Liquid-phase Adsorption from Binary Solutions on Silica Gel. The Apparent Separation Factors and the Distribution of Adsorption Sites

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The liquid-phase adsorption equilibrium of a cyclohexane-benzene mixture on a silica-gel surface, containing various quantities of physically-adsorbed water, has been studied at 30°C. The apparent separation factors (α^{ap}) have been determined on the assumption that this liquid-phase adsorption is of the Langmuir-type. It was found that the values of α^{ap} were, in general, markedly affected not only by the composition of binary solvents, but also by the amounts of physically-adsorbed water. In order to discuss this point quantitatively, the theoretical equation for estimating the apparent separation factors on a complicated solid surface having two or more types of adsorption sites has been derived on the basis of the theory of chemical equilibrium. The following three types of adsorption sites have been assumed to exist on the silica-gel surface used in this experiment: the surface silanol (σ_1), the monolayer of water (σ_2), and the multilayer of water (σ_3). The separation factors of the σ_1 and σ_3 were experimentally measured as 17.1 and 2.5. By best-fitting the above theoretical equation for α^{ap} with the observed values, the separation factor of the σ_2 site was taken to be 3.7 and the distribution of each adsorption site on the surface was determined.

It is well known that a solid surface consists of the various adsorption sites with different adsorptive capacities. In this sense, studies of the adsorption phenomena offer fundamental and interesting information on the distribution of the adsorption sites and on the chemical reactions on solid catalyst surfaces. Quantitative investigations of the adsorption behavior and the chemical structures of solid surfaces have long been made by using gravimetric methods,[1,2] spectroscopic methods,[3,4] thermodynamic methods,[5,6] and so on.[7,8] However, the quantitative studies have been restricted to the gas-solid interface, and sufficient systematic studies of the liquid-phase adsorption have not been made.[9-11]

In a previous paper,[12] the present authors studied the adsorption equilibria of various binary solutions on chromatographic silica-gel, and determined the separation factors and the numbers of moles in the adsorbed-phase. On the basis of this information, the microscopic behavior of the liquid-phase adsorption was discussed in relation to the adsorption models proposed.

In this study, the adsorption equilibria of cyclohexane-benzene mixtures have been studied on silica-gel, on which a small quantity of water had previously been adsorbed. The purposes of this work are (1) to elucidate the relationships between the apparent separation factor and the composition of solvents and/or the quantity of physically-adsorbed water, and (2) to gain information on the distribution of adsorption sites on the silica-gel surface on the basis of the simple models of adsorption sites.

Experimental

Materials. The spectro-grade cyclohexane and benzene were used as the adsorbates. They were dried with silica-gel and were then used without further purification. The adsorbent was silica-gel (100—200 mesh) for thin-layer chromatography; this silica-gel was commercially obtained. The silica-gel was dried at 160°C for 6 hr in an electric furnace,[13] and various amounts of water were physically-adsorbed to prepare four kinds of adsorbents (SG-1, 2, 3, and 4), which were of the different adsorptive capacities on the surface. The silica-gel dried at 160°C had the following characteristics: B.E.T. (N_2) area=380—420 m^2/g, and pH of aqueous suspension=7.0.

Adsorption Equilibrium. Portions (about 10 m*l*) of a cyclohexane(S_1)–benzene(S_2) solution of a known composition were added to about 4 g of an accurately-weighed adsorbent in a glass ampoule. The sealed ampoule was 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 by means of a Shimadzu gas-chromatography, GC-4AIT.

Determination of Amounts of Physically-adsorbed Water. The amounts of water physically-adsorbed on silica-gel were weighed by means of a Shimadzu micro-thermobalance, MTB-50.

Analysis of Experimental Data

The overall adsorption equilibrium of a binary solution (S_1–S_2) can be expressed as follows:

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[2] M. L. Hair and W. Hertl, *J. Phys. Chem.*, **73**, 4269 (1969).

[3] L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press Inc. (London) Ltd. (1966).

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[5] V. Ya. Davydov, A. V. Kiselev, and B. G. Kuznetsov, *Zhur. Fiz. Khim.*, **39**, 2058 (1965).

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[8] V. Ya. Davydov, A. V. Kiselev, and L. T. Zhuravlev, *Trans. Faraday Soc.*, **60**, 2254 (1964).

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

[10] E. Funakubo, I. Moritani, N. Toshima, and T. Nagai., *Kogyo Kagaku Zasshi*, **66**, 237 (1963).

