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The Heat of Adsorption from Solution. I. The Heat of Adsorption of Benzene on Silica Gel from the Benzene-Cyclohexane Solution

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The sensitivity and reliability of the improved-flow micro-calorimeter have been examined by supplying given amounts of electric energy to the calibration heater inserted in the calorimeter. The detection limit of the heat amount was found to be 0.01 mcal, and its probable error to be ±0.5 and ±0.3% at the heat evolutions of 10 and 40 mcal respectively. The heat of the adsorption of benzene on silica gel from a cyclohexane solution has been measured at 30°C by the calorimeter thus constructed. The adsorption calorimetry indicates that benzene is adsorbed reversibly on silica gel, and that the differential heat of the adsorption of benzene is independent of the amount of adsorbed benzene, but that it depends strongly on the pretreatment temperature of the silica gel. The heats of adsorption were found to be 1.2, 1.6, 2.0, and 3.8 kcal/mol on silica gel samples treated at 100, 300, 500, and 800°C respectively. The findings on the heats of adsorption have been elucidated in terms of the interaction between benzene molecules and silanol groups on silica gel.

The heat of adsorption from a solution is of great significance, since it is considered to be a measure of the interaction energy between the adsorbed molecules dissolved in the solution and the solid surface concerned.[1] Many reports have been published on the heat of adsorption from a solution, as calculated from the temperature dependence of the adsorption isotherm. The data obtained, however, seem to be lacking in reliability, because of such difficulties as the temperature effect on solubility and the uncertainties both in regard to the activity coefficient of the adsorbed molecules and in regard to the thickness of the adsorbed layer.[2,3]

So far, two direct calorimetric methods have been developed to measure the heat of adsorption from solu-

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[1] J. J. Kipling, "Adsorption from Solution of Nonelectrolytes," Academic Press, London-New York (1965), Chapter 10.

[2] *ibid.*, Chapter 14.

[3] F. E. Bartell, T. L. Thomas, and Y. Fu, *J. Phys. Chem.*, **55**, 1456 (1951).

tion. Young *et al.*[4] have developed a method of measuring the heat of adsorption from solution by means of the technique of the heat of immersion. On the other hand, Groszek[5] has constructed a flow micro-calorimeter, in which the heat of adsorption was measured by injecting a solution of a known concentration into a solvent flowing through an adsorbent bed placed in the column.

In the present investigation, a flow micro-calorimeter has been constructed which is suitable for the exact measurement of a small heat evolution. By using this calorimeter, the heat of adsorption has been measured on a system of silica gel and the benzene-cyclohexane solution. Several investigators have reported the preferential adsorption of an aromatic hydrocarbon dissolved in an aliphatic hydrocarbon on the surface of silica gel.[6-11] However, the direct calorimetric measurement of the heat of adsorption has not yet been made in this system. Here, it will be reported that the direct calorimetric measurement by our improved flow micro-calorimeter can give a highly precise value of the interaction energy of adsorption in the same system.

Experimental

Materials. Silica gel was prepared by the hydrolysis of ethyl orthosilicate. The latter was purified by fractional distillation, and the fraction between the boiling points of 167.1 and 167.8°C was used. Two hundred grams of ethyl orthosilicate and 1015 g of redistilled water were mixed violently at 97—99°C for 4 hr in a 2-*l* flask. In this process, silica gel was produced by the hydrolysis reaction. After that, the excess water was evaporated out at *ca.* 80°C. The silica gel thus obtained was dried at 100°C in an air-bath for 24 hr, calcined at 500°C in the atmosphere for 15 hr, and treated in an agate ball-mill. The benzene and cyclohexane were purified by the usual method.[12] Glass beads of 65—100 mesh, used as a column bed of the flow micro-calorimeter, were treated with hot concentrated hydrochloric acid, washed thoroughly with distilled water, and then dried at 100°C in an air-bath.

