Chem. Pharm. Bull.
26(12)3738—3742(1978)

UDC 547.269.1.08 : 541.123.04

Adsorption of Methanethiol on Porous Adsorbents

SEIKI TANADA and KEITO BOKI

Faculty of Pharmaceutical Science, Tokushima University of Arts and Science[1]

(Received June 5, 1978)

Adsorption of methanethiol on activated carbon, magnesium silicate, and zeolite, and the rate of adsorption on them were gravimetrically measured to elucidate the mechanism of this adsorption. The Dubinin-Astakhov equation was applicable to the adsorption isotherms of methanethiol on these adsorbents. The rate of adsorption was expressed by the fractional approach to the equilibrium, and the mechanism of the rate of adsorption was explained by the volume filling of the smallest pore to the pores of a certain dimension. Activated carbon No. 2 was suitable for practical purposes because it had a high adsorption capacity at high pressure, its rate of adsorption was relatively fast, and methanethiol was physically adsorbed on it. From the results of differential heat of adsorption, adsorption of methanethiol on activated carbon No. 2 was considered to be the volume filling of micropores and the adsorption of monolayers or multilayers on transitional pores.

Keywords——methanethiol; mechanism of adsorption; porous adsorbent; application of Dubinin-Astakhov equation; rate of adsorption; differential heat of adsorption; porous structure

Methanethiol is one of the offensive odor substances discharged from the kraft pulp mill.[2] Its threshold is 0.0011 ppm[3] or 0.00099 ppm[4] and its concentration is limited to the range of 0.002—0.004 ppm in Japan by the Offensive Odor Control Law. It is also one of toxic materials.[5] Many methods to control the odorous emission from the kraft pulp mill have been reported.[6] The adsorptive removal of methanethiol by activated carbon,[7] silica gel,[8] and zeolite[9] has been studied.

We have as yet very little information concerning the mechanism of adsorption of single methanethiol on porous adsorbents. In the present work the adsorption of methanethiol on activated carbon, magnesium silicate, and zeolite, and the rate of adsorption of methanethiol on them were measured to investigate this problem.

Experimental

Materials——Methanethiol was obtained from Matheson Gas Products, U.S.A., and its labeled purity was 99.07%. Activated carbon and zeolite used were commercial products, and $MgO \cdot SiO_2$ used was prepared in our laboratory. The particle size of adsorbents was 200—400 mesh.

---

1) Location: *Yamashiro-cho, Tokushima, 770, Japan.*
2) E.W. Thomas, *Tappi*, **47**, 587 (1964); D.F. Adams, R.K. Koppe, and W.N. Tuttle, *J. Air Pollution Control Assoc.*, **13**, 31 (1965).
3) W. Summer, "Methods of Air Deodorization," Elsevier Publishing Company, London, 1963, pp. 46—47.
4) F.V. Wilby, *J. Air Pollution Control Assoc.*, **19**, 96 (1969).
5) C. Sandage, U.S. Dept. Com., Office Tech. Serv., AD268783, 33 (1961).
6) L. Ruus, *Svensk. Papperstid*, **66**, 554 (1963); B. Bjellqvist, F.E. Eriksen, B. Widen, and T. Westermark, Rep. STU-69-488-U-355, 29 (1971); K. Popov, *Tr. Nauchno-Issled. Inst. Vodosnabdyavane, Kanaliz. Sanit. Tekh.*, **8**, 135 (1973); M.J. Paul, Br. Patent 1353909 (1974); S. Ioka, *Kami Pa Gikyoshi*, **28**, 257 (1974); S. Ueda, *Kami Pa Gikyoshi*, **28**, 72 (1974); I. Araki and S. Honda, *Hokkaidoritsu Kogyo Shikenjo Hokoku*, **230**, 9 (1974).
7) R.J. Grant, M. Manes, and S.B. Smith, *Am. Inst. Chem. Eng.*, **8**, 403 (1962); F.C. Alley, U.S. Patent 3598521 (1971).
8) W.J. Jones and R.A. Ross, *J. Chem. Soc.*, 1787 (1968).
9) M.M. Robert, U.S. Patent 3078641 (1959); R.J. Schoofs and R.J. Kulpurger, Ger., Offen., 1911669 (1969).