[11] T. Yagi, K. Shimizu, K. Uchimoto, and S. Maeda, *ibid.*, **68**, 335 (1965).

[12] T. Kagiya, Y. Sumida, and T. Tachi, This Bulletin, **44**, 1219 (1971).

[13] As will be described after, the fact that the physically-adsorbed water is nearly completely removed by the prolonged evacuation at about 160°C has been supported by many investigators, on the basis of the experimental data by the spectroscopic[3,4] and gravimetric techniques.[1]

$$(S_1)^\sigma + (S_2)^l \overset{\alpha^{ap}}{\rightleftharpoons} (S_1)^l + (S_2)^\sigma \tag{1}$$

where the σ and l superscripts represent the adsorbed-phase and the liquid-phase respectively. If the surface of the adsorbent is a heterogeneous one consisting of various adsorption sites, then the apparent separation factor (α^{ap}) is defined as follows:

$$\alpha^{ap} \equiv \frac{n_1{}^l n_2{}^\sigma}{n_2{}^l n_1{}^\sigma} = \frac{n_1{}^l \sum\limits_i n_2{}^{\sigma_i}}{n_2{}^l \sum\limits_i n_1{}^{\sigma_i}} \tag{2}$$

where σ_i is the i-th adsorption site on the adsorbent; where $n_1{}^l$ and $n_2{}^l$ are, respectively, the numbers of moles of S_1 and S_2 in the equilibrium mixture (mol); where $n_1{}^{\sigma_i}$ and $n_2{}^{\sigma_i}$ are, respectively, the numbers of moles of S_1 and S_2 adsorbed on the σ_i site (mol), and where $n_1{}^\sigma = \sum\limits_i n_1{}^{\sigma_i}$ and $n_2{}^\sigma = \sum\limits_i n_2{}^{\sigma_i}$.

The numbers of moles of S_1 and S_2 in the adsorbed-phase, namely, $\sum\limits_i n_1{}^{\sigma_i}$ and $\sum\limits_i n_2{}^{\sigma_i}$, can be related to the Gibbs surface excess (Γ), defined by Eq. (3), by means of the following Eq. (4):[14]

$$\Gamma_2 \equiv \frac{n^0}{mS} \Delta x_2{}^l \tag{3}$$

$$\Gamma_2 = \frac{1}{mS}\left(x_1{}^l \sum_i n_2{}^{\sigma_i} - x_2{}^l \sum_i n_1{}^{\sigma_i}\right) \tag{4}$$

In these equations, m is the weight of the adsorbent (g); S, the surface area per unit of mass of the adsorbent (m^2/g); n^0, the total number of moles of the original mixture (mol), and $\Delta x_2{}^l$, the change in the mole fractions of S_2 in the solutions between before and after the adsorption.

On the other hand, supposing that the adsorption is of the Langmuir-type and that the effective molecular occupancies (A) of the two components in the adsorbed-phase are known in advance, then the surface area should be given by:[15,16]

$$S = \frac{N_A}{m}\left(A_1 \sum_i n_1{}^{\sigma_i} + A_2 \sum_i n_2{}^{\sigma_i}\right) \tag{5}$$

As has been described in the previous paper,[12] it is known that the adsorption of a cyclohexane-benzene solution on silica-gel is of the Langmuir-type. If the surface is almost completely covered by the preferentially-adsorbed component (S_2=benzene), we have:

$$S = \frac{n^\sigma_{m2}}{m} A_2 N_A \tag{6}$$

where n^σ_{m2} is the number of moles of S_2 required to form a perfect monolayer.

Since the ratio of A_1 and A_2 is a constant ($\beta = A_2/A_1$), the following equations are derived from Eqs. (3), (4), (5), and (6):

$$\sum_i n_1{}^{\sigma_i} = \frac{\beta(n^\sigma_{m2} x_1{}^l + n^0 \Delta x_1{}^l)}{x_1{}^l + \beta x_2{}^l} \tag{7}$$

and

$$\sum_i n_2{}^{\sigma_i} = \frac{\beta n^\sigma_{m2} x_2{}^l + n^0 \Delta x_2{}^l}{x_1{}^l + \beta x_2{}^l} \tag{8}$$

Hence, the apparent separation factor should be expressed by Eq. (9):[17]

$$\alpha^{ap} = \frac{\left(\beta \dfrac{n^\sigma_{m2} x_2{}^l}{m} + \dfrac{n^0 \Delta x_2{}^l}{m}\right) x_1{}^l}{\beta\left(\dfrac{n^\sigma_{m2} x_1{}^l}{m} + \dfrac{n^0 \Delta x_1{}^l}{m}\right) x_2{}^l} \tag{9}$$

