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Adsorption Equilibria of Trimethylamine on Porous Adsorbents

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Adsorption equilibria of trimethylamine as the offensive odor substance was measured by a gravimetric method to elucidate the mechanism of its adsorption on activated carbon, silicate, and zeolite. The mechanism of adsorption was discussed on the basis of application of the Dubinin-Astakhov equation to the adsorption isotherms and relation between the characteristic energy (E), exponent (n) and pore size distribution. The Dubinin-Astakhov equation was well applicable to the adsorption isotherms of activated carbon, silicate, and zeolite. The exponent (n) of activated carbon, silicate, and zeolite was 2, 3, and 3, respectively. It was confirmed that the adsorption of trimethylamine on the adsorbents resulted in the volume filling of their micropores by the mechanism of capillary condensation, and that the two or three degrees of freedom in translation of trimethylamine was lost by its adsorption on the micropores or ultramicropores, respectively. The amount of trimethylamine adsorbed on the microporous adsorbents was determined by their micropore volume of pore radius less than about 20 Å.

Keywords——trimethylamine; porous adsorbent; mechanism of adsorption; Dubinin-Astakhov equation; theory of London-van der Waals force; micropore volume; volume filling

Trimethylamine, which is discharged from the treatment plant of human waste and from the fish and animal processing plants,[2–4)] has a typical fishy ammoniacal odor. Its threshold is 0.4 ppm[5)] and its concentration is limited to the range of 0.005—0.07 ppm by Offensive Odor Control Law in Japan.

Trimethylamine was catalytically oxidized to deprive the plant of its odor by natural zeolite and was oxidized to ammonia.[4)] Tezuka and Takeuchi[6)] discussed the adsorption of trimethylamine on amorphous silica-alumina, using isosteric heat of adsorption obtained from the adsorption isotherms. Chemisorption of trimethylamine on commercial silica-alumina catalyst was studied by infrared spectrum (IR) techniques.[7)] Adsorptive capacity of porous *m*-aminophenol resins for trimethylamine tended to increase with pore size of resins.[8)] In a recent paper,[9)] we showed that microporous activated carbon was the most suitable for removing trimethylamine and that the amount adsorbed on it was mainly determined by its microporous structure.

The present paper discusses the mechanism of the adsorption of trimethylamine on microporous activated carbon, silicate, and zeolite on the basis of the application of Dubinin-

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2) E. Tanikawa, T. Motohiro, and M. Aikiba, *Hokkaido Daigaku Suisan Gakubu Kenkyu Iho*, **15**, 42 (1964).
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Astakhov equation[10] to the adsorption isotherm, and on the basis of the relation between the characteristic energy of adsorption (E), the exponent (n), and the pore size distribution.

Experimental

Materials——Trimethylamine was obtained from Matheson Gas Products, U.S.A., and its labeled purity was 99.0%. Activated carbon and zeolite used were commercial products, and $MgO \cdot SiO_2$ and $CaO \cdot SiO_2$ used were prepared in our laboratory. The particle size of adsorbents was 200—400 mesh.

Procedure for Adsorption and Measurement of Pore Size Distribution——The apparatus and procedure for adsorption and measurement of pore size distribution of adsorbents were described previously.[11] The specific surface area was measured with the BET apparatus using argon gas as an adsorbate at liquid nitrogen temperature.

Results and Discussion

1. Adsorption Isotherm of Trimethylamine on Adsorbents

Figure 1 shows the adsorption isotherms of trimethylamine on adsorbents up to 50 Torr. The adsorption isotherm curves of activated carbon (No. 1—4) became concave towards the equilibrium pressure, and the amount adsorbed on it gradually increased with equilibrium pressure. The adsorption isotherms of magnesium silicate (No. 5 and 6) and zeolite (No. 8 and 9) rose sharply at pressures up to about 2 and 0.5 Torr, respectively, and reached their plateau which presumably corresponded to their limiting adsorption. The adsorption isotherms obtained in the experiment were compared with the analytical expressions proposed by Langmuir,[12] Freundlich,[13] Brunauer, Emmett, and Teller,[14] and Harkins and Jura.[15] None of these equations agreed with the data over a limited range of pressure up to 50 Torr. The relation well fitted for the adsorption isotherms was expressed by the equation of Dubinin-Astakhov.[10] Dubinin and Astakhov[10] advanced the thermodynamical equation of adsorption well fitted to express the characteristic of gas adsorption by a porous adsorbent on the basis of the potential theory of Polanyi.[16]

