigma/\gamma_1^\sigma\gamma_2^l$) can be approximated to unity, and (iv) the adsorbed components have similar molecular sizes in the adsorbed-phase or the S_2 covers the surface entirely, even in the low concentration range of S_2. Regarding assumption (ii), Yagi *et al.* have reported that the values of α in the *n*-heptane-aromatic hydrocarbon systems are constant over a wide concentration range ($0.2<x_2^l<1.0$).[6] Assumption (iii) cannot be checked at present because of the difficulties in measuring the activity coefficients

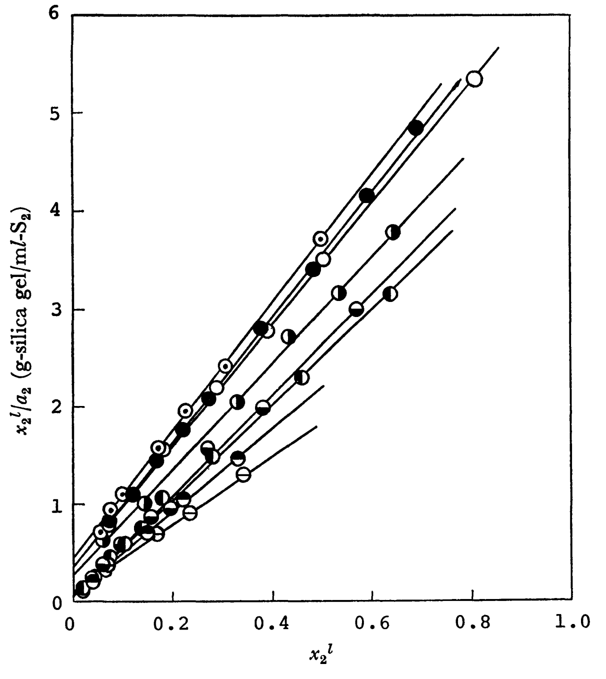

Fig. 2. Langmuir plots for cyclohexane (S_1) - second solvent (S_2) mixtures on silica gel.
S_2: ⊙, Chlorobenzene; ○, Benzene; ●, Toluene; ◑, *p*-Xylene; ◐, Anisole; ⊖, Dioxolane; ◓, 1,4-Dioxane; ◒, Tetrahydrofuran.

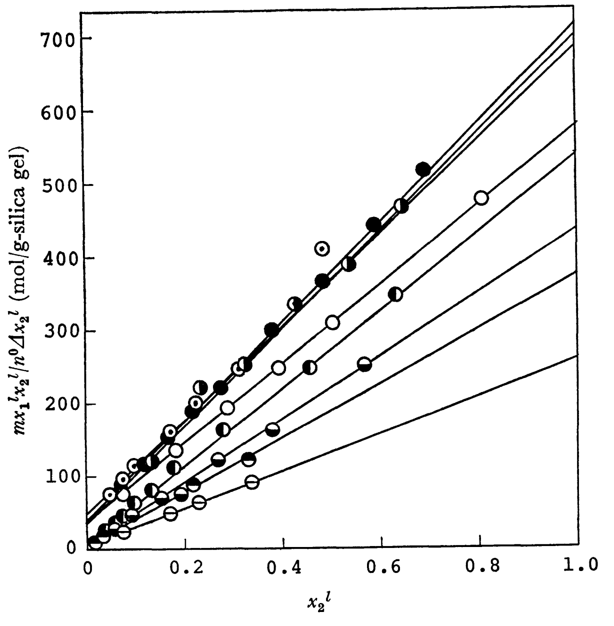

Fig. 3. Everett plots of $mx_1^lx_2^l/n^0\Delta x_2^l$ *vs.* x_2^l for cyclohexane (S_1) - second solvent (S_2) mixtures on silica gel.
S_2: ⊙, Chlorobenzene; ○, Benzene; ●, Toluene; ◑, *p*-Xylene; ◐, Anisole; ⊖, Dioxolane; ◓, 1,4-Dioxane; ◒, Tetrahydrofuran.

