Adsorption Properties of Methyl Sulfide and Methyl Disulfide on Activated Carbon, Zeolite, and Silicate, and Their Porous Structure

SEIKI TANADA, KEITO BOKI, and KAZUO MATSUMOTO

Faculty of Pharmaceutical Science, Tokushima University of Arts and Science, and Tokyo Food and Nutrition College

(Received October 11, 1977)

Adsorption of methyl sulfide and methyl disulfide as the offensive odor substances was measured by a gravimetric method to elucidate the mechanism of their adsorption on activated carbon, zeolite, and silicate. The mechanism of adsorption was discussed on the basis of the application of Dubinin-Astakhov equation ($W = W_{0} \exp\left(-\frac{A}{E}\right)$) to the adsorption isotherms and the pore size distribution in the range of pore radius 7.5 to 300 Å. Dubinin-Astakhov equation was well applicable to the adsorption isotherm on activated carbon and the exponent $n$ was 2. No straight line was found between log $W$ and $A^{n}$ ($n = 1-6$) of adsorption isotherm on zeolite. A plot of log $W$ against $A$ ($n = 1$) of adsorption isotherm on silica gel was found to be linear. It was confirmed that the adsorption of methyl sulfide and methyl disulfide on activated carbon and silica gel resulted in the volume filling of their micropores by the mechanism of capillary condensation, and that its adsorption was a physical adsorption. The amount of methyl sulfide and methyl disulfide adsorbed on the porous adsorbents was determined by their micropore volume of pore radius less than about 20 Å.

Keywords — methyl sulfide; methyl disulfide; mechanism of adsorption; Dubinin-Astakhov equation; porous structure; activated carbon; zeolite; silicate

Methyl sulfide and methyl disulfide smell of decayed cabbage and they are discharged particulary from the factories of oil refinery and paper making, and from the treatment plant of animals into the atmosphere. They are listed as the offensive odor substances in the Offensive Odor Control Law in Japan, and their concentration is limited by it to the range of 0.01—0.2 (CH$_3$SCH$_3$) and 0.009—0.1 (CH$_3$SSCH$_3$) ppm.

We had studied the adsorptive removal of methyl sulfide$^2$ and methyl disulfide$^3$ by a dry process. The present paper describes the mechanism of the adsorption of methyl sulfide and methyl disulfide on activated carbon, zeolite, and silicate on the basis of the application of Dubinin-Astakhov equation$^4$ to the adsorption isotherm, and the relation between the amount adsorbed and their micropore volume.

Experimental

Materials — Methyl sulfide was obtained from Seitetsu Kagaku Company, and its labeled purity was 98.0%. Methyl disulfide, commercially purified material, was purified by vacuum distillation. Activated carbon, zeolite, and silicate, except magnesium silicate, used were commercial products, and magnesium silicate was prepared in our laboratory.

Procedure of Adsorption — The adsorbent was dried at 110° for 1 hr at 1 × 10$^{-3}$ Torr before use. Equilibrium amount of methyl sulfide and methyl disulfide adsorbed, at pressures up to 550 and 35 Torr, respectively, was measured by a gravimetric method using B.E.T. apparatus with a spring balance at 30°.

1) Location: a) Yamashiro-cho, Tokushima 770, Japan; b) 11-23, Ikejiri 2-chome, Setagaya-ku, Tokyo 154, Japan.
Measurement of Pore Size Distribution—For the seven kinds of adsorbents the pore size distribution in the range of 7.5 to 300 Å was obtained by the method of Dollimore and Heal, the calculation being performed on a FACOM 203-28S computer (Fujitsu Co., Ltd.) using the FORTRAN program.