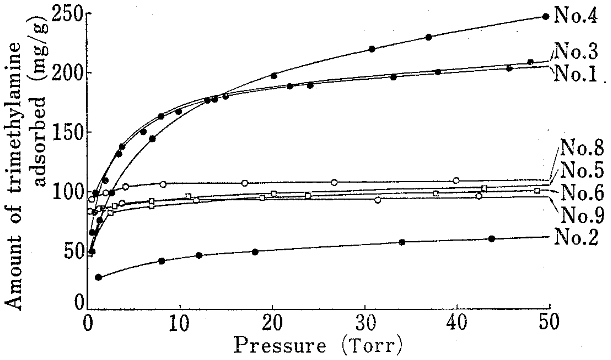

Fig. 1. Adsorption Isotherms of Trimethylamine on Adsorbents at 30°

$$W = W_0 \exp[-(A/E)^n] \quad (1)$$

$$A = RT \ln(P_s/P) \quad (2)$$

$$(q_{st})_{1/e} = \Delta H_0 + E \quad (3)$$

where W is the filled volume of the adsorption space, W_0 the limiting volume of the adsorption space, A the decrease of free energy in adsorption, E the characteristic energy of adsorp-

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tion, n the small integer, $\boldsymbol{R}$ the gas constant, T the absolute temperature, P_s the saturated vapor pressure, P the equilibrium pressure, $(q_{st})_{1/e}$ the isosteric heat of adsorption at the characteristic point ($W/W_0=1/e=0.368$), and ΔH_0 is the heat of vaporization.

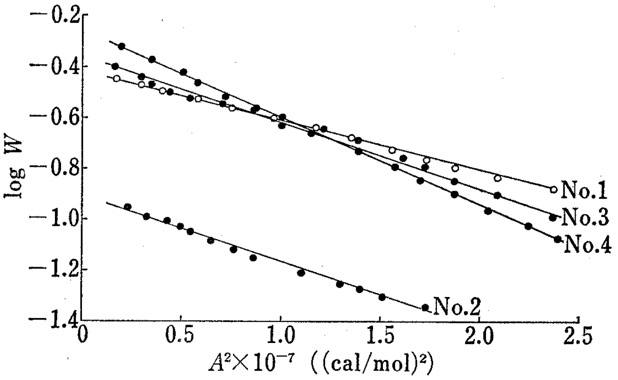

Fig. 2. Application of Dubinin-Astakhov Equation to Adsorption Isotherms of Trimethylamine on Activated Carbon

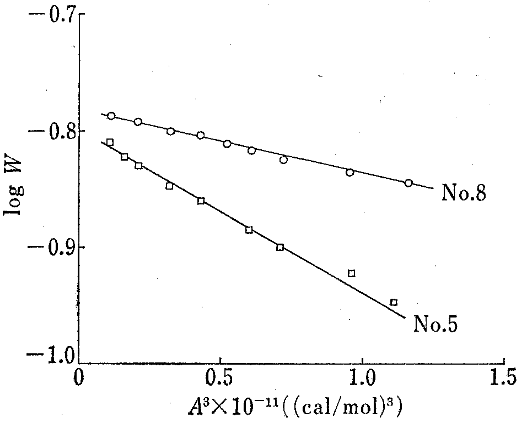

Fig. 3. Application of Dubinin-Astakhov Equation to Adsorption Isotherms of Trimethylamine on Silicate (No. 5) and Zeolite (No. 8)