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.10)

Results and Discussion

1. Adsorption Isotherms of Methanethiol on Adsorbents

Adsorption isotherms of methanethiol on activated carbon, magnesium silicate, and zeolite at 30° and pressure up to 50 Torr are shown in Fig. 1. The adsorption isotherms of activated carbon (No. 1—3) rose gradually up to 50 Torr. However, the adsorption isotherms of zeolite rose sharply at about 5 Torr and then reached their plateaux. It is now known that such adsorption isotherms (No. 6—8) very often result when the adsorbent is microporous. In this case, the limiting value of the adsorption is considered to be the filling of micropores rather than completion of a monolayer. The amount adsorbed on zeolite No. 6

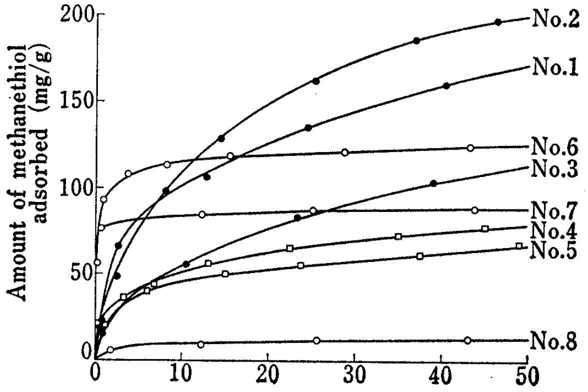

Fig. 1. Adsorption Isotherms of Methanethiol on Activated Carbon (No. 1—3), Magnesium Silicate (No. 4 and 5), and Zeolite (No. 6—8)

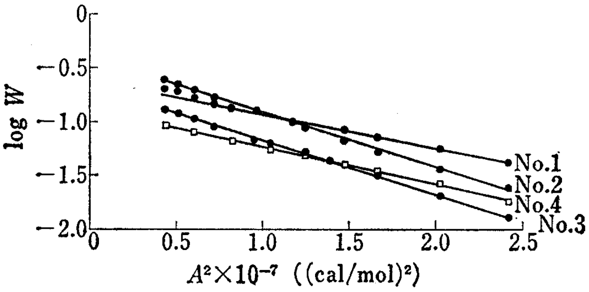

Fig. 2. Application of Dubinin-Astakhov Equation to Adsorption Isotherms of Methanethiol on Activated Carbon and Magnesium Silicate

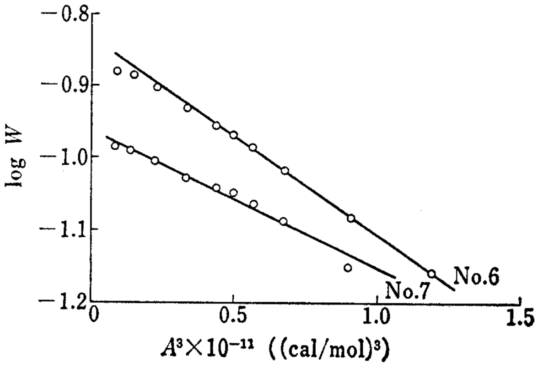

Fig. 3. Application of Dubinin-Astakhov Equation to Adsorption Isotherms of Methanethiol on Zeolite

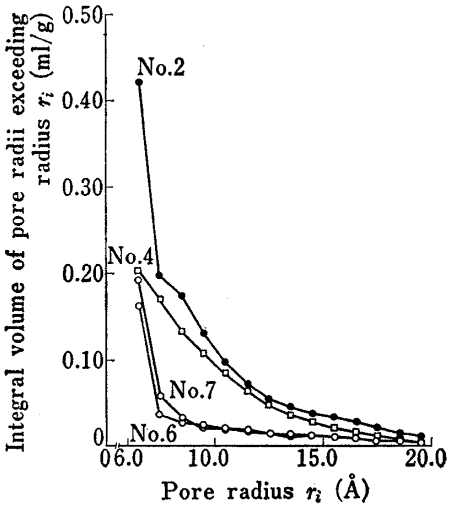

Fig. 4. Pore Size Distribution Curves of Activated Carbon (No. 2), Magnesium Silicate (No. 4), and Zeolite (No. 6 and 7)

---

10) S. Tanada, K. Boki, and K. Matsumoto, *Chem. Pharm. Bull.* (Tokyo), **26**, 1527 (1972).

at less than about 10 Torr was larger than that on activated carbon (No. 1 and 2) which had a high adsorption capacity at high pressure. It was concluded that zeolite No. 6 and activated carbon No. 2 were the most suitable adsorbents for removing methanethiol at low and high pressure, respectively.