Surface Area of Silica Gel. The specific surface area of the silica gel was determined by the BET method from the nitrogen adsorption at the temperature of liquid nitrogen. The surface areas of the samples pretreated *in vacuo* for 4 hr at 100, 300, 500, and 800°C were found to be 423, 422, 431, and 396 m^2/g respectively.

Flow Micro-calorimeter. The calorimeter was constructed by setting a heater circuit in the detection column of the liquid-column chromatograph manufactured by the Japan Electron Optics Laboratory Co., Ltd. The calorimeter, shown diagrammatically in Fig. 1, consisted of a constant flow pump, solvent and solution reservoirs, purification, reference and detection columns, exchange valves, and a metal thermostat. The flow rate was regulated by means of the constant flow pump. The thermistor was used as the temperature-sensitive element. A heater made of platinum wire with a diameter of 0.01 mm and a resistance of 12Ω was placed 1 cm above the thermistor in the detection column. The change in resistivity of the thermistor was amplified and recorded; it was caused by the temperature change due to the heat evolved by the adsorption on silica gel or by the electric current flowing through the heater. Furthermore, it should be noticed that this calorimeter performed excellently in several more points, *i.e.*, the method of injecting the solution, the temperature control of the metal thermostat, and the construction of the double-column system.

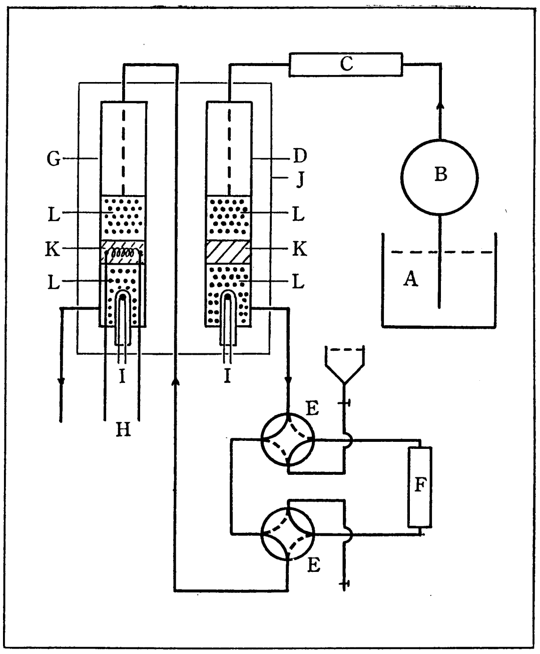

Fig. 1. Block diagram of flow micro-calorimeter.
A, solvent reservoir; B, constant flow pump; C, purification column; D, reference column; E, exchange valves; F, solution reservoir; G, detection column; H, calibration heater; I, thermistor; J, metal thermostat; K, silica gel (adsorbent); L, glass beads.

Adsorption Calorimetry. The primary purpose of the present adsorption calorimetry is to test the performance of the improved flow micro-calorimeter by applying it to the investigation of the interaction between the surface of silica gel and benzene molecules dissolved in cyclohexane. Silica gel (60—140 mg) was pretreated at a reduced pressure of 10^{-3} Torr for 4 hr at an elevated temperature and then placed in a bed at the same position as the calibration heater. In this case, care was taken so that the silica gel sample did not directly come in contact with the atmosphere. The silica gel bed, several millimeters thick, was sandwiched by glass beads (65—100 mesh) in the detection column. Both of them were similarly packed in the reference column. In the purification column, a large quantity of silica gel was used for the filteration of any impurities. At first, the cyclohexane used as a solvent was forced to flow through at the rate of 0.21 m*l*/min. The flow direction of cyclohexane is shown by arrows in Fig. 1. In order to reduce the fluctuation of the temperature in the detection column, the reference column

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[4] G. J. Young, J. J. Chessick, and F. H. Healey, *J. Phys. Chem.*, **60**, 391 (1956).

[5] A. Groszek, *J. Chromatogr.*, **3**, 454 (1960); *Chem. Ind.*, 482 (1965).

[6] C. L. Lloyd and B. L. Hariss, *J. Phys. Chem.*, **58**, 899 (1954).