As is obvious from Eq. (9), one can easily determine the apparent separation factor (α^{ap}) from the observed values of $x_1{}^l$ and $x_2{}^l$, if the values of β and n^σ_{m2}/m can be measured in any way. The effective molecular occupancies of benzene derivatives and cyclic ethers have already been reported.[12]

The value of n^σ_{m2}/m may be evaluated from the B.E.T. (N_2) area according to Eq. (6). However, there is a possibility of overestimating the value of S, because the molecular size of benzene is quite large compared with that of the nitrogen molecule. In order to avoid this risk, it is desirable to estimate directly the n^σ_{m2}/m value from the same experimental data of liquid-phase adsorption.

According to Everett,[14] the behavior of a perfect binary solution in contact with a Langmuir-type adsorbing surface can be discussed on the basis of the following equation:

$$\frac{x_1{}^l x_2{}^l}{n^0 \Delta x_2{}^l / m} = \frac{m}{n^\sigma}\left(x_2{}^l + \frac{1}{\alpha^{ap} - 1}\right) \tag{10}$$

where $n^\sigma = \sum\limits_i n_1{}^{\sigma_i} + \sum\limits_i n_2{}^{\sigma_i}$. Equation (10) shows that a good linear relationship holds over an entire concentration range between $m x_1{}^l x_2{}^l / n^0 \Delta x_2{}^l$ and $x_2{}^l$ if the values of α^{ap} and m/n^σ are both constant. In general, a curvature is observed in a low concentration range of a preferentially-adsorbed component (S_2) because of the existence of the various adsorption sites, the difference in the effective molecular occupancies of adsorbed components, and so on. It can, however, be expected that a linear relationship exists over a wide concentration range of S_2 when the adsorption power of S_2 is so large in comparison with that of S_1 that the surface can be almost entirely covered by S_2. The slope is nearly equal to m/n^σ_{m2}:

$$\frac{m}{n^\sigma} \simeq \frac{m}{n^\sigma_{m2}} \tag{11}$$

By substituting the n^σ_{m2}/m values obtained from the Everett plots and the β values into Eq. (9), one can examine the dependence of the composition of binary solvents on the apparent separation factors.

Results

The amounts of water adsorbed physically on silica-gel were measured; they are listed in Table 1.

TABLE 1. LISTS OF EXPERIMENTAL RESULTS OF LIQUID-PHASE ADSORPTION OF CYCLOHEXANE-BENZENE SOLUTION ON SILICA-GEL SURFACE

Adsorbent	ω (mmol/g)	n^σ_{m2}/m (mmol/g)	$\overline{\alpha}^{ap}$	$\alpha^{ap}(x^l_2=1.0)$	$\alpha^{ap}(x^l_2=0)$
SG–1	0	1.848	16.03	17.10	17.10
SG–2	1.12	1.854	11.36	15.70	8.10
SG–3	2.21	2.068	5.89	8.30	4.70
SG–4	4.14	1.799	3.56	5.05	3.00

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

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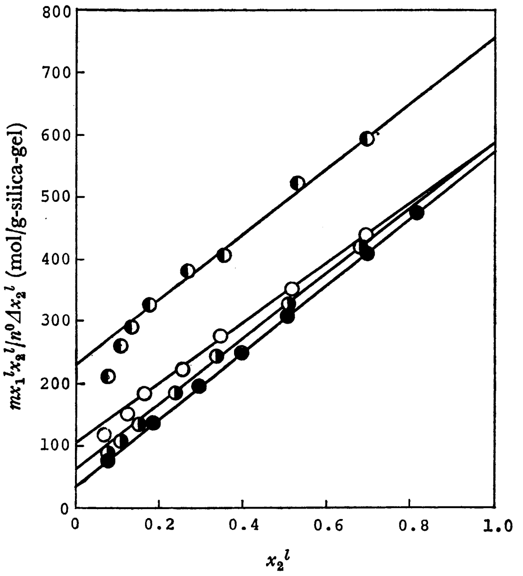

Fig. 1. Everett plots of $mx_1^lx_2^l/n^0\Delta x_2^l$ vs. x_2^l for cyclohexane (S_1)-benzene (S_2) mixture on various silica-gel surfaces. Silica-gel surface: ●, SG-1; ◑, SG-2; ○, SG-3; ◐, SG-4.