The application of Dubinin-Astakhov equation ($W=W_0 \exp[-(A/E)^n]$, where W is the filled volume of adsorption space, W_0 the limiting volume of the adsorption space, A the decrease of free energy in adsorption, E the characteristic energy of adsorption, and the exponent n is a small integer.) used in the previous paper[10] to the adsorption isotherms in Fig. 1 was examined. The Dubinin-Astakhov plots of activated carbon and magnesium silicate were linear for the relation of log W *vs.* A^2, as shown in Fig. 2. However, the relation between log W and A^3 of zeolite showed rough linearity, as shown in Fig. 3. The present experimental results showed that the adsorption of methanethiol on these adsorbents resulted in the volume filling of their pores.[11]

The porous structure of adsorbent is one of the characteristics which determines the amount adsorbed on an adsorbent. The pore size distribution was calculated by applying the Kelvin equation[12] (on the assumption of cylindrical pores) to the adsorption isotherm on adsorbent at −195.8°. 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 structures of the adsorbents. The curves of activated carbon No. 2 and magnesium silicate No. 4 exhibited a monotonous decrease at radii larger than 6.5 Å as the pore radius increased. The curves of zeolite No. 6 and 7 were mainly occupied by the pores of radii less than 7.5 Å. The results of the application of Dubinin-Astakhov equation to the adsorption isotherms of methanethiol on adsorbents and the pore size distribution curves showed that the adsorption of methanethiol on porous adsorbents resulted in the volume filling of pores of adsorbents which were occupied by the pores of radii less than 20 Å.

2. Rate of Adsorption of Methanethiol on Adsorbents

The rate of adsorption is one of the parameters required in choosing a suitable adsorbent for practical use and, therefore, the fractional approach to the equilibrium of methanethiol on adsorbent is shown in Fig. 5. The fractional approach to the equilibrium[13] is given by

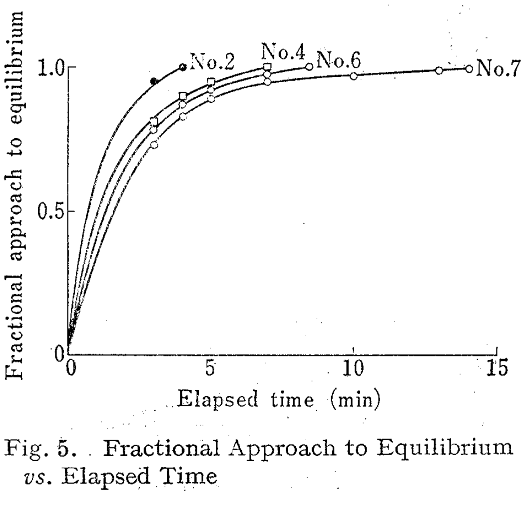

Fig. 5. Fractional Approach to Equilibrium *vs.* Elapsed Time

The rate of adsorption was gravimetrically measured at the initial pressure about 2 Torr and at 30°.

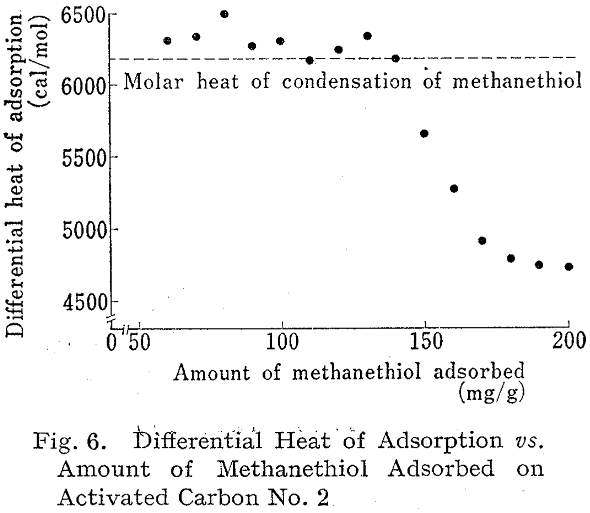

Fig. 6. Differential Heat of Adsorption *vs.* Amount of Methanethiol Adsorbed on Activated Carbon No. 2

---

[11] M.M. Dubinin and V.A. Astakhov, "Molecular Sieve Zeolite," Vol. II, ed. by E.M. Flanigen and L.B. Sand, Academic Press, Inc., London, 1971, p. 69.

[12] J. Kelvin, *Phil. Mag.*, **47**, 448 (1871).

[13] C.E. Dryden and W.B. Kay, *Ind. Eng. Chem.*, **46**, 2294 (1954).