[7] L. R. Snyder, *ibid.*, **67**, 2622 (1963).

[8] C. N. Rowe and R. W. Schiessler, *ibid.*, **70**, 787 (1966).

[9] B. C.-Y. Lu and R. F. Lama, *Trans. Faraday Soc.*, **63**, 727 (1967).

[10] S. K. Suri and R. W. Ramakriskna, *J. Phys. Chem.*, **72**, 1555 (1968).

[11] T. Kagiya, Y. Sumida, and T. Tachi, This Bulletin, **44**, 1291 (1971).

[12] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Organic Solvent," 2nd ed., Interscience Publishers, Inc., New York (1955), p. 306, 315.

was connected with the flow circuit and was positioned close to the detection column in the metal thermostat. After the thermal equilibrium had been established in the measuring system, a stable base line with no slope was recorded; then the flowing liquid was replaced with a benzene solution of a given concentration by using the exchange valves. Thus, the temperature rise caused by the adsorption of benzene was recorded. During the flow of the benzene solution, the temperature rose initially, passed through maximum, and then went down to the same level as the original base line. This means that the adsorption equilibrium of benzene has been attained. The A curve in Fig. 6 is an example of such an adsorption peak. The desorption peak was obtained after exchanging the flow of the solution with that of the solvent by means of the exchange valves, as is shown in the B curve in Fig. 6. The calibration of the calorimeter was made with the aid of the calibration heater; the peak area recorded was plotted against the electric energy supplied by the heater.

Adsorption Measurement of Benzene on Silica-gel from the Benzene-Cyclohexane Solution. The amount of benzene adsorbed on silica-gel from the cyclohexane solution was obtained from the difference in the concentrations before and after the adsorption. In a 2-m*l* ampoule, silica gel (0.5—1.0 g) was pretreated under the same conditions as those described in the adsorption calorimetry. A known amount (*e.g.*, 2 g) of the solution of a given concentration was poured into the ampoule, and then it was sealed. In this case, precaution was taken so that the solid powder did not come into direct contact with the atmosphere by cutting off the top of the ampoule in the solution. The sealed ampoule was shaken for 15 hr at 30°C; this resulted in the attainment of the adsorption equilibrium. The concentration of benzene in the supernatant solution was determined by means of absorption spectroscopy at the wave length of 254.5 mμ by using a spectrophotometer of the Hitachi 139 type.

Results and Discussion

Reliability and Sensitivity of the Flow Micro-calorimeter. In Fig. 2, several calibration peaks are illustrated. These peaks are recordings of the resistivity change in the thermistor set in the detection column when different amounts of electric energy were supplied to the calibration heater at the heat-evolution rate of 4.60 mcal/min and at the flow rate of the solvent of 0.21 m*l*/min. Figure 3 presents the relation between the peak area and the electric energy supplied, which was obtained by varying the rate of the solvent flow and that of the heat evolution. It may be seen from Fig. 3 that the peak area is exactly proportional to the heat evolved and that the slope of the straight lines varies with the flow rate of the solvent, independently of the heat-evolution rate. The slope for the straight lines in Fig. 3 increases with the flow rate of the liquid. This fact may be interpreted as follows: the heat generated in the detection column escapes in all directions of the column, but the enhanced flow rate of the liquid causes an increase in the heat sensitivity of the thermistor. Thus, it can be understood that, in flow calorimetry, it is necessary to operate the calorimeter at a constant flow rate.

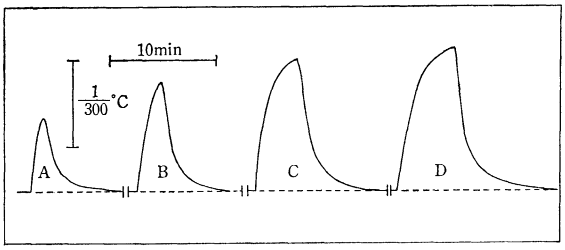

Fig. 2. Calibration peaks at 30°C.
Solvent, cylcohexane; flow rate, 0.21 m*l*/min; heat-evolution rate, 4.60 mcal/min. Peak A, 4.62 mcal; B, 9.28 mcal; C, 18.5 mcal; D, 23.2 mcal.

