Table II. Recovery of Bromazepam from Rat Blood

Sample	Bromazepam added (μg/ml)	Bromazepam recovered (μg/ml)	Recovery (%)
1	2	2.01	100.5
2	5	4.82	96.5
3	10	10.01	100.1
4	20	19.98	99.1
Mean			99.0
Whole blood[a]	100 (mg/kg)	$14.5+37$[b] (μg/ml)	

[a] Blood level in rats 1 hr after oral administration of 100 mg/kg of bromazepam.
[b] Mean ±SD. (10 rats).

Recovery of Bromazepam from Rat Blood

One milliliter of bromazepam sample (2 to 20 μg/ml) in 3% arabic gum solution was added to 2 ml of whole blood. After deproteinization, the solution was adjusted to pH 8.0 with Na_2CO_3 and assayed spectrometrically in accordance with the standard procedure. Recovery of added bromazepam ranged from 96 to 100.5% with a mean recovery of 99.18%. Bromazepam was also administered orally to rats, and the blood level of bromazepam determined at 1 hr after administration is shown Table II. The present procedure, utilizing a specific reaction for the determination of intact bromazepam, is suitable for identifying and quantitating bromazepam in prepared tablets and in biological fluids.

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Adsorption of Styrene on Activated Carbon and Regeneration of Spent Activated Carbon

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Adsorption of styrene on activated carbon was investigated on the basis of the adsorption isotherm, isosteric heat of adsorption, and compressed volume of condensed styrene. Regeneration of spent activated carbon was examined by the extraction of styrene with organic solvents. The Langmuir equation could be applied to the adsorption isotherms of styrene on activated carbon. The isosteric heats of adsorption of styrene on activated carbon Nos. 1—3 and 5 were less than twice the value of the heat of condensation of styrene ($\Delta H_0=9.64$ kcal/mol) in the range of θ 0.2 to 1.0, and therefore, styrene adsorbed in this range of θ seemed to be physisorbed on activated carbon. Styrene physisorbed on activated carbon seemed to be compressed in the pores. Spent activated carbon could be regenerated by extracting the styrene with acetone at about 30° and its adsorptive capacity became approximately equal to that of fresh activated carbon.

Keywords——styrene; activated carbon; adsorption; isosteric heat of adsorption; compression; regeneration

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Styrene is often discharged into the atmosphere from factories producing styrene resin and synthetic rubber, and it was listed as one of the offensive substances by the Offensive Odor Control Law in Japan in 1976. Styrene vapor has a stimulating action on the eye,[2] and membranes of the nose and trachea.[3] It also has toxic effects on blood cells, the liver,[4] and the nervous system.[5] The concentration of styrene permissible in the working environment is restricted to 1.2 ppm in the Soviet Union and Bulgaria, 50 ppm in Japan, or 100 ppm in Great Britain, Western Germany, Switzerland, and America.[6] We have previously studied the relationship between the amount of styrene adsorbed and the pore structure.[7]

In the present work, the adsorption isotherms of styrene on activated carbon at 30° and 40°, the isosteric heat of adsorption, and the compressed volume of styrene adsorbed were determined in order to elucidate the mechanism of adsorption of styrene on activated carbon. The regeneration of spent activated carbon was examined by the extraction of styrene with organic solvents.

Experimental

Materials——Styrene (commercially purified material) was purified by vacuum distillation. Activated carbon used was a commercial product, and its particle size was 4—16 mesh. The specific surface area of activated carbon was measured with the BET apparatus by using nitrogen gas at liquid nitrogen temperature, and the procedure for measurement of pore volume was described previously.[8] The specific surface area and the pore volume of activated carbon are shown in Table I.

Adsorption Procedure——Activated carbon was dried at 110° for 1 hr at 1×10^{-3} Torr before use. The equilibrium amount adsorbed at equilibrium concentrations up to 9 Torr was measured by a gravimetric method by using a BET apparatus with a spring balance at 30° and 40°.

Isosteric Heat of Adsorption——The isosteric heat of adsorption was calculated from the adsorption isotherms at two different temperatures (30° and 40°) by means of the Clausius-Clapeyron equation.[9] From the equation $(\partial \log p/\partial 1/T)_{A,n_s} = -q_{st}/2.3\boldsymbol{R}$ (q_{st}, isosteric heat of adsorption; $\boldsymbol{R}$, gas constant; A, a constant surface area; n_s, a constant amount of styrene adsorbed), the isosteric heat of adsorption was calculated.

Regeneration of Spent Activated Carbon——The spent activated carbon was washed with organic solvent in a flask at constant temperature under the following conditions: (1) spent activated carbon/solvent, 1% (w/v); (2) rate of stirring, 500 rpm; (3) time of stirring, 1 hr. It was then dried at 110° for 1 hr in a thermostat.

