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Effects of Surface Oxygen of Activated Carbon on Alkaloid Adsorption: A Molecular Dynamics Simulation Study

DIANXIA WANG, AKIYOSHI SAKODA AND MOTOYUKI SUZUKI
Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106-8558, Japan

Abstract. The influence of the density and the type of surface oxygen on the adsorption of berberine alkaloid onto activated carbon was investigated using the molecular dynamics simulation method in vacuum. The carbon surface consisted of a basal plane of graphite and surface oxygen groups which were bonded on the graphite plane in a regular square array with various densities. Two types of surface oxygen groups, =O and −OH, were employed. The simulation results showed that the berberine alkaloids were favorable to be adsorbed on the negative charged carbon surfaces. It was indicated that the vdw attraction of the carbon surface to the alkaloid molecule dominates the adsorption only at the lower surface density of oxygen. It is also indicated that a good adsorptive selectivity for a certain berberine alkaloid can be obtained by controlling the density of surface oxygen.

The adsorption simulation of berberine alkaloids onto activated carbon in the presence of water was also carried out by using a dome-shape molecular model for presenting the alkaloid/water/carbon system. It was found that the adsorption of berberine alkaloids on the activated carbon which has a higher density of surface oxygen was strongly inhibited by the presence of water.

Keywords: adsorption, molecular simulation, activated carbon, surface oxygen, alkaloids

1. Introduction

Activated carbons are known to be excellent and versatile adsorbents widely used for separations in the chemical, petroleum, and pharmaceutical industries, as well as in the removal of pollutants from water and air. This great flexibility in the applications of activated carbons arises from their wide range of not only physical surface properties but also chemical properties resulted from the presence of surface chemical groups such as hydroxyl, carboxyl, quinone, peroxide, aldehyde, etc. (Saito and Higashi, 1987; Tamon and Okazaki, 1993).

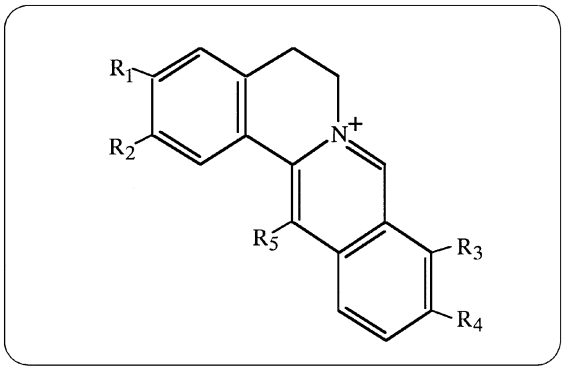
In view of the great interest in the surface chemical groups of activated carbon, many studies have been done in the respects of modifying and characterizing the surface chemical properties (Boehm, 1994; Leon y leon et al., 1992; McKee and Mimeault, 1973). However, by direct experimental methods, it is difficult to illustrate the microscopic mechanisms of the adsorption phenomena such as the orientation of adsorbates to adsorption sites and the effect of type, density and placement of the surface chemical groups on adsorption behaviors, since it is very difficult to prepare a well-characterized material. On the other hand, molecular simulation methods offer the possibility to study above respects individually and systematically. This is because that the carbon surface can be modeled precisely and the relevant variables can be investigated separately by computer (Muller et al., 1996; Ulberg and Gubbins, 1995).

So far only few researches relate to the fundamental molecular simulation of adsorption on modified activated carbon surface. Segarra and Glandt (1994) developed a graphitic platelet model of the activated carbon that incorporates surface functional groups as dipoles, evenly smeared around the edges of graphitic carbon platelet disks. Maddox et al. (1995) simulated the adsorption of water by mimicing the activated carbon as a COOH groups bonded graphite surface. In another series of contributions, researchers (Muller et al., 1995, 1996; Vega et al., 1996) have studied the behavior of

Lennard-Jones associating fluids in carbon slit pore models activated with specific surface sites capable of forming hydrogen like bonds with adsorbate.

In our previous work (Suzuki et al., 1997; Wang et al., 1997), a methodology for the molecular dynamics simulation of the liquid phase adsorption has been developed and the solvent effect on the adsorption was discussed by employing alkaloid as a model adsorbate and the graphite plane as a model adsorbent. Alkaloid is a kind of physiological active compounds obtained mainly from plant. It was chosen because of its important medicinal activity and the fact that the adsorption technique can be used to separate alkaloid efficiently (Payne and Shuler, 1988).

The present study is a part of this series work and alkaloid is also employed as the adsorbate here. The objective is to investigate the role of the surface oxygen in the adsorption of organic compounds on activated carbon by a molecular simulation method. Especially, the attention is focused on the effect of the type and the density of surface oxygen on the adsorption behaviors of alkaloid.



	R_1	R_2	R_3	R_4	R_5
Berberine	O—CH_2—O		OCH_3	OCH_3	H
Coptisine	O—CH_2—O		O—CH_2—O		H
Worenine	O—CH_2—O		O—CH_2—O		CH_3
Jateorrhizine	OH	OCH_3	OCH_3	OCH_3	H
Palmatine	OCH_3	OCH_3	OCH_3	OCH_3	H

Figure 1. Structural formula of berberine alkaloids.

2. System Model

2.1. Alkaloids

The five berberine alkaloids, namely, berberine, coptisine, worenine, jateorrhizine and palmatine, were employed as adsorbates. They are consisted in *Coptis japonica* Makino and have been used as antibacterial medicines. Their molecular structures are shown in Fig. 1. The partial charges of them were calculated by using the charge equilibration method (Rappe and Goddard III, 1991). As an example, Fig. 2 shows the partial charges of berberine.