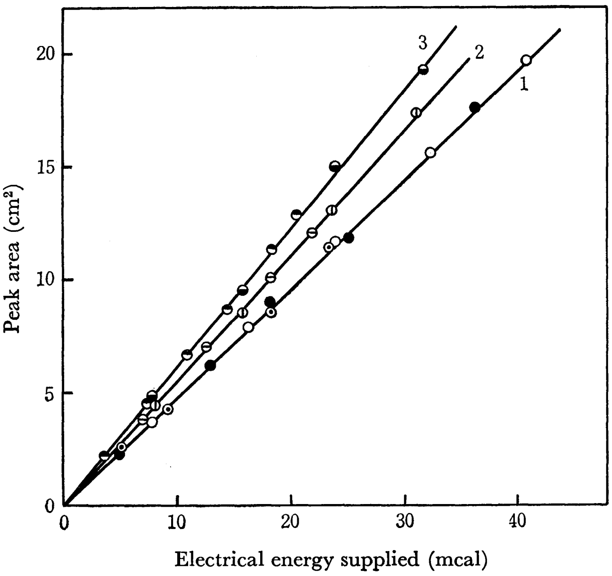

Fig. 3. Relation between peak area and heat.
1: flow rate, 0.21 m*l*/min; heat-evolution rate, ⊙: 4.60 mcal/min, ●: 12.7 mcal/min, ○ 16.3 mcal/min.
2: flow rate, 0.31 m*l*/min; heat-evolution rate, ⊖: 3.67 mcal/min, ⦶: 15.9 mcal/min.
3: flow rate, 0.46 m*l*/min; heat-evolution rate, ◓: 3.72 mcal/min, ◒: 15.9 mcal/min.

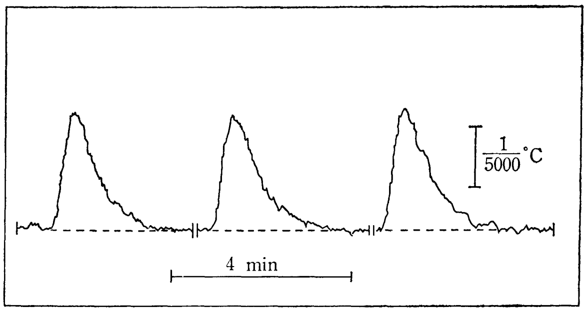

Fig. 4. Response of flow micro-calorimeter for 0.1 mcal at 30°C.
Solvent, cyclohexane; flow rate, 0.21 m*l*/min.

Next, the accuracy of the calorimeter was examined for the heat amounts of 10 and 40 mcal. Five measurements were repeated in each case. The peak area obtained gives probable errors of ±0.5 and ±0.3% for 10 and 40 mcal respectively. The sensitivity of the calorimeter was also tested. Figure 4 shows the three peaks obtained for 0.1 mcal. Although there is appreciable noise, the peak area can be measured within an error of ±5%, which corresponds to the detection limit

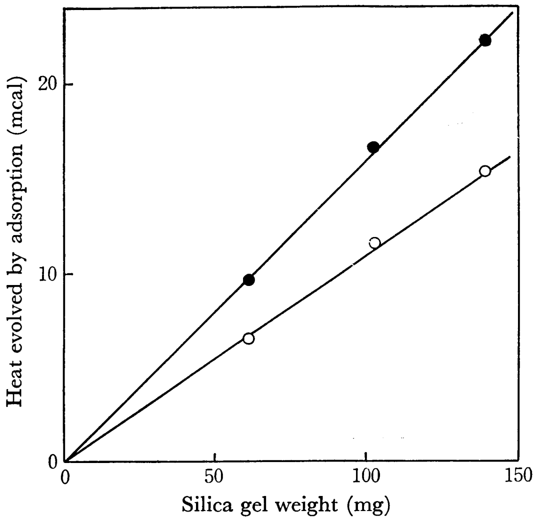

Fig. 5. Relation between heat evolved by adsorption of benzene and silica gel weight in flow micro-calorimeter. Pretreatment temperatrue of silica gel, 100°C; benzene concentration,
○: 0.050 molality, ●: 0.085 molality.

of the heat of 0.01 mcal.