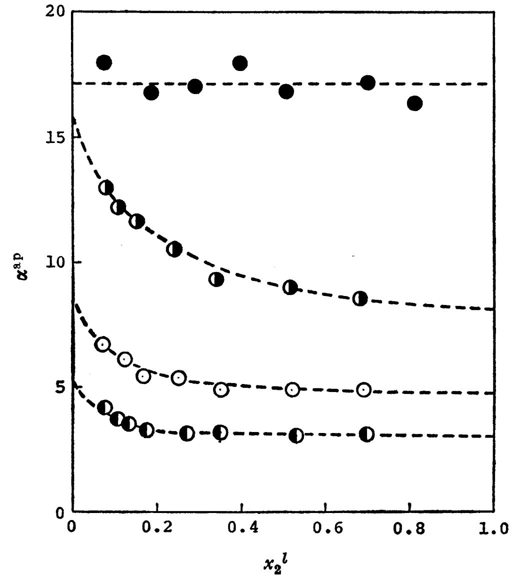

Fig. 2. Changes in apparent separation factors of cyclohexane (S_1)-benzene (S_2) mixture on various silica-gel surfaces. Silica-gel surface: ●, SG-1; ◑, SG-2; ○, SG-3; ◐, SG-4.

Figure 1 shows the analytical results for the adsorption of cyclohexane(S_1)-benzene(S_2) plotted according to Eq. (10). Although good linear relationships hold in the high concentration range of S_2, pronounced deviations are observed in the low concentration range. The degrees of deviations become larger as the amounts of adsorbed water increase. From the solpe and the intercept of the linear part in Fig. 1, the numbers of moles of adsorbed components in the high concentrations of S_2 were determined; they are listed in Table 1, together with the $\overline{\alpha^{ap}}$ values which correspond to the average values of the apparent separation factors at the high concentrations of S_2. It is obvious in Table 1 that the value of $\overline{\alpha^{ap}}$ decreases remarkably with the increase in the amount of adsorbed water, whereas the value of n^s_{m2}/m is constant within the limits of experimental error. More noticeable is the fact that there exists a linear relationship over an entire concentration range when using silica-gel (SG-1) containing no physically-adsorbed water. As will be discussed below, the effective molecular occupancy of benzene is nearly equal to that of cyclohexane. Taking this fact into account, the correlation obtained for SG-1 may indicate that the α^{ap} value is to be regarded as a constant, independent of the composition of the solvents. In other words, it may be suggested that there is only one type of adsorption site on the surface of SG-1. Joining this suggestion with the results of the infrared-spectroscopic analysis of the structures of the silica-gel surface,[3,4] the surface of SG-1 is considered to be maximally hydroxylated.[1]

On the other hand, the effective molecular occupancy of benzene was reported in a previous paper to be 34.41 Å²/molecule.[12] That of cyclohexane was calculated to be 38.46 Å²/molecule from its molar volume on the assumption of a cube-shaped molecule. The β value is 0.895.

Using this β value and the n^s_{m2}/m value in Table 1, the apparent separation factor in Eq. (9) was determined and plotted against the x_2^l, as is shown in Fig. 2. It was evident in Fig. 2 that the apparent separation factors (α^{ap}) decrease markedly with the increase in the quantity of adsorbed water. This corresponds to the fact that the adsorptive capacity of a site become small during the physical adsorption of water. Of interest is the fact that the α^{ap} value approaches the preferential coordination constant ($\alpha^{H_2O}=2.5$) of a cyclohexane-benzene solution to liquid water, which is the separation factor in the liquid-liquid interface.[18,19] It should also be noted that the α^{ap} values for SG-1 are constant, regardless of the solvent compositions,

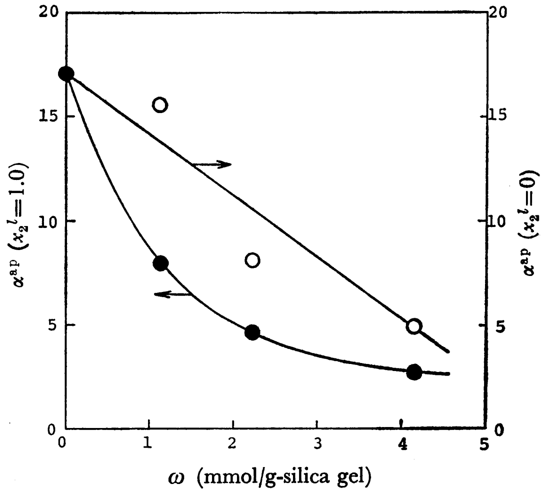

Fig. 3. Relationships between limited values of α^{ap} of cyclohexane (S_1)-benzene (S_2) mixture and amounts of physically-adsorbed water.
●, α^{ap} (x_2^l=1.0); ○, α^{ap} (x_2^l=0).