Results and Discussion

1. Adsorption of Styrene on Activated Carbon

Figure 1 shows the adsorption isotherms of styrene on activated carbon at 30° and at pressures up to 9 Torr. The adsorption isotherms rose sharply at about 0.5 Torr and then reached plateaux, which presumably correspond to the limiting adsorption. Since the amount adsorbed on activated carbon No. 2 was larger than those on other activated carbons at pressures up to 9 Torr, it was concluded that the activated carbon. No. 2 was a preferable adsorbent for removing styrene. It is known that adsorption isotherms of the type shown in Fig. 1 are very often obtained when the adsorbent is microporous.[10] The adsorption isotherm has

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[2] R.D. Stewart, H.C. Dodd, E.D. Baretta, and A.W. Schaffer, *Arch. Environ. Health*, **16**, 656 (1968).

[3] R.W. Stephenson and L.B. Fosdick, *Amer. Ind. Hyg. Assoc. J.*, **21**, 522 (1960).

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[5] L.B. Bourne and F.J.M. Milner, *Brit. J. Industr. Med.*, **20**, 100 (1966).

[6] Special Committee for Japanese Translation of Foreign Literature (ed.), "Suchiren Monomā no Dokusei Kenkyu Shiryo" (Toxicologie du Styrene Monomere, ed. by M. Oltramare, E. Desbaumes, C. Imhoff, and W. Michiels), Japan Medical Center, Tokyo, 1976, p. 19.

[7] K. Boki, S. Tanada, and T. Kita, *Bull. Environm. Contam. Toxicol.*, **24**, 185 (1980).

[8] K. Boki, *Nippon Eiseigaku Zasshi*, 32, 482 (1977).

[9] V. Ponec, Z. Knor, and S. Cerny, "Adsorption on Solids," (English translation edited by B.A. Smith and N.G. Adams), Butterworths, London, 1974, pp. 310—311, 372—373.

[10] R. Aveyard and D.A. Haydon, "An Introduction to the Principles of Surface Chemistry," Cambridge University Press, London, 1973, pp. 153—154.

been explained by Ponec *et al.*[9] in terms of the potential theory of adsorption of Polanyi,[11] that is, the influence of opposite walls frequently overlaps in narrow pores and the intensity of adsorption force fields is substantialy increased, so that the amount adsorbed rises very little with increased pressure after the micropores have been completely filled. The limiting values of adsorption at 30° and 40° were found to correlate with the micropore volume rather than the specific surface area (Table I). The limiting value of adsorption is considered to be the amount corresponding to filling of the micropores rather than that corresponding to completion of a monolayer. The results are consistent with the finding that the amount of styrene adsorbed on activated carbon was dominated by its micropore volume.[7] Figure 2 shows Langmuir plots of the adsorption isotherms of styrene on activated carbon at 30°. The

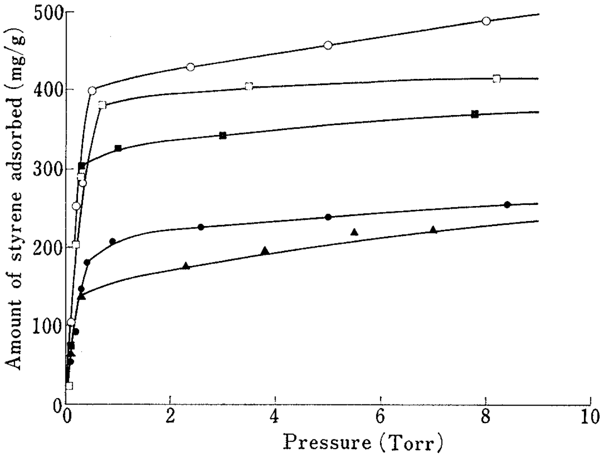

Fig. 1. Adsorption Isotherms of Styrene on Activated Carbon at 30°

—●— No. 1, —○— No. 2, —■— No. 3, —□— No. 4,
—▲— No. 5.

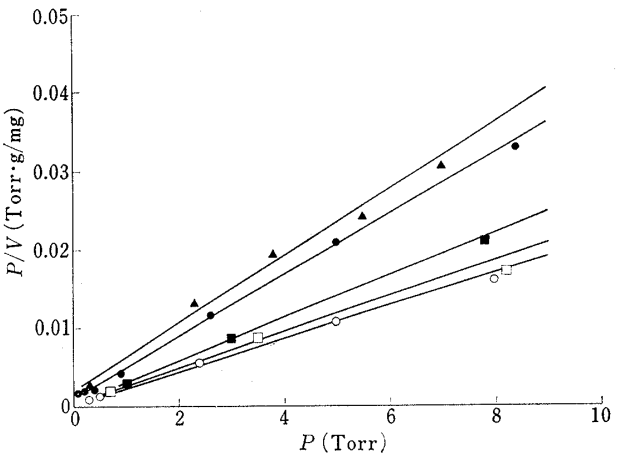

Fig. 2. Langmuir Plots of the Adsorption Isotherms of Styrene on Activated Carbon at 30°

—●— No. 1, —○— No. 2, —■— No. 3, —□— No. 4,
—▲— No. 5,
P: equilibrium pressure. V: amount adsorbed.