Finally, the relation between the amount of the heat evolved by adsorption and the weight of the adsorbent used for the calorimetry was examined at a constant concentration of benzene. The results obtained are shown in Fig. 5, which indicates that the heat evolved by the adsorption of benzene is proportional to the weight of the silica gel used within the range of the present experiments. The above examinations prove that the present flow micro-calorimeter is useful for the measurement of the heat of adsorption from solution, especially for the investigation of a system with a weak interaction energy.

In comparison with the micro-calorimeter employed by Groszek,[5] the following points are improved in the present calorimeter: (1) the temperature of the metal thermostat is regulated within an error of $\pm 10^{-3}$°C, (2) the noise arizing from the fluctuation in the flow rate of the liquid and in the temperature of the metal thermostat is eliminated by adopting the double-column system, and (3) the solution in the reservoir is smoothly injected into the detection column by using the exchange valves. The sensitivity of his calorimeter was approximately the same as that of the present one. He reported that the slope was recorded by the base line, and that the peak areas are nearly linearly related to the heat produced by the heater up to 20 mcal. On the contrary, the present results give a straight base line, one with no slope over a prolonged period, and a good linearity between the peak area and the amount of heat supplied.

Heat of Adsorption of Benzene on Silica Gel from the Benzene-Cyclohexane Solution. Figure 6 shows the response of the flow micro-calorimeter, including both the exothermic peak due to the adsorption of benzene on silica gel and the endothermic one due to the desorption from silica gel. The silica gel samples used in the experiments in Fig. 6 were pretreated at 100°C *in vacuo*. In each sample of silica gel, no matter what the pretreatment temperature, the area of the adsorption peak is in good agreement with that of the desorption peak within the limits of experimental error. This agreement establishes that benzene molecules are adsorbed reversibly on the silica gel surface.

Taking into account the specific surface area of silica gel, the heat evolved by the adsorption of benzene, H, can expressed in calories per 100 Å^2 of silica gel. This is plotted in Fig. 7 as a function of the concentration. The silica-gel samples used were pretreated at 100, 300, 500, and 800°C *in vacuo*. It can be seen from Fig. 7 that the value of H increases with an increase in the concentration of benzene. Moreover, the H value

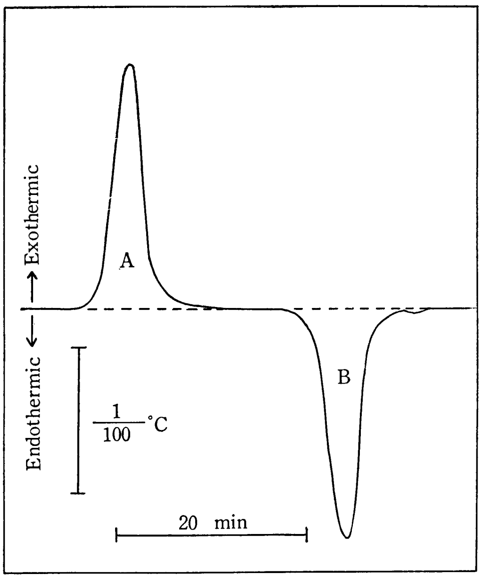

Fig. 6. Adsorption and desorption peaks of benzene at 30°C. A, adsorption peak; B, desorption peak. Solvent, cyclohexane; flow rate, 0.21 m*l*/min; benzene concentration, 0.095 molality; silica gel weight, 120 mg.