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[10] Yagi *et al.* pointed out that the adsorption of the *n*-heptane - aromatic hydrocarbon systems on silica gel was of the Freundlich type.[6]

[11] D. H. Everett, *Trans. Faraday Soc.*, **60**, 1803 (1964); D. H. Everett, *ibid.*, **61**, 2478 (1965).

Table 1. Separation factors and numbers of moles of adsorbed components in cyclohexane - preferentially adsorbed component mixtures

Preferentially adsorbed components	α	$n^{\sigma}/m \times 10^4$ (mol/g)
Chlorobenzene	14.0_6	15.3_8
Benzene	16.0_3	18.4_8
Toluene	18.5_5	14.8_0
p-Xylene	19.3_8	15.0_4
Anisole	49.2_4	18.9_9
Dioxolane	37.8_0	40.3_2
1,4-Dioxane	63.2_2	27.6_6
Tetrahydrofuran	80.0_2	23.4_5

of the components in the adsorbed-phase.[11–13]

Figure 3 shows the analytical data for various binary solutions plotted according to Eq. (2). The good linear relationships may indicate that the above assumptions are almost satisfied over the concentration range used in this experiment, in spite of the difference in the chemical structures of S_2. The separation factor (α) and the number of moles in the adsorbed-phase per unit mass of adsorbent (n^{σ}/m) are listed in Table 1.[14] It should be noted in Table 1 that the α and n^{σ}/m values of dioxolane, 1,4-dioxane, and tetrahydrofuran are sufficiently large in comparison with those of the aromatic hydrocarbons. This suggests difference in the adsorption behavior, *i.e.*, the adsorption power and the orientation of adsorption.

The Separation Factors and the Electron-donating Properties of Solvents. It may be considered that the values of log α, indicating the power of the nucleophilic adsorption of S_2 on the silica-gel surface covered with cyclohexane (S_1), are related to the electron-donating properties of S_2. The log α of the aromatic hydrocarbons and derivatives are plotted against the ionization potentials (I_p) and the Hammett's substituent constants (σ_p) in Fig. 4.[15] The log α increased linearly as the ionization potentials became smaller and as the electron-relieving properties of the substituents became larger. This suggests that the adsorption of the aromatic hydrocarbons is mainly caused by the π-electrons of the benzene nuclei.[19] The deviation of chlorobenzene from the log α-I_p line may imply that the first ionization of chlorobenzene was not caused by the benzene ring. On the other hand, the declination of anisole from both lines can be inferred to indicate the existence of strong adsorption by the oxygen atom rather than weak adsorption by the benzene nuclei.

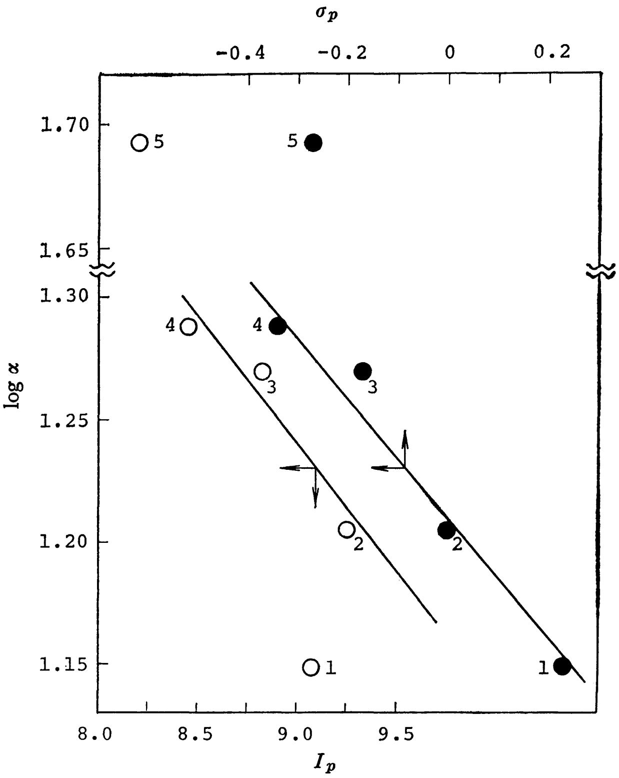

Fig. 4. Relation between log α and ionization potentials (I_p) or Hammett's substituent constants (σ_p) for substituted benzene derivatives.