2.2. Carbon Surface

The solid phase was taken to be a basal plane of graphite with dimensions of 4.66 × 4.67 nm, in which carbon atoms were organized in a hexagonal array. To mimic the activated carbon surface, the active sites were placed on the graphite surface in a regular square array of periodicity a, namely, the graphite surface was divided into N square segments and one active site was placed at the center of each square. Thus, the surface density of active site equals to $1/a^2$ or N/A sites per unit area (A is the area of the graphite surface). It should be pointed out that the graphite surface is approximated as a continuum one here, so that the active sites can be located at will (Muller et al., 1996).

Two types of oxygen group, =O and —OH, were employed as active sites in this study, since the oxygen atoms contained in the functional groups on activated carbon surface usually take these two basic types. =O and —OH groups were designated with the structural parameters such as atom type, bond length, bond angle, partial charges, etc., as same as those of the same parts in benzoic acid and phenol molecules, respectively. =O group was bonded to carbon atom in graphite plane with a bond length of 0.125 nm and —OH group was bonded with a bond length of 0.136 nm with identical orientation as shown in Fig. 3. Both =O and —OH groups protruded from the surface. The parameters of =O and —OH are listed in Table 1.

Table 1. Parameters of =O and —OH bonded on graphite surface.

	=O	—OH	
Bond	graphite=O	graphite—O	O—H
	0.125 nm	0.136 nm	0.098 nm
Angle	—	graphite—O—H	
		105.81°	
Atom type	O_2	O_3	H_A
Partial charges	−0.94e	−0.71e	0.33e

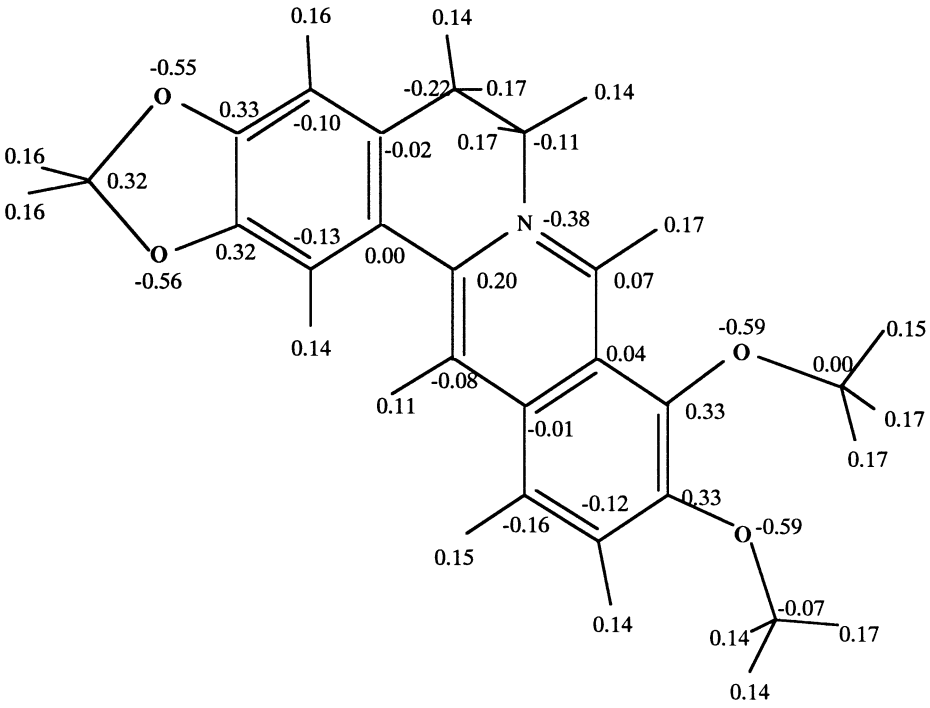


Figure 2. Partial charges of berberine molecule.

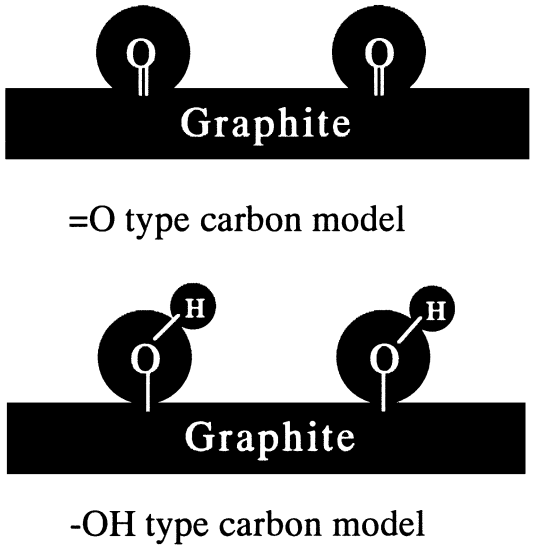


Figure 3. Model of activated carbon surface.

From the typical experiments (Baudu et al., 1993; Buczec et al., 1995), it is known that the site density of activated carbon commercially used ranges from 0.2 to 1.44 sites/nm^2. Maddox et al. (1995) adapted the site density of 0–1.5 sites/nm^2, and Muller et al. (1995) employed the site density from 0 to 1.77 sites/nm^2. In the present study, seven surface densities of oxygen group range from 0 to 1.66 sites/nm^2 were discussed.