Table I. Physical Properties of Activated Carbon, Limiting Values of Amount of Styrene Adsorbed on Activated Carbon, and Residual Amounts at 30°

No.	Specific surface area[a] (m^2/g)	Micropore volume[b] (ml/g)	Total pore volume[c] (ml/g)	V_m at 30° (ml/g)	V_m at 40° (ml/g)	Residual amount[d] (%)
1	906.0	0.395	0.557	0.296	0.271	71.1
2	866.4	0.532	0.607	0.556	0.422	71.6
3	1141.4	0.454	0.650	0.424	0.389	75.3
4	378.0	0.485	0.523	0.538	0.445	68.1
5	642.9	0.267	0.347	0.235	0.229	61.2

a) N_2–BET method.
b) Micropore volume is the volume at pore radii less than 15.5 Å.
c) Total pore volume is the volume at $p_e/p_s=1.0$.
d) Residual amount of styrene was determined after outgassing under 1×10^{-2} Torr for 2 hr at 30°.

Langmuir equation was applicable to the adsorption isotherms of styrene on activated carbon. From the slopes of plots of P/V against P, the limiting values of the amount adsorbed (V_m) at 30° were obtained (Table I). The spent activated carbon must be regenerated before the amount of styrene adsorbed reaches the limiting values shown in Table I. After evacuation at 30° and at 1×10^{-2} Torr for 2 hr ,61—75% of the limiting values were retained on the ac-

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11) M. Polanyi, *Trans. Faraday Soc.*, **28**, 316 (1932).

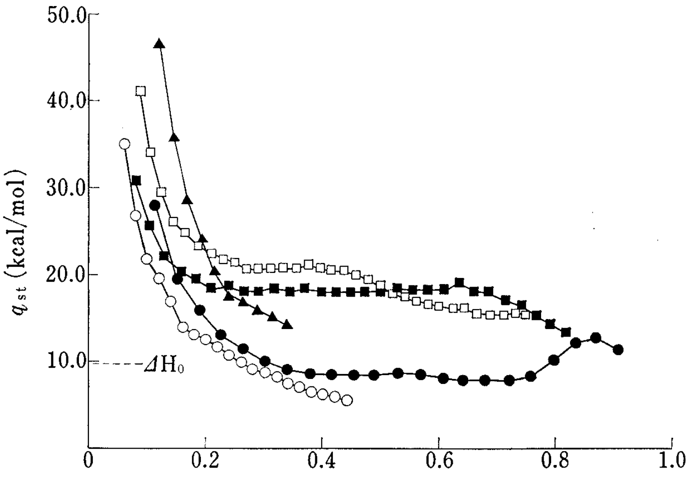

Fig. 3. Isosteric Heat of Adsorption *vs.* Adsorption Ratio

—●— No. 1, —○— No. 2, —■— No. 3, —□— No. 4, —▲— No. 5,
ΔH_0: heat of condensation of styrene

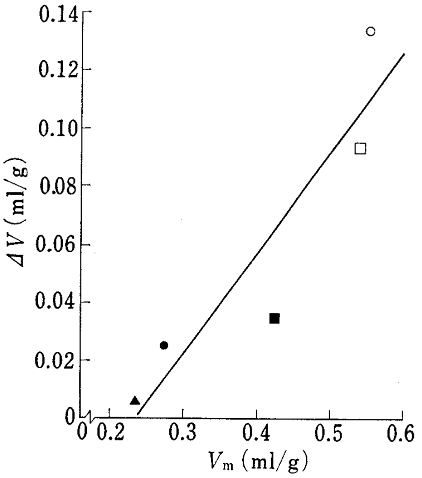

Fig. 4. Relationship between Compressed Volume and Limiting Volume of Amount Adsorbed

● No. 1, ○ No. 2, ■ No. 3,
□ No. 4, ▲ No. 5.