1, Chlorobenzene; 2, Benzene; 3, Toluene; 4, *p*-Xylene; 5, Anisole.

The Separation Factors and the Hydrogen-bonding Interaction with the Surface Silanol or Liquid Trimethylsilanol. In order to make clear the liquid-phase adsorption phenomenon, we discussed the separation factors, *i.e.*, the liquid-phase adsorption powers, in connection with the strengths of the solid-gas and liquid-liquid hydrogen-bonding interactions. The strength of the solid-gas hydrogen bond can be evaluated by the IR technique as the difference ($\Delta\nu^S_{OH}$) in the adsorption frequencies of the free O-H band and the bonded O-H band caused by the monolyaer adsorption of gas on silica gel:[20,21)]

$$\Delta\nu^S_{OH} = \nu^S_{OH}(\text{free}) - \nu^S_{OH}(\text{bonded})$$

That of the liquid-liquid hydrogen bond can be similarly estimated by means of the frequency shift ($\Delta\nu^L_{OH}$) of liquid trimethylsilanol caused by the solvent, which has a chemical structure (SiO-H bond) analogous to the silanol group on the silica-gel surface:[22]

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12) a) S. K. Suri and V. Ramakrishna, *J. Phys. Chem.*, **72**, 1555 (1968); b) S. K. Suri and V. Ramakrishna, *Trans. Faraday Soc.*, **65**, 1690 (1969).

13) B. C.-Y. Lu and R. F. Lama, *ibid.*, **63**, 727 (1967).

14) In the cyclohexane - benzene systems, the value of n^{σ}/m was independent of the adsorption temperature.

15) This order of the adsorption powers of the benzene derivatives agrees well with the experimental results of Brown,[16] Giles *et al.*,[17] and Kiselev *et al.*[18] However, Funakubo *et al.* reached the reverse conclusion on the basis of their findings on the ultraviolet adsorption spectrum of the adsorbed-phase.[5b]

16) H. C. Brown, *J. Amer, Chem. Soc.*. **74**, 3570 (1952).

17) C. H. Giles and R. B. Mckay, *J. Chem. Soc.*, **1961**, 58.

18) G. A. Galkin, A. V. Kiselev, and V. I. Lygin, *Trans. Faraday Soc.*, **60**, 431 (1964).

19) N. Okuda, *Nippon Kagaku Zasshi*, **82**, 1118 (1961).

20) a) V. Ya. Davydov, A. V. Kiselev, and V. I. Lygin, *Dokl. Akad. Nauk, SSSR*, **147**, 131 (1962); b) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, London–New York (1966), p. 274.

21) 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.[18]

22) a) T. Kagiya, Y. Sumida, and T. Tachi, This Bulletin, **43**, 3716 (1970); b) T. Kagiya, Y. Sumida, T. Watanabe, and T. Tachi, *ibid.*, **44**, 923 (1971).

TABLE 2. EFFECTIVE MOLECULAR OCCUPANCIES AND ORIENTATION ANGLES OF PREFERENTIALLY ADSORBED COMPONENTS ON SILICA GEL

Preferentially adsorbed components	A_2 (Å^2/molecule)	d_2 a) (Å)	h_2 a) (Å)	θ (degree)	A_2 b) (Å^2/molecule)	S b) (m^2/g)
Chlorobenzene	41.3_4	5.45_9	7.34_2	3	30.9_1	$286._4$
Benzene	34.4_1	5.45_9	6.30_3	0	27.9_2	$310._8$
Toluene	42.9_6	5.45_9	7.53_8	5	31.4_6	$280._5$
p-Xylene	42.2_8	5.45_9	8.74_5	11	34.7_3	$314._7$
Anisole	33.4_8	5.45_9	7.71_5	17	31.9_5	$365._5$
Dioxolane	15.7_7	5.37_8	5.11_5	77	23.8_0	$578._1$
1,4-Dioxane	22.9_9	5.38_3	6.21_6	90	27.1_5	$452._4$
Tetrahydrofuran	27.1_1	5.65_0	5.37_1	86	26.0_0	$367._2$

a) Values calculated from Eq. (6).
b) Values calculated from the assumption of the spherical molecules for the preferentially adsorbed components.