3. Simulation Methods

3.1. Potential Energy

The simulations were carried out using the molecular mechanics (MM) and molecular dynamics (MD) modules provided in POLYGRAF^{TM}. The intramolecular and intermolecular interactions were calculated via the DREIDING force field (Mayo et al., 1990; Rappe and Goddard III, 1991). The total potential energy is given by:

$$E = \sum_{\text{bonds}} \frac{1}{2} K_b (R_b - R_{b0})^2 + \sum_{\text{angles}} \frac{1}{2} K_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedral}} \sum_{n=1}^{6} \frac{1}{2} K_{\varphi,n} [1 - d \cos(n\varphi)] + \sum_{\text{inversion}} \frac{1}{2} K_\omega (\cos\omega - \cos\omega_0)^2$$

$$+ \sum_{\substack{R_{ij}<R_{\text{cut}} \\ [\text{excl}(1\text{–}2,1\text{–}3)]}} (D_0)_{ij} \left\{ \left[\frac{(R_0)_{ij}}{R_{ij}} \right]^{12} - 2 \left[\frac{(R_0)_{ij}}{R_{ij}} \right]^{6} \right\}$$

$$+ \sum_{\substack{R_{ij}<R_{\text{cut}} \\ [\text{excl}(1\text{–}2,1\text{–}3)]}} \frac{Q_i Q_j}{\varepsilon R_{ij}} + \sum_{R_{ij}<R_{\text{cut}}} (D_{0h})_{ij}$$

$$\times \left\{ 5 \left[\frac{(R_{0h})_{ij}}{R_{ij}} \right]^{12} - 6 \left[\frac{(R_{0h})_{ij}}{R_{ij}} \right]^{10} \right\} \quad (1)$$

where the first four terms of the right-hand side of Eq. (1) represent bond interactions such as bonds stretching, valence angle vibrations, torsional vibrations, and inversion potentials, respectively. The last three terms are non-bond interactions such as van der Waals (vdw) interaction given by Lennard-Jones potential, electrostatic interaction, and hydrogen bond interaction. The potential parameters used in Eq. (1) were from Mayo et al. (1990) and Rappe and Goddard III (1991).

The adsorption energy, ΔE_B^{ad}, was defined as the difference between the total potential energy of alkaloid-carbon complex, E_{BC}, and the sum of the total potential energy of alkaloid alone, E_B^0, and that of the carbon surface alone, E_C^0:

$$\Delta E_B^{\text{ad}} = E_{BC} - \left(E_B^0 + E_C^0 \right) \quad (2)$$

3.2. Simulation Details

Through our simulations, the particle number, the volume and the temperature (300 K) were kept constants. The MM calculations were based on the conjugate gradient algorithm method. The equations of motion were solved by using the standard Verlet algorithm. The time interval used for the dynamics integration was 0.001 ps. The non-bond interactions were truncated at 0.9 nm. The hydrogen-bond interactions beyond hydrogen bond cut-offs of donor-acceptor distance of 0.5 nm and donor-H-acceptor angle of 90° were omitted.

In order to investigate the effects of the density and the type of the surface oxygen on the alkaloid adsorption directly, the adsorption simulations in vacuum were carried out mainly for a single alkaloid molecule onto various carbon surfaces. The position of the alkaloid molecule and the potential energy of the adsorption system were monitored as the functions of MD simulation time.

The alkaloid molecule was oriented initially with its molecular plane parallel to the carbon surface for all of the adsorption simulations. This initial orientation was chosen based on two facts which were found in preliminary simulations. One is that the adsorbed alkaloid molecule on the carbon surface is oriented with its molecular plane parallel to the carbon surface regardless of the initial orientation of the alkaloid or the type of the carbon surface. The another one is that the alkaloid molecule with this initial orientation needs shortest time to reach the carbon surface.

To reduce the computational time, we adapted 0.8 nm, instead of the cut-off distance of 0.9 nm, as the initial position of alkaloid for all of the adsorption simulations. That is, the alkaloid molecule was located 0.8 nm over the carbon surface.

During the MD simulation, all of the atoms in the alkaloid molecule were movable, while the atoms in the carbon surface were fixed.

The simulations of the alkaloid on the carbon in the presence of water were also carried out in this work. In addition to the basic methods described above, the special points related to the adsorption simulation in water are addressed in Section 4.3.

4. Results and Discussions

4.1. Density Effect of the Surface Oxygen on Berberine Alkaloid Adsorption

4.1.1. Adsorption Energy. To investigate the density effect of the surface oxygen on the alkaloid adsorption, the simulations were carried out for the alkaloid molecule onto the carbon surfaces on which =O was bonded with the densities of 0, 0.05, 0.18, 0.41, 0.74, 1.15 and 1.66 sites/nm^2, respectively.

As an example, Fig. 4 shows the variation of an energy change, ΔE, with MD simulation time for a berberine molecule onto the carbon surfaces. Here, ΔE is the difference between the total potential energy of the adsorption system, including an berberine molecule and a carbon surface, and the sum of the total potential energy of alkaloid alone and that of the carbon surface alone. It is found that the berberine molecule reached near the surface at the same time approximately (about 1 ps) even for the carbon surface bonded with a higher density of oxygen. However, with the increase of =O density from 0 to 1.66 sites/nm^2, the simulation time for the berberine molecule reaching the energetic equilibrium state increased from about 2 ps to 8 ps. This is because that the berberine molecule needs longer time to set down in the most stable configuration if the