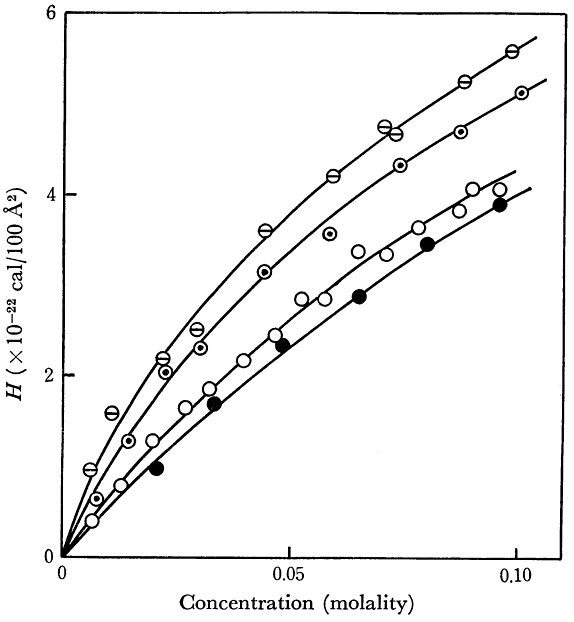

Fig. 7. Heat evolved by adsorption of benzene, H, on silica gel from cyclohexane solution at 30°C.
Pretreatment temperature of silica gel,
○: 100°C, ⊙: 300°C, ⊖: 500°C, ●: 800°C.

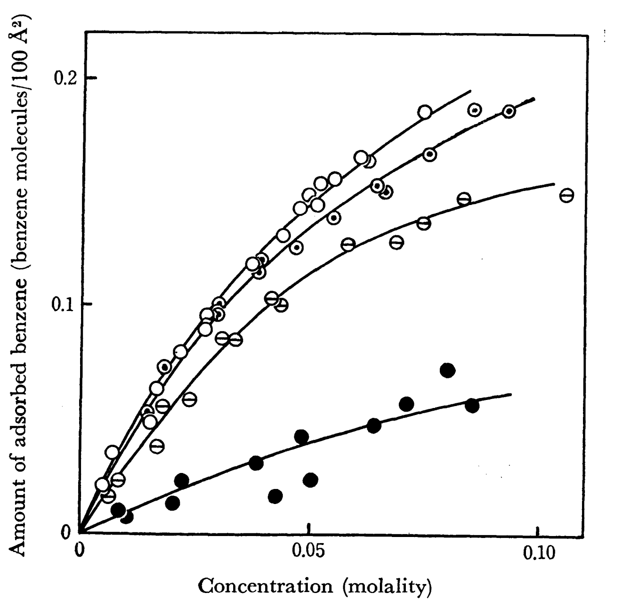

Fig. 8. Adsorption isotherm of benzene on silica gel at 30°C. Pretreatment temperature of silica gel,
○: 100°C, ⊙: 300°C, ⊖: 500°C, ●: 800°C.

depends on the pretreatment temperature, *i.e.*, it increases in the order of 800, 100, 300, and 500°C treatment.

On the other hand, the adsorption isotherm of benzene on silica gel from the benzene-cyclohexane solution is as is shown in Fig. 8, where the amount of adsorbed benzene is expressed in benzene molecules per 100 Å^2 of silica gel. An appreciable fluctuation is observed in the experimental data on the amount of benzene adsorbed on the silica gel samples pretreated at 800°C, probably because of the remarkably reduced amount of adsorption. Taking the molecular area of benzene adsorbed in the close-packed state on graphitized carbon black to be 40 Å^2,[13] it may be seen from Fig. 8 that only a small part of the silica gel surface is covered by benzene molecules within the concentration range examined here. Furthermore, it can be seen from Fig. 8 that the higher the pretreatment temperature of silica gel, the smaller the amount of benzene adsorbed.