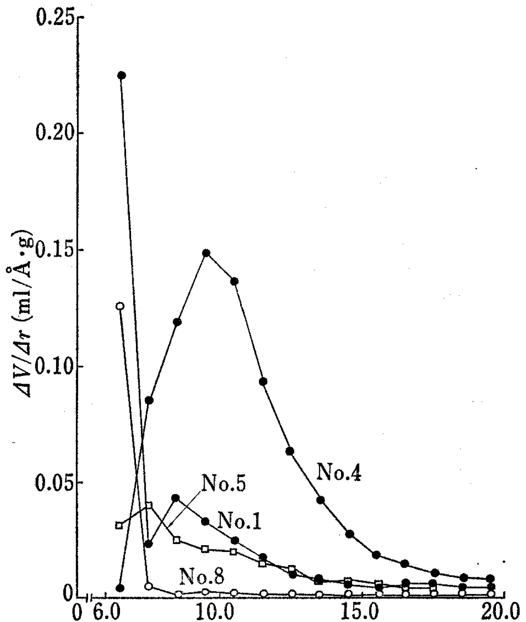

Fig. 4. Pore Size Distribution Curves of Activated Carbon (No. 1 and 4), Magnesium Silicate (No. 5) and Zeolite (No. 8)

Fig. 2 shows the application of Eq. (1) to adsorption isotherms of trimethylamine on activated carbon (No. 1—4). No straight lines were found between log W and A or A^3 but a plot of log W *vs.* A^2 on activated carbon gave a straight line. In this case, the exponent n in Eq. (1) was found to be 2. Dubinin-Astakhov equation ($n=2$) could be applied to the adsorption isotherms of trimethylamine on activated carbon No. 1—4, and it was therefore concluded that adsorption of trimethylamine on them resulted not in a successive formation of adsorption layers on the surface of the micropores but the volume filling of their micropores by the mechanism of capillary condensation, and that this was mainly a physical adsorption.[10,17]

Fig. 3 shows the application of Eq. (1) to the adsorption isotherms of trimethylamine on magnesium silicate (No. 5) and zeolite (No. 8). The relationship between log W and A^n was best plotted as a straight line with the co-ordinates given by log W *vs.* A^3. The exponent n in Eq. (1) was 3. The result obtained was similar to that of adsorption isotherms of ethane, ethylene, and nitrogen on molecular sieve carbons.[17b] The numerical difference in the exponent was explained by the difference in pore size of the adsorbents, that is, the fact that the exponent n was 2 and 3 was explained by its adsorption on micropores and ultramicropores, respectively, of the adsorbents.[17b]

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17) *a*) K. Kawazoe, V.A. Astakhov, and T. Kawai, *Seisan Kenkyu*, **22**, 373 (1970); *b*) K. Kawazoe, V.A. Astakhov, and T. Kawai, *Seisan Kenkyu*, **22**, 491 (1970); *c*) K. Kawazoe, V.A. Astakhov, T. Kawai, and Y. Eguchi, *Kagaku Kôgaku*, **35**, 1006 (1971).

2. Pore Size Distribution of Adsorbents

The pore size distribution curves in the range of radii 6.5 to 300 Å were obtained in this experiment and Fig. 4 shows them, particularly in the range of radii 6.5 to 19.5 Å to clarify the microporous structure of the adsorbents. The curves in Fig. 4 express the increment of pore volume corresponding to a differential increase in their radii, and the maxima in the curves correspond to the radii of the pores present in greatest abundance. Activated carbon No. 1 was mainly occupied by micropores of radii of less than 7.5 Å. The curve (activated carbon No. 4) had a maximum at a radius of about 10 Å, and it was mainly occupied by micropores in the broard range of radii of 6.5 to 19.5 Å. The curve No. 5 (magnesium silicate) exhibited a monotonous decrease at larger radii above 7.5 Å as the pore radius increased. Zeolite No. 8 was occupied by micropores of radii of less than 7.5 Å and had no pores of radii above 8.5 Å.

3. Relation between Type of Adsorption Isotherm and Pore Size Distribution

The results of adsorption isotherms, application of Dubinin-Astakhov equation to adsorption isotherms, and the pore size distribution gave the following description. When the adsorbent contained a large number of micropores, the dimensions of which were comparable to that of trimethylamine (d=6 Å[18]), the amount of trimethylamine adsorbed increased little with increasing equilibrium pressure after micropores had been filled with trimethylamine.