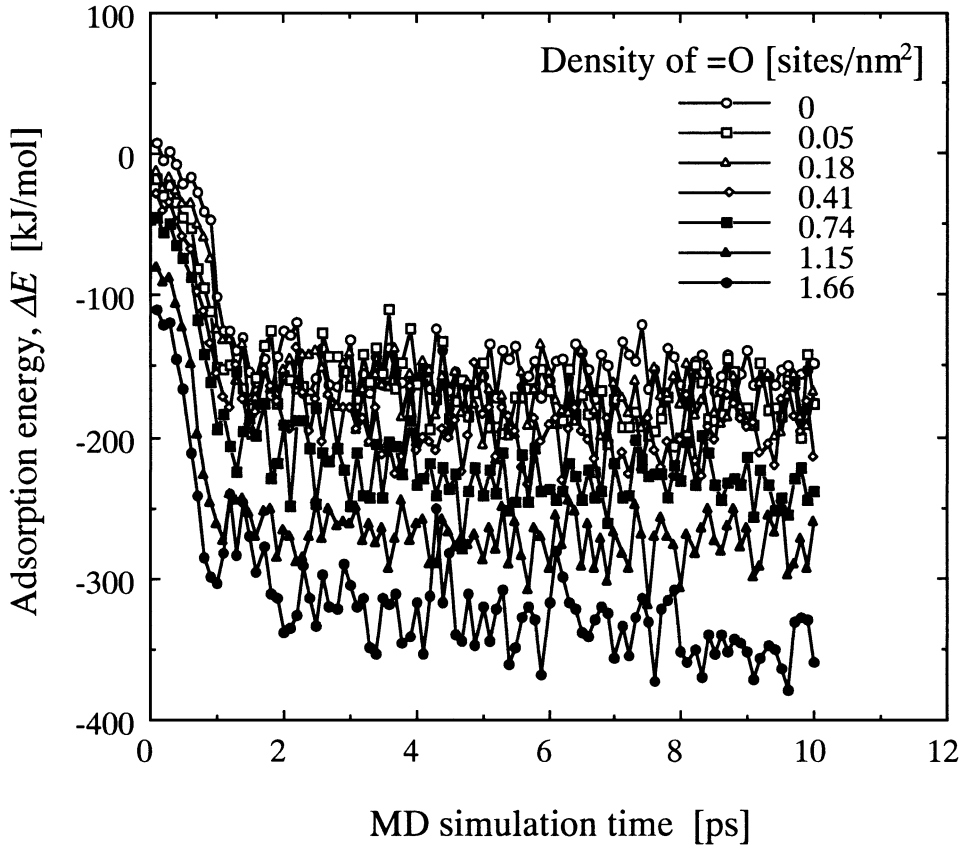


Figure 4. Variation of adsorption energy with MD simulation time for a single berberine molecule onto =O type carbon surface.

carbon surface has a higher density of the surface oxygen. It is obviously that the value of ΔE in the energetic equilibrium state equals to the adsorption energy defined in Eq. (2). Therefore, Fig. 4 also shows that the adsorption energy decreased greatly with the increase in surface density of =O.

It should be pointed out that the adsorption energy given in Fig. 4 is a total potential energy including both van der Waals potential component and electrostatic potential component. However, to develop or design a new adsorbent, it is also necessary to get a knowledge about the dominate attractive interaction of alkaloid onto active carbon surface. For this reason, the contributions of vdw term and electrostatic term to total adsorption energy are given in Fig. 5. The horizontal axis is the surface density of =O. The vertical axis presents the potential terms which are the time average from 8 to 10 ps (cf. Fig. 4).

As mentioned in Section 3.2, the molecular plane of the adsorbed alkaloid in the stable configuration parallels the carbon surface. This observation indicated that the adsorbed alkaloid molecule can attach to carbon plane directly even if =O density is the highest (1.66 sites/nm^2). Therefore, the vdw term is almost constant in Fig. 5. However, the electrostatic term decreases greatly with the increase in surface density of =O. This is because that more than one part of alkaloid molecule can attach to more than one =O in the stable configuration, and more electrostatic interaction partner can be found from the carbon surface which has a higher density of =O.

From the above analyses, the following conclusions may deduced: (1) the change of the total adsorption energy is attributed mainly to the change of the electrostatic interaction between alkaloid molecule and =O, (2) the alkaloid molecule is favorable to be adsorbed on the negative charged surface, (3) the adsorption of alkaloid on carbon surface is dominated mainly by vdw attraction at the lower surface density of =O, however, with the increase of the density of =O in the carbon surface, the electrostatic attraction should be paid more attention.

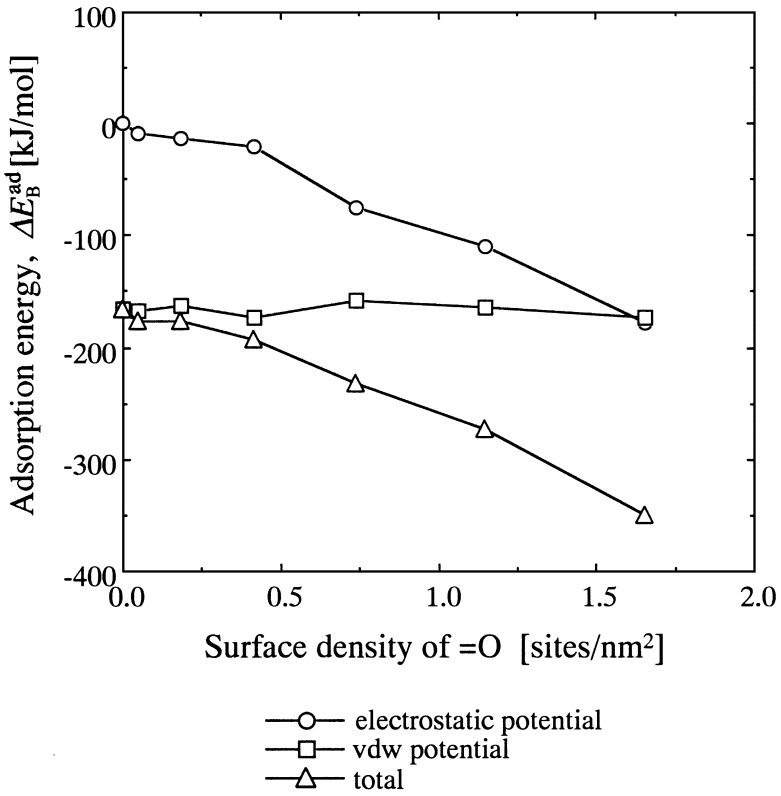


Figure 5. Dependence of adsorption energy and its contributions of vdw and electrostatic potentials on surface density of =O for berberine adsorption on =O type carbon.