From the smooth curves shown in Figs. 7 and 8, the relation between H and the amount of adsorbed benzene is obtained (*cf.* Fig. 9). A good linear relationship holds between them, and the slope increases with the pretreatment temperature of silica gel. Since the slope directly indicates the differential heat of adsorption, it can be seen from Fig. 9 that the differential heat of adsorption of benzene on silica gel from the cyclohexane solution is independent of the amount of adsorbed benzene within the concentration range examined. Therefore, we can conclude that the surface of silica gel is energetically homogeneous for the adsorption of benzene from the cyclohexane solution at a low coverage of benzene. Furthermore, it should be noticed that the heat of the adsorption of benzene depends greatly on the pretreatment temperature; the values are 1.2, 1.6, 2.0, and 3.8 kcal/mol on the samples pretreated at 100, 300, 500, and 800°C respectively. These values show that the interaction between the silica gel surface and benzene molecules is relatively weak compared to that between the same surface and polar molecules.[14]

In the present calorimetric measurements, the heat of dilution should be a factor in addition to the heat evolved by adsorption. In the benzene-cyclohexane system, the heat of dilution can be calculated from the heat of the mixing of benzene with cyclohexane. Ac-

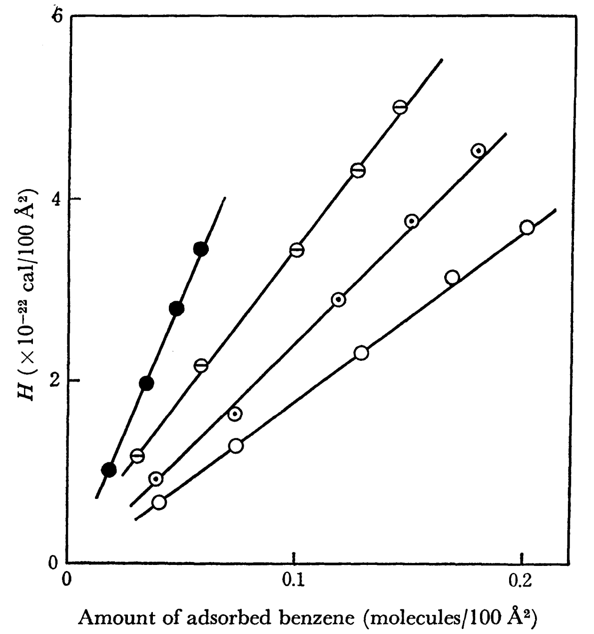

Fig. 9. Relation between H and amount of adsorbed benzene pretreatment temperature of silica-gel,
○: 100°C, ⊙: 300°C, ⊖: 500°C, ●: 800°C,

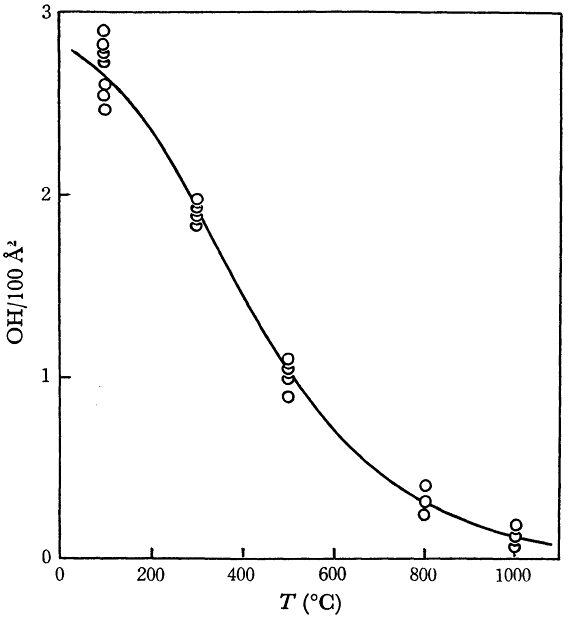

Fig. 10. Relation between silanol content and pretreatment temperature of silica gel, T.

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[13] A. A. Isirikyan and A. V. Kiselev, *J. Phys. Chem.*, **65**, 601 (1961).

[14] T. Morimoto and H. Naono, Unpublished data.

cording to the data reported by Maagek *et al.*,[15] the heat of dilution is less than 5 cal/mol in the concentration range of benzene examined here; this is negligibly small compared with the heat of the adsorption of benzene.