The relation between the type of adsorption isotherm and the pore size distribution could also be explained by the theory of London-van der Waals force.[19] The dispersion force (*i.e.*, the force of attraction) between the adsorbate and the surface of adsorbent is inversely proportional to the distance to the sixth power of the adsorbate from the surface. It may safely be assumed that the force of attraction between trimethylamine and the adsorbent is determined by the area of contact of trimethylamine with its surface, that is, adsorption in the smallest micropores into which trimethylamine can enter is more preferred to that at plane surfaces. The conclusions based on the above theory and experimental results of the type of adsorption isotherm and the pore size distribution were that the adsorption isotherm at low equilibrium pressure corresponded to the adsorption mainly for small micropores, dimensions of which were comparable to that of trimethylamine, and that the

Table I. Specific Surface Area of Adsorbents Used and Amount of Trimethylamine Adsorbed on Them

No.	Adsorbent	Specific surface area (m^2/g)	Amount of trimethyl amine adsorbed (mg/g)
1	Activated carbon	1209.0	204.0
2	Activated carbon	1237.0	61.2
3	Activated carbon	495.0	208 2
4	Activated carbon	1922.5	246.0
5	Magnesium silicate	428.6	104.2
6	Magnesium silicate	324.5	100.2
7	Calcium silicate	33.2	6.5
8	Synthetic zeolite F-9	525.6	108.8
9	Molecular sieve 13X	352.6	94.6
10	Natural zeolite	7.2	5.4
11	Synthetic zeolite A-3	3.0	2.2

Amount of trimethylamine adsorbed was measured at 30° and 50 Torr.

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18) The diameter of trimethylamine was calculated by using the Emmett and Brunauer equation [P.H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 1553 (1937)].

19) F. London, *Z. Phys.*, **63**, 245 (1930).

adsorption isotherm at higher pressure corresponded to the adsorption for large pores, and additionally, that these results could be explained by assuming that adsorption by the force of attraction for small micropores was greater than that for large pores.

4. Relation between Amount of Trimethylamine Adsorbed and Micropore Volume

From the result of the adsorption isotherm in Fig. 1, the amount of trimethylamine adsorbed on activated carbon except No. 2 was about 1.5 to 2.5 times that on magnesium silicate or zeolite at equilibrium pressure of 2 to 50 Torr. Table I shows the specific surface area of adsorbents and the amount of trimethylamine adsorbed on them. Activated carbon No. 1, 3, and 4 showed a larger amount adsorbed than others at 30° and 50 Torr, and they were found to be the most suitable adsorbents among eleven kinds of adsorbents for the removal of trimethylamine. If it is assumed that the amount of trimethylamine adsorbed is proportional to the specific surface area obtained from the BET equation based on multilayer adsorption, then the specific surface area of No. 3 is estimated to be larger than that of No. 1. Table I indicates that the amount of trimethylamine adsorbed on these adsorbents could not be explained by their specific surface areas. Fig. 5 shows the amount adsorbed versus micropore volume up to radius of 20 Å. The fact that the graph illustrating the amount adsorbed versus micropore volume lay nearly on a straight line could best be explained by assuming that the adsorption of trimethylamine in micropores of the adsorbents resulted in their volume filling. This was consistent with the result obtained from application of the Dubinin-Astakhov equation to the adsorption isotherm.