tivated carbon. The isosteric heat of adsorption was determined in order to clarify whether the residual styrene was chemically or physically adsorbed. Figure 3 shows the isosteric heat of adsorption *vs.* adsorption ratio. If the isosteric heat of adsorption does not exceed twice the value of the heat of condensation, the process is defined as physical adsorption.12) The heat of condensation of styrene (ΔH_0=9.64 kcal/mol) was evaluated by fitting the Clausius–Clapeyron equation to the data.13) The isosteric heats of adsorption of activated carbon Nos. 1—3 and 5 were less than twice the value of the heat of condensation in the range θ 0.2 to 1.0. According to the above definition,12) styrene thus seems to be physisorbed on activated carbon in this range. The isosteric heats of adsorption on activated carbon Nos. 1—3 and 5 fall smoothly from initial high values to values close to twice the values of the heat of condensation. Styrene seems to be chemisorbed on activated carbon at the initial stage of adsorption because the isosteric heats of adsorption are larger than twice the heats of condensation in this range. These results indicate that the bulk of the residual styrene is physisorbed on activated carbon. That is to say, large amounts of styrene resident in activated carbon, as shown in Table I, must be physically retained in the micropores of activated carbon.

The relationship between the compressed volume and the limiting volume was determined in order to elucidate the state of adsorption of styrene in the pores of activated carbon, as shown in Fig. 4. If the density of styrene condensed in pores is equal to that of common liquid styrene, V_m(ml/g) of styrene at 30° is considered to be the same as that at 40°. The liquid densities of styrene at 30° and 40° were reported to be 0.893 and 0.884 g/ml, respectively.13) The limiting values of the amount of styrene adsorbed, V_m(ml/g), was calculated by dividing the limiting amount adsorbed per unit weight (mg/g), obtained by application of the Langmuir equation to the adsorption isotherm, by the liquid density at each temperature. If there was a difference in V_m at 30° and 40°, ΔV was obtained by deducting V_m at 40° from V_m at 30°. On the assumption that the pore structure of activated carbon is not transformed by adsorption of styrene, ΔV is considered to be a compressed volume.14) A linear relationship between the compressed volume and the limiting value of the amount

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12) W.J. Jones and R.A. Rose, *J. Chem. Soc.*, **1968**, 1787.
13) R.W. Gallant, *Hydrocarbon Processing*, **49**, 112 (1970).
14) Y. Morioka, K. Aoyama, S. Kashiwada, J. Kobayashi, and I. Higuchi, *Nippon Kagaku Kaishi*, **1975**, 2065.

Table II. Treatments of Regeneration of Spent Activated Carbon Nos. 1, 2, and 3 and Adsorptive Capacity of Reactivated Carbon

Treatment	Adsorptive capacity (%)		
	No. 1	No. 2	No. 3
Non-treatment	13.9—21.0	18.3—25.7	10.2—15.1
Dry (110°)	40.9—46.0	46.6—51.6	28.6—37.7
CH_3COOH (20°)	62.0—64.9	58.8—64.0	77.6—83.0
CH_3OH (20°)	58.2—64.9	66.0—70.9	59.0—68.1
C_2H_5OH (20°)	60.3—63.5	58.4—63.8	67.3—76.5
C_6H_6 (20°)	68.5—72.4	60.3—65.9	70.6—78.6
CH_3COCH_3 (20°)	76.3—82.4	78.2—83.5	80.3—87.8
(30°)	88.6—92.2	82.4—88.4	79.0—88.5
(40°)	85.4—87.6	78.4—83.5	82.2—89.7

An adsorptive capascity of reactivated carbon was obtained at an equilibrium pressure 9 Torr at 30°.

adsorbed on each activated carbon was seen. This result demonstrates that liquid styrene is compressed in pores and that the compressed volume due to adsorption is proportional to the limiting volume of the amount adsorbed.

2. Regeneration of Spent Activated Carbon

Table II shows the treatments tested for the regeneration of spent activated carbon Nos. 1—3 with large residual amounts of styrene (Table I) and the adsorptive capacities of the reactivated carbons. In general, the regeneration of spent activated carbon is accomplished by thermal means. One difficulty in this case is that styrene monomer is polymerized by thermal treatment before the temperature of the spent activated carbon is raised to the point at which styrene will be desorbed. It is, therefore, preferable to utilize a solvent in order to extract styrene adsorbed on activated carbon. The results of Table II indicate that the extraction of styrene with various solvents can restore the adsorptive capacity. The cross-sectional areas of these solvents are estimated to be smaller than that of styrene (36.1 Å^2),15) and therefore styrene retained in the pores of activated carbon can be extracted and replaced by these solvents. Although we have as yet little information as to the precise values of solubility of styrene in various solvents, the finding that adsorptive capacities were different in extracted carbons can perhaps be explained in terms of the differences of solubiltiy of styrene in the extractants. The adsorptive capacities of these spent activated carbons Nos. 1—3 could be well restored by washing with acetone at about 30° and by drying the washed activated carbons at 110°.

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15) S. Tanada and K. Boki, *Bull. Environm. Contam. Toxicol.*, **23**, 524 (1979).