4.1.2. Preferential Adsorption. Figure 6 shows the comparison of the changes in the adsorption energy with the surface density of =O for five berberine alkaloids. It is shown that the adsorption energies of all alkaloids decreased with the increase in surface density of =O, however, the speed of this decrease is different for every alkaloid. If we use the adsorption energy as a measure of adsorption ability of alkaloid (Suzuki et al., 1995), then the preferential adsorption behavior of alkaloid can be investigated by employing the difference of adsorption energies as a measure. It is found that the absolute value of the difference of adsorption energies between any two alkaloids changed when the surface density of =O increased. This observation implies that the separation of these alkaloids may become easier by changing the surface density of =O. For example, the absolute values of the difference between worenine and coptisine are 27.82, 36.78 and 50.21 kJ/mol corresponding to =O densities of 0, 0.74 and 1.66 sites/nm^2, respectively. It means that the adsorptive selectivity for copstisine from worenine increased 1.8 times due to increasing the density of =O from 0 to 1.66 sites/nm^2. It is also indicated that palmatine and jateorrhizine are difficult to be separated at =O density of 0 sites/nm^2, but when the density of =O increased from 0 to 1.66 sites/nm^2, the absolute value of the difference of adsorption energies between them increased from 0.46 to 46.02 kJ/mol. It suggests that the adsorptive selectivity of palmatine from jateorrhizine is enhanced about 100 times. On the other hand, the cross points indicate that those two alkaloids cannot be separated by the adsorption onto the carbon bonded with those surface density of =O on it, since they have the same adsorption energy.

The another interesting observation found in Fig. 6 is that the change of the adsorption energy with the surface density of =O holds the similar trend for berberine, worenine and coptistine, while holds the similar trend for palmatine and jateorrhizine. In the former group, the change of the adsorption energy with the surface density of =O shows a positive curvature, while in the later group the change of adsorption energy shows a negative curvature. The explanation of this observation may be attempted by analyzing the molecular structures

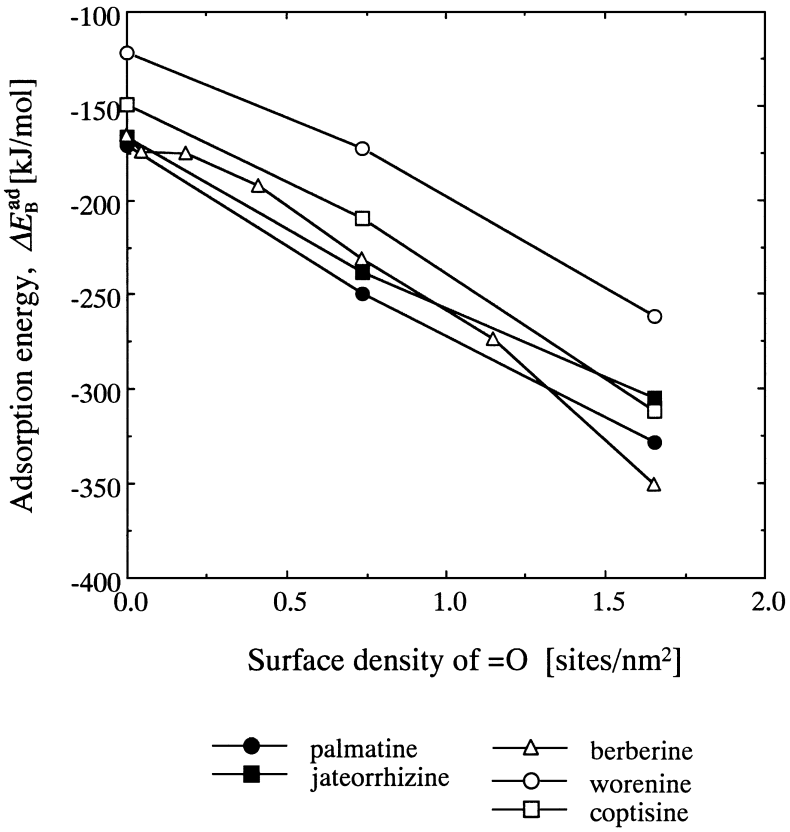


Figure 6. Comparison of the changes in adsorption energies with surface density of =O for the five berberine alkaloids.

and the partial charge contributions of berberine alkaloids as shown in Figs. 1 and 2. It is found that all of berberine, worenine and coptisine have the COCOC ring in their molecular structures, while both palmatine and jateorrhizine have four COC chains instead of COCOC ring in their molecules. On the other hand, although one COCOC ring and two COC chains are contained in a berberine molecule, it seems that the COCOC ring plays a more important role in affecting adsorption behavior of berberine on =O contained carbon surfaces. It is realized that more detailed work should be carried out in the future to support the above discussion.

4.2. Type Effect of Surface Oxygen on Berberine Alkaloids Adsorption

To test the effect of the oxygen type, hydroxyl (−OH) was employed as another example of the surface oxygen bonded on carbon plane in adsorption simulations of berberine alkaloids onto activated carbon. The comparison of the adsorption energies of alkaloid onto different type carbon surfaces was particularly focused on here.