$$\Delta\nu^L_{OH} = \nu^L_{OH}(\text{bonded by benzene}) - \nu^L_{OH}(\text{bonded})$$

where benzene is conveniently employed as a reference solvent. As is shown in Fig. 5, good correlations between logα and $\Delta\nu^S_{OH}$ or $\Delta\nu^L_{OH}$ were obtained; that is, the values of logα increased linearly with the increase in the $\Delta\nu^S_{OH}$ or the $\Delta\nu^L_{OH}$. From the relationships, we may conclude that the liquid-phase adsorption on silica gel is mainly governed by the proton-accepting properties of solvents. A comparison of $\Delta\nu^S_{OH}$ and $\Delta\nu^L_{OH}$ shows a large proton-donating property of surface silanol.[22]

The Orientation Angles of the Components Adsorbed on the Surface. According to Schay and Nagy,[12b,23] if the effective molecular occupancies (A) of the two components in the adsorbed-phase are known, the total surface area per unit mass of solid (S) is given by the following equation:

$$S = N\left(\frac{n_1^\sigma}{m}A_1 + \frac{n_2^\sigma}{m}A_2\right) \qquad (4)$$

where n_1^σ and n_2^σ are, respectively, the number of moles of S_1 and S_2, and where N is the Avogadro number. When the α of S_2 is so large that the surface is preferentially covered with S_2, or when $A_1 = A_2$, Eq. (4) can be approximated with Eq. (5):

$$S = \frac{n^\sigma}{m}A_2N \qquad (5)$$

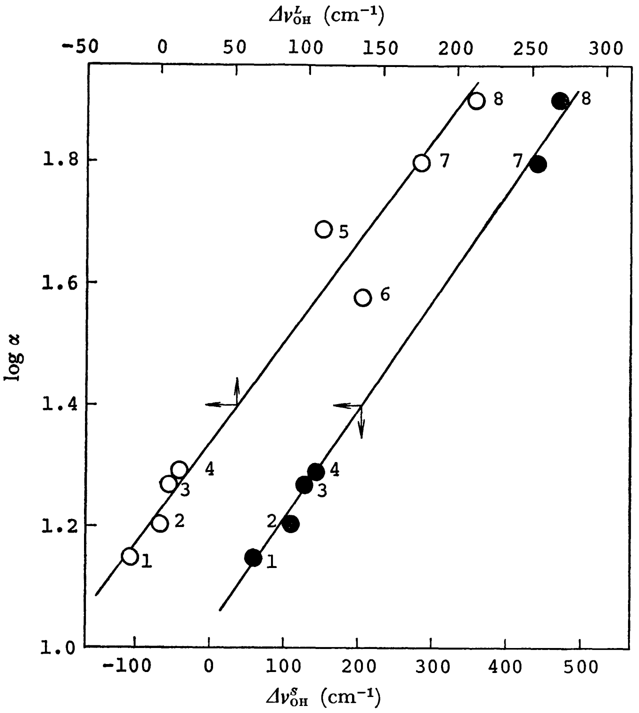

Fig. 5. Relationship between log α and O–H frequency shifts ($\Delta\nu^S_{OH}$) of silica gel surface silanol by gas-phase adsorption or O–H frequency shifts ($\Delta\nu^L_{OH}$) of trimethylsilanol by solvents. 1, Chlorobenzene; 2, Benzene; 3, Toluene; 4, *p*-Xylene; 5, Anisole; 6, Dioxolane; 7,1,4-Dioxane; 8, Tetrahydrofuran.