Results and Discussion

1. Application of Dubinin-Astakhov Equation to Adsorption Isotherms

In general, adsorbents contain various sizes of pores, however, adsorption properties of an adsorbent are associated with its porous structure, the smallest pores (micropores) playing the principal role in adsorption. Dubinin proposed, for the theory of gas adsorption by a microporous adsorbent, the following equations which are based upon the adsorption potential theory of Polanyi.

\[ A = RT \ln \left( \frac{P_s}{P} \right) \]  
\[ W = W_0 \exp \left[-(k_0 A)^n \right] \]

where \( A \) is the decrease of free energy in adsorption, \( R \) the gas constant, \( T \) the absolute temperature, \( P_s \) the saturated vapor pressure, \( P \) the equilibrium pressure, \( W \) the filled volume of the adsorption space, \( W_0 \) the limiting volume of the adsorption space, and \( k_0 \) is a constant. The theory of physical adsorption of a gas in micropores which he proposed is explained in terms of the theory of the volume filling of micropores. Dubinin and Astakhov expressed Eq. (2) as the thermodynamical equation of adsorption (3) in the general form.

\[ W = W_0 \exp \left[-(A/E)^n \right] \]

where \( E \) is the characteristic energy of adsorption and the exponent \( n \) is a small integer. According to equation (3), \( E \) is equal to \( A \) at the characteristic point \( W/W_0 = 1/e = 0.368 \). From Eq. (3) and by the application of Clausius-Clapeyron equation to the vapor-liquid equilibrium and the adsorption equilibrium, the isosteric heat of adsorption is given by

\[ (q_{st})/e = \Delta H_0 + E \]

![Graph](image1.png)

Fig. 1. Application of Dubinin-Astakhov Equation to Adsorption Isotherms of Methyl Sulfide on Adsorbents

- ○, No. 1; ■, No. 2; □, No. 4; ■, No. 5.

Numbers in all the graphs refer to adsorbent No. in Table III.

![Graph](image2.png)

Fig. 2. Application of Dubinin-Astakhov Equation to Adsorption Isotherms of Methyl Disulfide on Adsorbents

- ○, No. 1; ■, No. 2; □, No. 4; ■, No. 5.

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where \((q_0)_{1/6}\) is the isosteric heat of adsorption at the characteristic point and \(\Delta H_0\) is the heat of vaporization.

The data obtained in the experimental work have been compared with the analytical expressions proposed by Langmuir,9) Freundlich,10) Brunauer, Emmett, and Teller,11) and Harkins and Jura.12) None of these equations agreed with the data over any extended range of variables. The most useful relation between the amount adsorbed \((\log W)\) and the decrease of free energy was expressed by the Dubinin-Astakhov equation. Fig. 1 and 2 show the application of Dubinin-Astakhov equation \((n=2)\) to adsorption isotherms of methyl sulfide and methyl disulfide, respectively, on activated carbon. No straight lines were found between \(\log W\) and \(A\) or \(A^n\) but a plot of \(\log W\) vs. \(A^n\) of activated carbon gave a straight line. In this case, the exponent \(n\) in Eq. (3) was found to be 2. Dubinin-Astakhov equation \((n=2)\) could be applied to adsorption isotherms of methyl sulfide and methyl disulfide on activated carbon No. 1, 2, 4, and 5, and it was therefore concluded that adsorption of methyl sulfide and methyl disulfide 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 adsorption was a physical adsorption.7,13)

No straight lines were found between \(\log W\) and \(A^n\) \((n=1—6)\) of adsorption isotherms on zeolite (No. 7—9). The adsorption isotherms of methane on zeolite L and carbon dioxide on Na, K-erionite were reported to be a well-suited application of Eq. (3) to them.13b) The mechanism of adsorption of methyl sulfide and methyl disulfide on zeolite remains obscure.

Fig. 3. shows the relation between \(\log W\) and \(A\) of adsorption isotherms on silica gel No. 10. The exponent \(n\) in Eq. (3) was 1. The result obtained was similar to that of adsorption isotherms of benzene on porous carbon black,14) and hydrocarbon gases on silica gel,15) The fact that the exponent \(n\) was 1 in the adsorption isotherms of hydrocarbon gases on silica gel was explained by their adsorption on relatively large-pore of silica gel because its pore diameter was about 80—100 Å and was far larger than the diameter of adsorbates.15) The mechanism of adsorption on silica gel No. 10 can also be accounted for by the adsorption on relatively large-pore adsorbent because its pore diameter is about 30—40 Å (Fig. 5), and the diameters of methyl sulfide and methyl disulfide are 5.56 and 5.92 Å, respectively (Table I).