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18) T. Kagiya, Y. Sumida, and T. Tachi, unpublished data.

19) T. Kagiya, Y. Sumida, T. Watanabe, and T. Tachi, This Bulletin, **44**, 923 (1971).

while the α^{ap} values for SG-2, 3, and 4 vary with the changes in the solvent compositions. This may imply the existence of two or more types of adsorption sites on the silica-gel surface of SG-2, 3, and 4, the adsorptive capacities of which differ from each other. This problem will be discussed in the next section in connection with the models of various adsorption sites.

By extrapolating the α^{ap}–$x_2{}^l$ curves to $x_2{}^l \rightarrow 0$ and $x_2{}^l \rightarrow 1$, the limited values of α^{ap} were determined; they are summarized in the last two columns of Table 1. Figure 3 shows the relationships between these limited values and the amounts of adsorbed water (ω); the $\alpha^{ap}(x_2{}^l=1.0)$ value decreases exponentially with the increase in the ω value, while the $\alpha^{ap}(x_2{}^l=0)$ value decreases almost linearly.

When we define $x_2{}^\sigma$ as the mole fraction of S_2 in the whole adsorbed-phase, the values of $x_2{}^\sigma$ can be expressed as follows:

$$x_2{}^\sigma = \frac{\alpha^{ap} x_2{}^l}{x_1{}^l + \alpha^{ap} x_2{}^l} \tag{12}$$

The relationships of $x_2{}^l$ *vs.* $x_2{}^\sigma$ are demonstrated in Fig. 4. The non-symmetric curves for SG-2, 3, and 4 are obviously due to the fact that the α^{ap} values change greatly with the compositions of the binary solvents.[19]

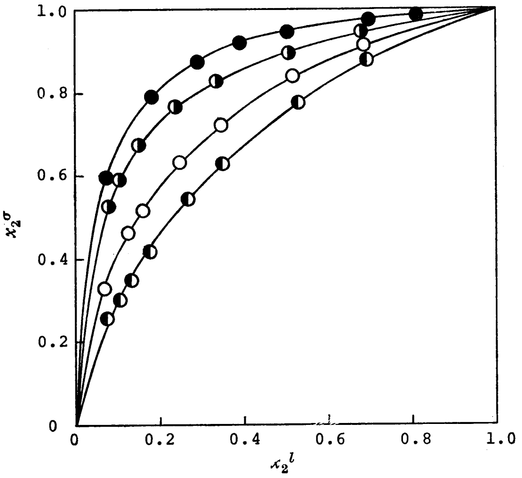

Fig. 4. Relationships between mole fractions of benzene in whole adsorbed-phase ($x_2{}^\sigma$) and mole fractions of benzene in equilibrium mixtures ($x_2{}^l$).
Silica-gel surface: ●, SG-1; ◑, SG-2; ○, SG-3; ◐, SG-4.

Discussion

Estimation of Apparent Separation Factors on the Basis of the Theory of Chemical Equilibrium. In the previous section, it has been indicated that the apparent separation factors are remarkably affected by both the quantity of physically-adsorbed water and the composition of the solvents. On the basis of the theory of chemical equilibrium, we examined first of all the dependence of both factors on the apparent separation factors.

In general, the silica-gel surface is well known to be a so-called heterogeneous adsorption surface, on which various adsorption sites with different adsorptive capacities are distributed. It can be considered, therefore, that the overall adsorption equilibrium of the binary solvents on such a solid surface can be expressed as the summation of the adsorption equilibria on all the adsorption sites:

$$\begin{array}{l} (\mathrm{S}_1)^{\sigma_1} + (\mathrm{S}_2)^l \overset{\alpha^{\sigma_1}}{\rightleftarrows} (\mathrm{S}_1)^l + (\mathrm{S}_2)^{\sigma_1} \\ (\mathrm{S}_1)^{\sigma_2} + (\mathrm{S}_2)^l \overset{\alpha^{\sigma_2}}{\rightleftarrows} (\mathrm{S}_1)^l + (\mathrm{S}_2)^{\sigma_2} \\ \quad\vdots \qquad\quad \vdots \qquad\qquad\quad \vdots \qquad\quad \vdots \\ (\mathrm{S}_1)^{\sigma_i} + (\mathrm{S}_2)^l \overset{\alpha^{\sigma_i}}{\rightleftarrows} (\mathrm{S}_1)^l + (\mathrm{S}_2)^{\sigma_i} \\ \quad\vdots \qquad\quad \vdots \qquad\qquad\quad \vdots \qquad\quad \vdots \end{array} \tag{13}$$

where $(\mathrm{S})^{\sigma_i}$ is the solvent component adsorbed on the adsorption site σ_i; $(\mathrm{S})^l$ is the solvent in the equilibrium mixture, and α^{σ_i} is the separation factor of the binary solvents on the σ_i site.

Each of the separation factors can be defined by:

$$\alpha^{\sigma_i} \equiv \frac{n_1{}^l n_2{}^{\sigma_i}}{n_2{}^l n_1{}^{\sigma_i}} \tag{14}$$

Hence, the apparent separation factor on the whole adsorption surface can be given as follows:

$$\alpha^{ap} = \frac{n_1{}^l \sum_i n_2{}^{\sigma_i}}{n_2{}^l \sum_i n_1{}^{\sigma_i}} = \frac{\sum_i n_2{}^{\sigma_i}}{\sum_i n_2{}^{\sigma_i}/\alpha^{\sigma_i}} \tag{15}$$

By using Eq. (14), the number of moles of adsorbed components on the σ_i site is:

$$n^{\sigma_i} = n_1{}^{\sigma_i} + n_2{}^{\sigma_i} = \left(1 + \frac{n_1{}^l}{\alpha^{\sigma_i} n_2{}^l}\right) n_2{}^{\sigma_i} \tag{16}$$

If the θ^{σ_i} is defined as the ratio of n^{σ_i} to the total number of moles of adsorbed components in the adsorbed-phase, then:

$$\theta^{\sigma_i} \equiv \frac{n^{\sigma_i}}{\sum_i n^{\sigma_i}} \tag{17}$$

Since the effective molecular occupancies of cyclohexane and benzene are nearly equal ($A_1 \simeq A_2$), the values of $\sum_i n^{\sigma_i}$ and n^{σ_i} can be approximated as follows:

$$\sum_i n^{\sigma_i} \simeq \frac{mS}{N_A A_2} \tag{18}$$

$$n^{\sigma_i} \simeq \frac{mS^{\sigma i}}{N_A A_2} \tag{19}$$

where S^{σ_i} represents the surface area of the σ_i site, *i.e.*, $S = \sum S^{\sigma_i}$. Accordingly,

$$n_2{}^{\sigma_i} = \frac{\alpha^{\sigma_i} x_2{}^l}{x_1{}^l + \alpha^{\sigma_i} x_2{}^l} \theta^{\sigma_i} \frac{mS}{N_A A_2} \tag{20}$$

By substituting Eq. (20) into Eq. (15), we obtain:

$$\alpha^{ap} = \frac{\sum_i \alpha^{\sigma_i} \theta^{\sigma_i}/(x_1{}^l + \alpha^{\sigma_i} x_2{}^l)}{\sum_i \theta^{\sigma_i}/(x_1{}^l + \alpha^{\sigma_i} x_2{}^l)} \tag{21}$$

In Eq. (21), the α^{σ_i} value is the constant characteristic of the combination of the adsorption site and the binary solvent system, and the θ^{σ_i} is the factor (S^{σ_i}/S) depending on the distribution of the adsorption sites (or the adsorptive capacities) of the silica-gel surface. Therefore, even when using the same silica-gel and the same binary solvents, if there is a distribution of the adsorption sites on the surface, the apparent separation factor should change with the composition of the solvents. When $x_2{}^l$ approaches 1.0, the α^{ap} values converge to a constant value:

$$\alpha^{ap}(x_2^l=1.0)=\frac{1}{\sum\limits_i \theta^{\sigma}{}_i/\alpha^{\sigma}{}_i} \qquad (22)$$

Similarly, by extrapolating to $x_2^l \to 0$:

$$\alpha^{ap}(x_2^l=0)=\sum_i \alpha^{\sigma}{}_i\theta^{\sigma}{}_i \qquad (23)$$