Figure 7(a) shows the comparison of adsorption energy for the adsorption of berberine onto =O type and −OH type carbon surfaces. The components of the adsorption energy which include vdw and electrostatic potential terms are also given here. It is found that the vdw term is close for =O type and −OH type carbons. This is because of the same reason as described in Section 4.1.1. However, with the increase in the surface density of the surface oxygen, the electrostatic interaction between berberine and =O type carbon becomes stronger than that between berberine and −OH type carbon. This phenomenon may be due to that more negative charges held in =O group than in −OH group. This character may result in a larger amount of berberine adsorbing on =O type carbon surface than on −OH type carbon surface.

For the adsorption of jateorrhizine, the case becomes more complicated. Figure 7(b) shows the comparison of the adsorption energy and its components for the adsorption of jateorrhizine onto =O type and

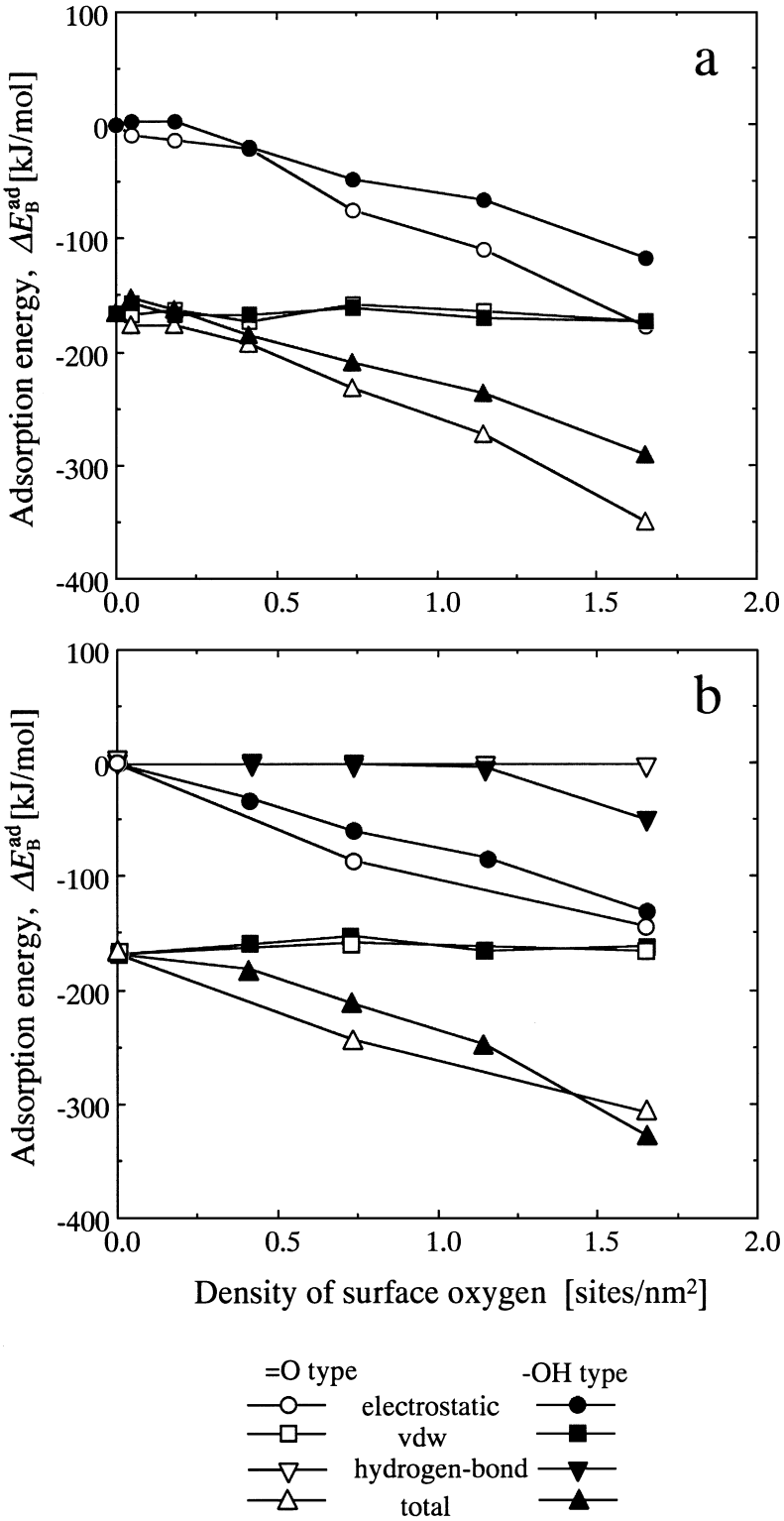


Figure 7. Effect of the type of surface oxygen on adsorption energy: (a) adsorption of berberine on ═O type and ─OH type carbons, and (b) adsorption of jateorrhizine on ═O and ─OH type carbons.

—OH type carbon surfaces. Since a hydroxyl group is contained in jateorrhizine molecule, the hydrogen bond interaction occurred also between jateorrhizine and —OH as well as vdw and electrostatic interactions. The hydrogen bond interaction is not found or is reasonable to be neglected (the absolute value is less than 2.09 kJ/mol, which is less than 1.2% of total adsorption energy) for the cases of all berberine alkaloids on =O type carbon surface and the another four berberine alkaloids on —OH type carbon surface in a range of —OH density from 0 to 1.66 sites/nm^2. As shown in Fig. 7(b), the hydrogen bond interaction between jateorrhizine and —OH type carbon cannot be neglected except for the lower surface density of —OH. The result is that the interaction between jateorrhizine and —OH type carbon becomes stronger than that between jateorrhizine and =O type carbon if the surface oxygen density is larger than 1.40 sites/nm^2.

Although the above results were obtained without concerning the solvent effect, it is believed that the information is useful for understanding the adsorption mechanisms.