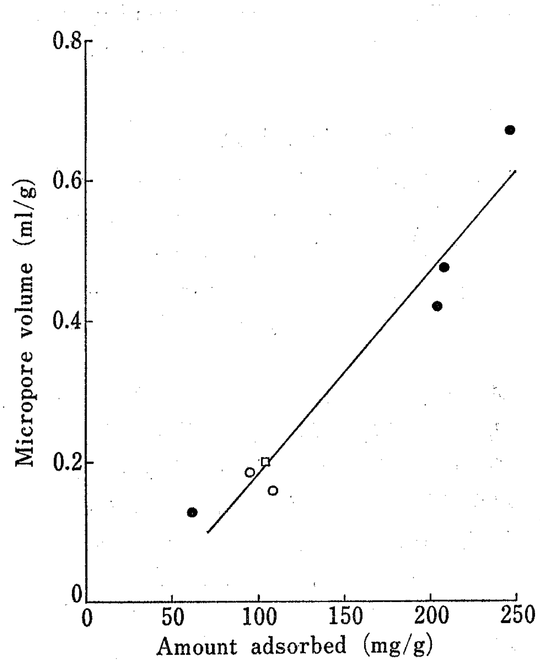

Fig. 5. Amount of Trimethylamine Adsorbed *vs.* Micropore Volume

●: activated carbon, □: silicate, ○: zeolite,
Amount of trimethylamine adsorbed was measured at 30° and 50 Torr.

5. Effect of n and E in Dubinin-Astakhov Equation on Pore Size Distribution

Table II shows the limiting volume of adsorption space, characteristic free energy of adsorption, n value of the Dubinin-Astakhov equation, and relation of E *vs.* ΔH_0. The exponent n is the degrees of freedom in the translation of a molecule,[17b)] and it is closely

Table II. Limiting Volume of Adsorption Space, Characteristic Free Energy of Adsorption, n Value of Dubinin-Astakhov Equation, and Relation of E *vs.* ΔH_0

No.	W_0 (ml/g)	E (cal/mol)	n	E *vs.* ΔH_0
1	0.3225	5158	2	$\Delta H_0 > E > 2/3\ \Delta H_0$
2	0.1230	4068	2	$E = 2/3\ \Delta H_0$
3	0.4365	4171	2	$E = 2/3\ \Delta H_0$
4	0.5470	3521	2	$1/3\ \Delta H_0 < E < 2/3\ \Delta H_0$
5	0.1594	6255	3	$E = \Delta H_0$
8	0.1647	9300	3	$E = 3/2\ \Delta H_0$

$\Delta H_0 = 6132$ cal/mol (heat of vaporization of trimethylamine was evaluated by fitting the Clausius-Clapeyron equation to the data [Chemical Society of Japan (ed.) "Kagaku Binran Kisohen II," (Handbook of Chemistry II) 2nd., Maruzen, Tokyo, 1975, p. 722].)

related to the mean radius of the pore of an adsorbent. The exponent n of activated carbon No. 1—4 was 2, and that of magnesium silicate (No. 5) and zeolite (No. 8) was 3 (Table II). The mean radii of a pore of activated carbon Nos. 1 and 4 were larger than those of magnesium silicate No. 5 and zeolite No. 8 (Fig. 4). A molecule has three degrees of freedom in its translation before it is adsorbed on the adsorbent, but some of the degrees of freedom in its translation are lost by its adsorption on the adsorbent. The narrower the mean radius of a pore, the less are the degrees of freedom in the translation of a molecule in its pore. The adsorption of trimethylamine on activated carbon, and on magnesium silicate and zeolite was explained by its adsorption on micropores and ultramicropores, respectively,[17b] of the adsorbents and by the loss of two and three degrees of freedom in its translation, respectively.

The characteristic energy (E) is related to the exponent n and the pore size distribution.[17b,20] When the exponent n was 2, the characteristic energy was divided into the following three groups, $\Delta H_0 > E > 2/3 \Delta H_0$, $E = 2/3 \Delta H_0$, and $1/3 \Delta H_0 < E < 2/3 \Delta H_0$. The relation between the characteristic energy of Nos. 1 and 4 and their pore size distribution seemed to indicate that the larger the mean radius of a micropore, the larger was the characteristic energy, and that their characteristic energy was in the range of ΔH_0 and $1/3\ \Delta H_0$. The characteristic energy was above ΔH_0 when the exponent n was 3. The fact that the characteristic energy of zeolite (No. 8) was larger than that of magnesium silicate (No. 5) could be explained by assuming that the radius of trimethylamine was comparable with the radius of ultramicropores of zeolite rather than that of magnesium silicate.

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20) K. Kawazoe and T. Kawai, "Zeolite-Fundamentals and Applications," ed. by N. Hara and H. Takahashi, Kôdanshya, Tokyo, 1975, pp. 89—94.