Models of Adsorption Sites on the Silica-gel Surface. In order to discuss the analytical results obtained in Fig. 2 by using Eq. (21), we must determine the various types of adsorption sites on the silica-gel surface on which a small quantity of water has been previously adsorbed. Many experimental studies of the change in the silica-gel surface upon the adsorption of water have been made, and much reliable informations have been gathered.[3,20]

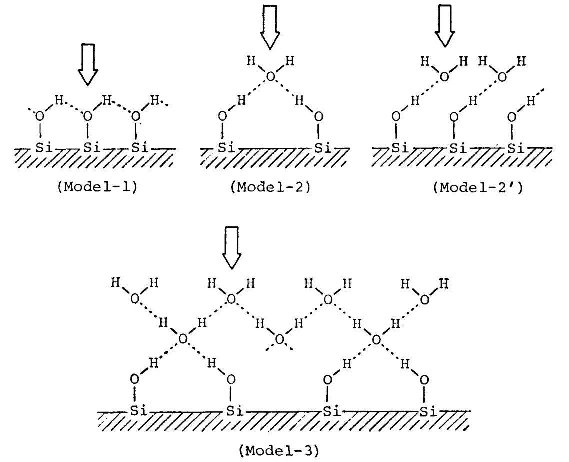

Fig. 5. Adsorption sites on silica-gel surface containing physically-adsorbed water.

From these combined infrared and gravimetric data,[1,3] it has been concluded that the physically-adsorbed water on silica-gel surface is almost completely removed by prolonged evacuation at 150—170°C, leaving a hydrogen-bonding surface formed between the adjacent silanol groups (Site Model-1 in Fig. 5). This has also been approximately, though not seriously, supported by Fripiat *et al.*[7] and Kiselev *et al.*[8] Moreover, Kiselev *et al.*[8] estimated, from their experimental results on the surface chemical reaction, that the number of surface hydroxyl groups is about 4.8 OH/100 Å^2, corresponding to one OH group per silicon atom on the surface. However, recent spectroscopic studies[21-23] have suggested the existence of three types of surface silanol, *i.e.*, the single, geminal, and paired silanol groups. In this study, the proper amounts of water were artifically adsorbed on silica-gel heated at 160°C. Therefore, the surface should be entirely covered with bridged silanol O–H groups.

The models of physically-adsorbed water have not been clear enough to permit the drawing of exact conclusions.[20] On the adsorption of a very small quantity of water, Kiselev *et al.*[7,24] proposed that a 1 : 2 hydrogen bonding was formed between one molecule of water and two adjacent surface silanols (Site Model-2), while Morimoto *et al.*[25] presented a 1 : 1 hydrogen bond mechanism (Site Model-2'). The 1 : 2 and 1 : 1 mechanisms may, of course, coexist on the surface.[20] If there are no clear-cut differences in the adsorptive capacities of the cyclohexane-benzene system on the 1 : 2 and 1 : 1 hydrogen-bonding surfaces, we can identify Model-2' with Model-2 with respect to the adsorptive capacity. This is almost certain, because the liquid-phase adsorptions on both Model-2 and Model-2' take place on the monolayer of water molecules bonded "directly" to the surface silanol.[26] A further physical-adsorption of water forms the multilayer coverage of water molecules (Site Model-3), where the liquid-phase adsorption occurs on the multilayer of water molecules bonded "indirectly" to the silanol.[26]

On the basis of such speculations, we conventionally classified the adsorption sites of silica-gel containing the physically-adsorbed water into the following three groups: Model-1 (the surface silanol, σ_1), Model-2 (the monolayer of water, σ_2), and Model-3 (the multilayer of water, σ_3).

Distribution of Adsorption Sites on the Silica-gel Surface. The next problem is to determine the separation factor

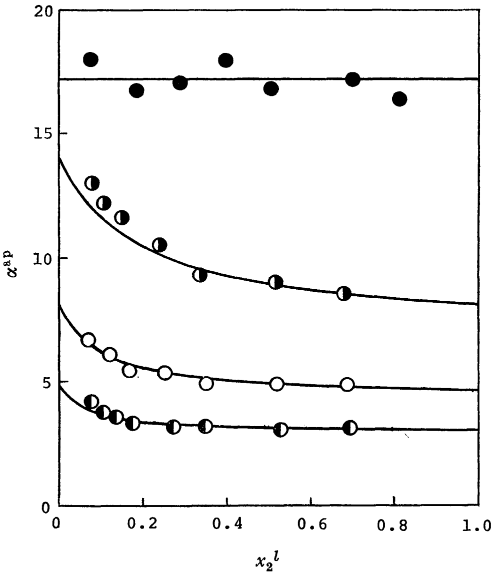

Fig. 6. Simulation of apparent separation factors of cyclohexane (S_1)-benzene (S_2) mixture on various silica-gel surfaces. Silica-gel surface:
●, SG-1; ◑, SG-2; ○, SG-3; ◐, SG-4.
The solid line represents the theoretical curve.