Table II lists the results obtained from the application of Eq. (3) to the adsorption isotherms. The limiting volume of adsorption space \(W_0\) was estimated by extrapolation of the

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### Table I. Physical Properties of Methyl Sulfide and Methyl Disulfide

<table>
<thead>
<tr>
<th></th>
<th>Methyl sulfide</th>
<th>Methyl disulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>CH₃SCH₃</td>
<td>CH₃SSCH₃</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>62.1</td>
<td>94.2</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>38.0</td>
<td>109.7</td>
</tr>
<tr>
<td>d³⁰</td>
<td>0.846</td>
<td>1.0647</td>
</tr>
<tr>
<td>Olfactory threshold (ppm)</td>
<td>0.02³⁰</td>
<td>0.015⁷</td>
</tr>
<tr>
<td>Concentration limit of regulation (ppm)</td>
<td>0.01~0.2³⁰</td>
<td>0.009~0.1³⁰</td>
</tr>
<tr>
<td>Cross-sectional area (Å²)</td>
<td>26.8</td>
<td>30.4</td>
</tr>
<tr>
<td>Diameter of molecule (Å)</td>
<td>5.56</td>
<td>5.92</td>
</tr>
<tr>
<td>Heat of vaporization (cal/mol)</td>
<td>6820</td>
<td>9150</td>
</tr>
</tbody>
</table>

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*b) Kogai to Taisaku (ed.), *Kogai to Taisaku*, 12, 1976.*
*c) The cross-sectional area and the diameter of a molecule was calculated by using the Emmett and Brunauer’s equation (F.H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, 59, 1553 (1937)).
*d) Heat of vaporization was evaluated by fitting the Clausius-Clapeyron equation to the data (Chemical Society of Japan (ed.) *Kagaku Binran Kishō II,* (Handbook of Chemistry, General II) 2nd Ed., Maruzen, Tokyo, 1975, p. 723, 731).
*e) Estimate.

### Table II. Limiting Volume of Adsorption Space, Characteristic Free Energy of Adsorption, and n Value of Dubinin-Astakhov Equation

<table>
<thead>
<tr>
<th>Adsorbent No.</th>
<th>CH₃SCH₃</th>
<th>CH₃SSCH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wₐ(ml/g)</td>
<td>E(cal/mol)</td>
</tr>
<tr>
<td>1</td>
<td>0.3236</td>
<td>4250</td>
</tr>
<tr>
<td>2</td>
<td>0.1276</td>
<td>3660</td>
</tr>
<tr>
<td>4</td>
<td>0.6412</td>
<td>2830</td>
</tr>
<tr>
<td>5</td>
<td>0.2937</td>
<td>3310</td>
</tr>
<tr>
<td>10</td>
<td>0.3443</td>
<td>2650</td>
</tr>
</tbody>
</table>