4.3. Adsorption Behavior of Berberine Alkaloids on Activated Carbon in the Presence of Water

Unlike adsorption in vacuum, the adsorption from aqueous solution is greatly affected by the competitive adsorption of water. Maddox et al. (1995) and Muller et al. (1995, 1996) indicated that the adsorption of water is remarkably enhanced by the presence of an appreciable surface density of the active site. In this section, the adsorption simulations in water were performed to investigate the effect of the density of the surface oxygen on adsorption behavior of berberine alkaloids on activated carbon in the presence of water.

Water molecules were involved explicitly by using the 3-site model with a positive charge on hydrogen and a negative charge on oxygen ($Q_O = 2Q_H$) as shown in Fig. 8. A dome-shape molecular model (Suzuki et al., 1997) for presenting the alkaloid/water/carbon adsorption system was employed. This model consists of a single alkaloid molecule, a solvation shell constructed around the alkaloid molecule with water molecules, and a carbon surface. To prevent the water molecules in the solvation shell from escaping, a thin reflecting wall composing by water molecules was created outer the solvation shell. The schematic diagram is shown in Fig. 9. In the simulations, all of the atoms in the alkaloid molecule and the water molecules of the solvation shell were movable, while the atoms of water molecules composing the reflecting wall and the atoms in carbon surface were fixed. The position of the alkaloid molecule and the interactions between alkaloid and water, between alkaloid and carbon surface, and between water and carbon surface were monitored during simulations.

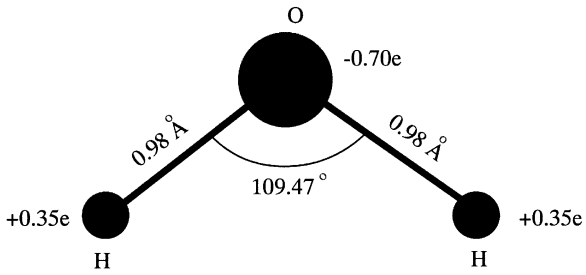


Figure 8. 3-site model of water.

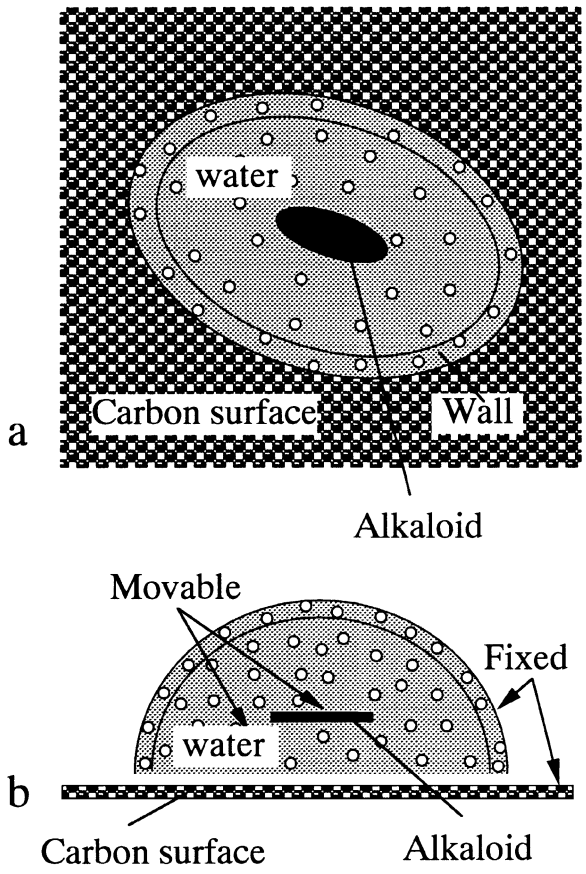


Figure 9. Schematic diagram of the semi-spherical dome-shape model for alkaloid/water/carbon surface system: (a) top view, and (b) side view.

The interaction energy between alkaloid and carbon surface in water is defined as follows (Suzuki et al., 1995; Kumagai et al., 1993):

$$\Delta E'_{BC} = E'_{BC} - E'_B - E'_C \tag{3}$$

where, E'_B, E'_C and E'_{BC} present the total potential energies of alkaloid molecule, carbon surface and alkaloid-carbon complex in water, respectively. The interactions between alkaloid and water, between carbon surface and water are not included in E'_B, E'_C and E'_{BC} explicitly. However, the effects of water, such as hydrophobic interaction and solvation effect, etc., are included undoubtedly in Eq. (3). This is because that the molecular configuration of the alkaloid/water/carbon system used to calculate E'_B, E'_C and E'_{BC} was obtained after interacting among alkaloid, water and surface for a certain time. $\Delta E'_{BC}$ presents the interaction energy between alkaloid and carbon surface in the presence of water effect. Therefore, $\Delta E'_{BC}$ can be used as a measure for discussing the difference of the water effect on the adsorption of alkaloid onto carbon surfaces which have different type or different amount of surface group. Moreover, since $\Delta E'_{BC}$ is a time dependence value during simulation, the behavior of the alkaloid molecule reaching the carbon surface from the bulk liquid phase can be monitored by calculating the change of ΔE_{BC} with simulation time.