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21) J. B. Peri and A. L. Hensley, Jr., *J. Phys. Chem.*, **72**, 2926 (1968).

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26) In the case of binary solvent system in which the proton-accepting power of solvent component is considerably large, compared with that of water, the solvent component may destroy the coverage of water molecules to adsorb "directly" to the surface silanol. However, the possibility can be neglected in the cyclohexane-benzene system employed here.

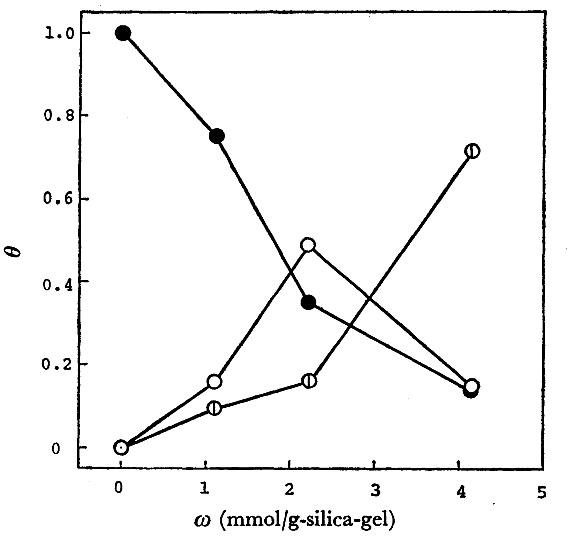

Fig. 7. Distribution of adsorption sites on silica-gel surfaces containing physically-adsorbed water.
Adsorption site: ●, σ_1; ○, σ_2; ⦶, σ_3.

(α^{σ_i}) of cyclohexane-benzene on each adsorption site, σ_i. According to the above speculations, the surface of SG-1 is a so-called homogeneous σ_1 site. Therefore, the $\alpha^{\sigma}{}_1$ value can be taken to be 17.1 from the experimental data in Table 1. Supposing that, in Model-3, the silanol groups exert little influence on the adsorptive capacity of the adsorption surface, the value of α^{σ_3} on the multilayer of water may be considered to be approximately equal to the preferential coordination constant ($\alpha^{H_2O}=2.5$) to liquid water.[18,19]

The value of α^{σ_2} cannot be measured by the use of this experimental technique, since it is impossible to prepare artifically a complete monolayer of water molecules on the silica-gel surface. However, we calculated the α^{σ_2} value by using Eq. (21). That is, by simulating the experimental points of the apparent separation factors obtained from Eq. (9) with Eq. (21), in which the values of x_1^l, x_2^l, α^{σ_1}, and α^{σ_3} are known, the best-fitting α^{σ_2} value was determined, together with θ^{σ_1}, θ^{σ_2}, and θ^{σ_3} values. The value of α^{σ_2} was calculated to be 3.7. It is reasonable that the α^{σ_2} value is slightly larger than the α^{σ_3} value.

The agreement between the experimental results and the theoretical curves of Eq. (21) is shown in Fig. 6. Though slight deviations are observed in the low concentration range of benzene, they may be overcome by considering four or more types of adsorption sites. However, it can be considered, on the basis of the fairly good accordance, that the above speculation regarding adsorption sites is quite reasonable.

In Fig. 7, each of the calculated θ^{σ} values is plotted against the amounts of physically-adsorbed water (ω). The curves represent the distribution of the adsorption sites on the silica-gel surface. On the silica-gel surface (SG-2) containing a very small quantity of adsorbed water, the σ_1 site gradually decreases and the σ_2 and σ_3 sites gradually increase. On the surface of SG-3, the σ_2 site occupies about half of the adsorption surface. The further adsorption of water (SG-4) brings about decreases in the σ_1 and σ_2 sites and a prominent increase in the σ_3 site. These tendencies are also in harmony with chemical intuition.

On the basis of this discussion, it may be reasonable to conclude that Eq. (21) is useful in offering not only valuable information on the liquid-phase adsorption on complicated solid surface, but also microscopic information on the structures of the surface.