$Er=q/q_\infty$, where Er is the fractional approach to equilibrium, q the amount adsorbed at various elapsed time, and q_∞ is the equilibrium amount adsorbed. The rate of adsorption was gravimetrically measured at the initial concentration about 2 Torr and at 30°, and the equilibrium amount adsorbed (q_∞) was estimated from the stretching of a spring balance which became constant at a certain elapsed time after the adsorption took place. It is thought that the shorter the time at $Er=1.0$, the faster will be the rate of adsorption. Adsorption to approach $Er=0.5$ was completed within about 1.5 min but the adsorbents except No. 2 took a long time to approach $Er=1.0$ and, in particular, zeolite No. 7 took about 15 min. The rate of adsorption on activated carbon No. 2 was relatively fast and therefore, this is suitable for practical purposes. The rate of adsorption on porous adsorbent is considered to be determined by its pore size distribution. Activated carbon No. 2 with the fast rate of adsorption contained various sizes of pores, but zeolite No. 6 and 7 contained mainly the pores of radii of less than 7.5 Å, as ahown in Fig. 4. The rate of adsorption of methanethiol on porous adsorbents can be explained by the differences of their pore size distributions.

3. Differential Heat of Adsorption of Methanethiol on Activated Carbon No. 2

The adsorption is customarily divided into two classes, physical adsorption and chemisorption. The striking difference between the two types of adsorption is the magnitude of the heat of adsorption and, in physical adsorption, the heat of adsorption[14] is in the range of heat of condensation of the adsorbate. Physically adsorbed molecules are easily removed or desorbed from the surface of adsorbent by lowering of the pressure of adsorbate. If methanethiol is physically adsorbed on the adsorbent, the adsorbent used is considered to be easily reproduced by evacuation.

The differential heat of adsorption of activated carbon No. 2 with a high adsorption capacity was obtained by applying the Clapeyron-Clausius equation[13] to the adsorption isotherms at 20° and 30°, and it is shown in Fig. 6. The differential heat of adsorption of activated carbon No. 2 was in the range of condensation of methanethiol. This result showed that the adsorption of methanethiol on activated carbon No. 2 was physical adsorption and that the adsorbent used can be reproduced.

It was noted that the differential heat of adsorption of methanethiol was approximately constant in the range of 50 to 140 mg/g of the amount adsorbed, but then it declined markedly with increasing amount adsorbed. From these results, it is assumed that two kinds of types of adsorption of methanethiol exist on activated carbon No. 2, adsorption in the range of heat of condensation and another adsorption in the range of less than the heat of condensation existing on it. The fact[15] that the differential heat of adsorption of methanol for sodium chloride and potassium chloride had smaller values than the heat of condensation of methanol at a certain amount adsorbed was interpreted in the such a way that an interaction between methanol and the polar groups in the formerly adsorbed molecule was expected to be depressed on further adsorption of methanol, *i.e.*, a two-layer adsorption, and the differential heat of adsorption would be small at this stage. According to the adsorption of methanol on activated carbon, adsorption on porous adsorbents was classified into two types, the volume filling of micropores (radii $<$15 Å) and adsorption of monolayers or multilayers on transitional pores (15 Å$<$radii).[16,17]

The limiting volume of adsorption space of activated carbon No. 2 obtained from its amount adsorbed (Table I) was equal to the pore volume (0.4176 ml/g) of radii less than 19.5 Å and, therefore, its limiting volume (amount adsorbed) is considered to be the sum of the

---

[14] A.W. Adamson, "Physical Chemistry of Surface," 2nd, Interscience Publishers, New York, 1967, pp. 310—311, 565—568.

[15] M. Chikazawa and T. Kanazawa, *Bull. Chem. Soc. Jpn.*, **50**, 2837 (1977).

[16] R. Tsunoda, *Bull. Chem. Soc. Jpn.*, **50**, 2058 (1977).

[17] R. Tsunoda, *Bull. Chem. Soc. Jpn.*, **51**, 341 (1978).

amount adsorbed on micropores and on transitional pores. From the results of its limiting volume and its differential heat of adsorption, adsorption of methanethiol on activated carbon No. 2 is considered to be the volume filling of micropores and adsorption of monolayers or multilayers on transitional pores.

Table I. Limiting Volume of Adsorption Space of Adsorbents

No.	W_0 (ml/g)	No.	W_0 (ml/g)
1	0.2400	4	0.1288
2	0.4145	6	0.1472
3	0.1995	7	0.1086

The limiting volume of adsorption space was estimated by extrapolation of the intercept at $A^2=0$ or $A^3=0$ in Fig. 2 and 3.