So far, it has been clarified that the silanol groups play an important role in the interaction between the silica gel surface and aromatic hydrocarbon molecules, whether in the gaseous or in the liquid phase.[7,11,16,17] In the present investigation, the surface silanol groups were determined by an analysis of the active hydrogen atoms;[18] the results are presented in Fig. 10 as a function of the pretreatment temperature of silica gel. Figure 10 shows that the silanol content decreases remarkably with an increase in the pretreatment temperature. On the other hand, as is shown in Fig. 8, the amount of benzene adsorbed on the silica gel surface also decreases with an increase in the pretreatment temperature. These results suggest that benzene molecules are selectively adsorbed on silanol groups on the silica gel surface. Moreover, a benzene molecule may be considered to interact with a single silanol group on the basis of the following facts. Assuming that the surface silanol groups are distributed uniformly, the area of silica gel per silanol group can be calculated from the data in Fig. 10: the area are 38, 53, 100, and 320 Å^2 for the surfaces treated at 100, 300, 500, and 800°C respectively. Thus, the area per silanol group is almost equal to, or is larger than, the molecular area of benzene (40 Å^2) mentioned above.[13]

In order to examine the quantitative relationship between the amount of benzene adsorbed and the silanol content, the ratio of the former to the latter was replotted against the concentration of benzene (*cf.* Fig. 11). First, it may be seen from Fig. 11 that the ratio is always far less than unity over the concentration range of benzene examined; this indicates that the surface silanol groups are only partly covered by benzene molecules over the range of the amount of adsorbed benzene examined, in spite of a quite small population of silanol groups. Figure 11 also shows that the higher the pretreatment temperature, the larger the ratio. This latter fact implies that the silanol groups on the surfaces treated at higher temperatures can attract benzene molecules more strongly than those on the surfaces treated at lower temperature; this corresponds with the results in Fig. 9. The heat treatment of silica gel at higher temperatures may change the structure of the surface and make it feasible to adsorb benzene molecules.

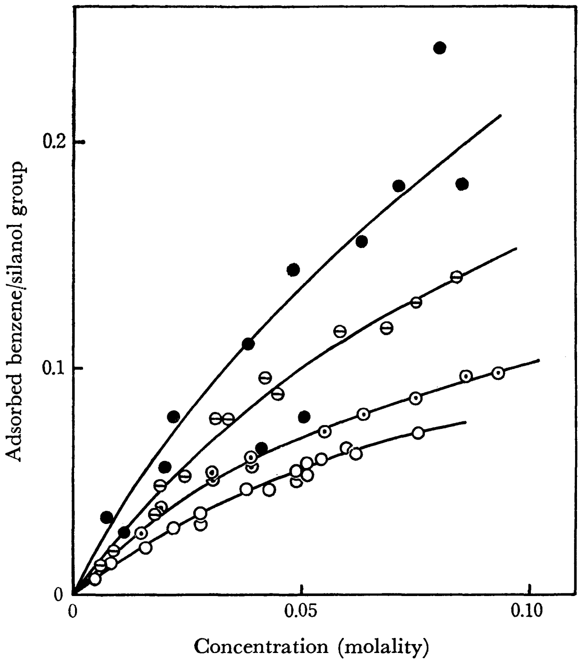

Fig. 11. Effect of pretreatment temperature of silica gel on the ratio of adsorbed benzene to silanol group.
○: 100°C, ⊙: 300°C, ⊖: 500°C, ●: 800°C.

The authors wish to thank Dr. M. Nagao for the measurements of the specific surface area of silica gel and Mrs. K. Moori for her assistance in a part of experiments.

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[15] R. V. Maagek and H. C. Van Ness, *A. I. Ch. E. Journal*, **7**, 190 (1966).

[16] N. Okuda, *Nippon Kagaku Zasshi*, **82**, 1118 (1961).

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

[18] The experimental details will be published in the next report; *cf.* J. J. Fripiat and J. Uytterhoeven, *J. Phys. Chem.*, **66**, 800 (1962).