The above conditions can be considered to be satisfied for the binary mixtures in this paper. By assuming that the specific surface area is equal to the B.E.T. (N_2) area, the effective molecular occupancies were calculated from Eq. (5); they are summarized in the second column of Table 2. The values of A in the sixth column of Table 2 are calculated from A$=(V_M/N)^{2/3}$.[12b,24]This calculation rests on the assumption that the adsorbed molecules are cube-shaped and have the same packing on the surface as the molecules of the adsorbed liquid have in the neat solution. The specific surface area, listed in the last column of Table 2, was calculated with the n^σ/m values and the A_2 values obtained with the latter method. It appears that the S values calculated by the above method yield lower values for the aromatic compounds and higher values for the cyclic ethers in comparison with the B.E.T. (N_2) area of 383 m^2/g for the adsorbent.[12] This disagreement in the areas provides negative support for the assumption of the spherical molecules in the adsorbed phase and suggests the orientation of the adsorbed components on the surface.

We then tried to estimate the orientation of the adsorption by the use of the effective molecular occupancy. If the preferentially-adsorbed molecules with six- or five-membered rings are cylindrical (diameter$=d$(Å) and height$=h$(Å)), then we can approximately obtain the following equation:

$$\pi\left(\frac{d}{2}\right)^2 h\cdot N = V_M \qquad (6)$$

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23) a) G. Schay, L. Gy. Nagy, and T. Szekrenyesy, *Periodica Polytechnica*, **6**, 91 (1962); b) L. Gy. Nagy, *ibid.*, **7**, 75 (1963).

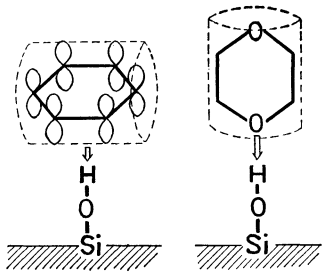
24) F. Paneth and W. Vorwerk, *Z. Phys. Chem.*, **101**, 445 (1922).

Between the diameter and the height, these relations may hold; $d=h\cdot\cos 30°$ for benzene and 1,4-dioxane, and $h=d\cdot\cos 18°$ for tetrahydrofuran and dioxolane. By substituting the above relations into Eq. (6), the diameters and the heights of S_2 molecules were calculated. The diameters of the other aromatic derivatives were taken to be that of benzene.

When the preferentially-adsorbed component adsorbs with an orientation angle (θ) on the surface, it should be given by the following equation:

$$A_2 = \pi\left(\frac{d}{2}\right)^2 \sin\theta + hd\cdot\cos\theta \qquad (7)$$

The values of θ obtained are also listed in the fifth column of Table 2. It is obvious from Table 2 that the adsorptions of all the aromatic compounds except anisole are nearly flat to the surface and that those of the cyclic ethers are nearly perpendicular (Fig. 6-a,b). The orientation angle ($\theta=77°$) for dioxolane may be understood as the simultaneous adsorption by two oxygen atoms in a dioxolane molecule, although it cannot be exactly illustrated. If the adsorption of anisole is caused only by the interaction force between the oxygen atom in an anisole molecule and the surface, the orientation angle should be nearly equal to 30°. On the contrary, for the adsorption due to the benzene nuclei, it should be nearly zero. Therefore, it can be considered that the orientation angle ($\theta=17°$) obtained for anisole suggests the existence of the two kinds of interactions, that of the strong adsorption by the oxygen atom and that of the weak adsorption by the benzene nuclei.[25] This consideration also agrees with the discussion of the large deviation of anisole from both straight lines of log α *versus* I_p and σ_p. This conclusion corresponds well to the spectroscopic data that the two unassociated O-H vibrational bands of trimethylsilanol appear in the anisole solution; the one showing the large shift and intensity is assigned to the O-H band due to the hydrogen bond formed by the lone-pair-electrons of ether oxygen, and the other, showing the small shift and intensity, to that formed by the benzene nuclei.[22a]



(a) Benzene (b) 1,4-Dioxane

Fig. 6. Adsorption models of benzene and 1,4-dioxane on silica gel.

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[25] M. J. D. Low and J. A. Cusumano, *Can. J. Chem.*, **47**, 3906 (1969).