As an example, Fig. 10 shows the variation of the interaction energy between alkaloid and carbon surface with MD time for a palmatine molecule onto the carbon surfaces with =O densities of 0, 0.74 and 1.15 sites/nm^2. It was found that the interaction energy between alkaloid and carbon surface in the energetic equilibrium state decreased with the increase in the density of =O. This is in agreement with the adsorption simulation results in the absence of water. However, the absolute value of the interaction energy in the energetic equilibrium state was the same as that in vacuum only for the case of on graphite, while for the oxygen-contained carbon surface, the absolute value of the interaction energy was little smaller than that in vacuum. Moreover, with the increase in the surface density of oxygen, much longer time was needed for palmatine molecule reaching the carbon surface. These observations are due to the fact that with the increase in the surface density of oxygen, the adsorption of water was enhanced and the water molecules previously adsorbed

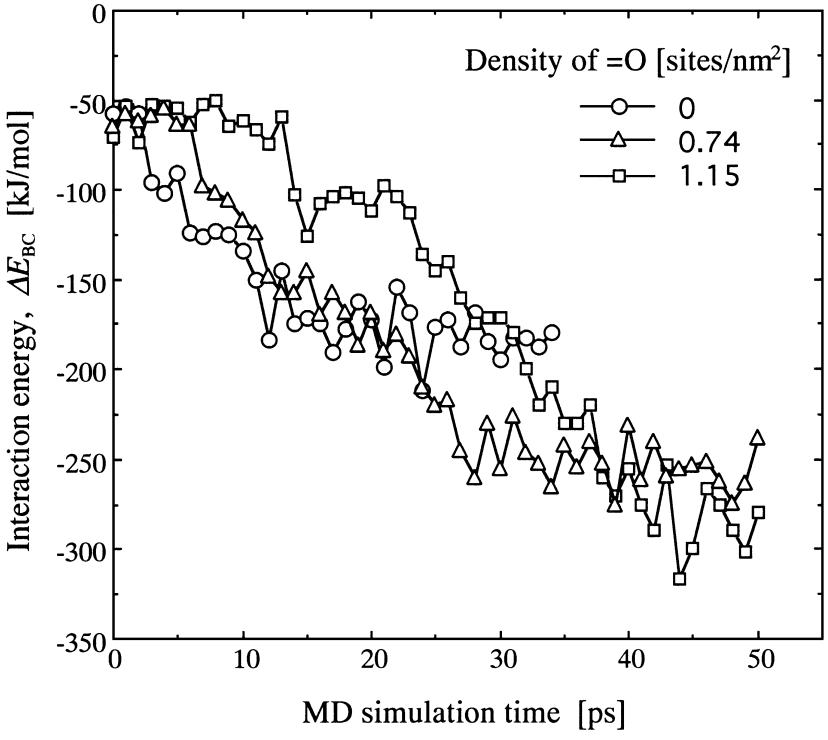


Figure 10. Variation of palmatine-surface interaction energy with MD simulation time for a single palmatine molecule onto =O type carbon surfaces.

on surface were difficult to be replaced by palmatine molecule. From the above results, it may be deduced that the adsorption of palmatine on activated carbon from water may be difficult to occur when the density of the surface oxygen is over some value, since the palmatine molecule may not penetrate the water film formed on the carbon surface.

5. Conclusions

Two types of surface oxygen, =O and −OH, bonded on a basal graphite plane were employed to study the adsorption behavior of berberine alkaloids on activated carbon surface using the MD simulation method. Particularly, the effect of the density and the type of surface oxygen on the adsorption were investigated.

The results showed that the adsorption energy decreased as the oxygen density increased, and that this change of the adsorption energy was mainly due to the electrostatic interaction, combining with the hydrogen bond interaction for the −OH type carbon surface, between the alkaloid molecule and the carbon surface. It was indicated that the vdw attraction of the carbon surface to the alkaloid molecule dominates the adsorption only at the lower surface density of oxygen. It was also indicated that the hydroxyl group holding alkaloid preferred to be adsorbed on =O type carbon at lower oxygen density, while, preferred to be adsorbed on −OH type carbon at higher oxygen density.

Moreover, the knowledge about the adsorptive selectivity of five berberine alkaloids were obtained. It was revealed that the adsorptive selectivity of berberine alkaloids on activated carbon can be improved by changing the density of surface oxygen. This is meaningful for the isolation of alkaloid.

The adsorption simulation studies in the presence of water showed that the effect of water on the adsorption of berberine alkaloids on activated carbon surface is enhanced by the increase in the surface density of surface oxygen.

Nomenclature

a	periodicity of square array	—
A	area of graphite surface	nm^2
d	phase factor, $d = +1$, *cis* is the minimum for $d = +1$, *cis* is the maximum for $d = -1$	—
D_0	van der Waals bond strength (well depth)	kJ/mol
D_{0h}	hydrogen bond strength	kJ/mol
$(D_0)_{ij}$	$\sqrt{(D_0)_{ii}(D_0)_{jj}}$	kJ/mol
E	total potential energy	kJ/mol
ΔE_B^{ad}	adsorption energy	kJ/mol
$\Delta E'_{BC}$	interaction energy	kJ/mol
H	hydrogen atom	—
K_β	force constant	(kJ/mol)/nm^2
K_θ	force constant	kJ/mol
K_ω	force constant	kJ/mol
$K_{\phi,n}$	one-half the rotational barrier	kJ/mol
n	periodicity of the potential, $n = 1, 2, \ldots, 6$	—
N	number of active site	—
O	oxygen atom	—
Q	charge of atom	C
R_0	van der Waals bond length	nm
$(R_0)_{ij}$	$1/2[(R_0)_{ii} + (R_0)_{jj}]$	nm
R_{0h}	distance between donor and acceptor atoms	nm
R_b	bond distance	nm
ε	dielectric constant	—
θ	angle between bonds	°
φ	dihedral angle, $\varphi = 0°$ for *cis* configuration, $\varphi = 180°$ for *trans* configuration	°
ω	angle between *IL* axis and *IJK* plane	°

Superscript

$'$	in water
ad	adsorption
0	in a free state

Subscript

0	equilibrium
b	bond
B	absorbate (alkaloid)
BC	adsorbate-adsorbent complex
C	adsorbent (carbon surface)
h	hydrogen bond
θ	angle
φ	dihedral angle
ω	angle between *IL* axis and *IJK* plane

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