### Table III. Amount of Methyl Sulfide and Methyl Disulfide Adsorbed on Adsorbents

<table>
<thead>
<tr>
<th>No.</th>
<th>Adsorbent</th>
<th>CH₃SCH₃</th>
<th>CH₃SSCH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Activated carbon (4—7 mesh)</td>
<td>3.66</td>
<td>4.50</td>
</tr>
<tr>
<td>2</td>
<td>Activated carbon (4—7 mesh)</td>
<td>1.33</td>
<td>1.73</td>
</tr>
<tr>
<td>3</td>
<td>Activated carbon (4—7 mesh)</td>
<td>5.56</td>
<td>3.76</td>
</tr>
<tr>
<td>4</td>
<td>Activated carbon (4—7 mesh)</td>
<td>5.34</td>
<td>8.10</td>
</tr>
<tr>
<td>5</td>
<td>Activated carbon (4—7 mesh)</td>
<td>2.95</td>
<td>3.70</td>
</tr>
<tr>
<td>6</td>
<td>Molecular-sieved carbon (4—7 mesh)</td>
<td>2.08</td>
<td>1.68</td>
</tr>
<tr>
<td>7</td>
<td>Molecular sieve 13X (1—16 mesh)</td>
<td>2.42</td>
<td>2.14</td>
</tr>
<tr>
<td>8</td>
<td>Molecular sieve 5A (1—8 mesh)</td>
<td>0.41</td>
<td>1.32</td>
</tr>
<tr>
<td>9</td>
<td>Synthetic zeolite T-9 (4—8 mesh)</td>
<td>2.19</td>
<td>1.73</td>
</tr>
<tr>
<td>10</td>
<td>Silica gel (7—9 mesh)</td>
<td>2.29</td>
<td>3.50</td>
</tr>
<tr>
<td>11</td>
<td>Acid clay (100—145 mesh)</td>
<td>0.31</td>
<td>1.09</td>
</tr>
<tr>
<td>12</td>
<td>Activated clay (100—145 mesh)</td>
<td>0.48</td>
<td>1.13</td>
</tr>
<tr>
<td>13</td>
<td>Magnesium silicate (100—200 mesh)</td>
<td>1.88</td>
<td>1.38</td>
</tr>
<tr>
<td>14</td>
<td>Magnesium silicate (100—200 mesh)</td>
<td>1.72</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Amount of methyl sulfide and methyl disulfide adsorbed was measured at 30° and 30 Torr.
intercept at $A^2=0$ or $A=0$. Since, according to the theory of volume filling, $W_0$ is a property of the adsorbent, it is independent of the adsorbate and implies the total micropore volume. $W_0$ of adsorbents except that of No. 2 did not vary with the adsorbate. From the heat of vaporization and the characteristic energy, we have the isosteric heat of adsorption at the characteristic point (Eq. (4)). The values of $(q_a)_t$ of methyl sulfide and methyl disulfide were 9450—11070 and 11750—13920 cal/mol, respectively. According to the definition by Benton and White,\textsuperscript{16} if the heat of adsorption exceeds 10 kcal/mol, then the process is deemed to be chemisorption but, if the heat falls short of 10 kcal/mol, then the physical adsorption is occurring. This classification, however, is not without uncertainty.\textsuperscript{17} Although the isosteric heat of adsorption exceeded 10 kcal/mol, it may be considered that methyl sulfide and methyl disulfide were physically adsorbed by the volume filling in microporous adsorbent because the characteristic energy was less than the heat of vaporization. A similar interpretation of the data obtained had been made by Barrer and Langley.\textsuperscript{18}

2. Relation between the Porous Structure and the Amount Adsorbed

Table III shows the amount of methyl sulfide and methyl disulfide adsorbed at 30° and 30 Torr on 14 kinds of adsorbents. The amount adsorbed was obtained from the adsorption isotherm at 30°. The activated carbon No. 1, 3, and 4 showed the most amount of adsorption

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figs.png}
\caption{Pore Size Distributions of Adsorbents in the Range of 7.5—300 Å in Radius}
\end{figure}

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\caption{Amount of Methyl Sulfide and Methyl Disulfide Adsorbed vs. Micropore Volume}
\end{figure}

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\centering
\includegraphics[width=\textwidth]{figs.png}
\caption{Amount of Methyl Sulfide and Methyl Disulfide Adsorbed vs. Micropore Volume}
\end{figure}

among the 14 kinds of adsorbents. They were found to be suitable adsorbents for the removal of these adsorbates.

Fig. 4 and 5 show the pore size distribution of several adsorbents. The curves except No. 7 and 9 (zeolite) became concave towards the pore radius and they approached the constant pore volume at the radius about 40 Å. Fig. 4 and 5 indicate that the pore volume at radii less than about 20—40 Å occupied most of the pore volume of up to radius 300 Å.

Fig. 6 shows the amount of methyl sulfide and methyl disulfide adsorbed at 30 Torr vs. micropore volume of up to radius 20 Å. An approximately linear relationship existed between the two, and it was confirmed that the amount adsorbed was determined by their micropore volume of less than 20 Å. The diameters of methyl sulfide and methyl disulfide are 5.56 and 5.97 Å (Table I), respectively, and therefore, they can enter into the micropore of adsorbents. The results of well-suited application of Dubinin-Astakhov equation to adsorption isotherms and Fig. 6 indicate that adsorption of methyl sulfide and methyl disulfide in micropores of adsorbents resulted in their volume filling.