

A Theoretical Study on a Series of Alkylamines on Silica

by

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(Received June 17, 1986)

Abstract

Silica surface covered with silanols round PZC detaches protons from the surface in alkaline ranges to increase surface negative charges of oxygen. The charge distributions of nitrogen of aminium ions are neutral, while those of amine molecules are negative. The positive charges of hydrogen connected to nitrogen of the aminium ions become greater than those of the amine molecules. The interaction between amines and silica is mainly coulombic. The bonds between amines and silica are almost the same as, or less in strength, than the hydrogen bond of a water dimer. The aminium ions are easy to adsorb on silica in alkaline ranges rather than round PZC. Both the aminium ion and the amine molecule prefer to adsorb on silica energetically by exchanging water molecules and sodium ions existing in the diffuse layer, or on the double layer. A series of aminium ions is easier to adsorb on silica as the chain length of the alkyl group becomes longer. The stabilization energy of the adsorption of a series of aminium ions is theoretically evaluated 0.25 kT per CH_2 group.

INTRODUCTION

The separation of silica or quartz from valuable minerals has been extensively studied since the flotation of non-sulfide minerals was put in practice in the field of mineral processing. Cationic amine collectors as dodecylamine chloride and dodecylammonium acetate are widely used in the flotation of silica, silicates, and some oxide minerals, except that anionic collectors are used after the activation of minerals by metal ions^{1,2)} (Fuerstenau and Cummins, 1967; Fuerstenau, 1975). The silica-amine system has been researched by measuring the adsorption amount of collectors³⁾ (Smith, 1963), the contact angles⁴⁾ (Smith and Lai, 1966), and the zeta potentials⁵⁾ (Smith and Akhtar, 1976) including the flotation tests⁶⁾ (Bleier et al, 1976), though the nice relationship of these factors was revealed by⁷⁾ Fuerstenau (1957). Amine adsorption on these types of sur-

faces is thought to involve not only aminium ions through coulombic interaction, but also amine molecules, especially at alkaline pH, which exists in abundant quantity by the hydrolysis of amine salts. Successively, Iwasaki et al concentrated their study on the adsorption of dodecylamine chloride or dodecylammonium acetate on metals such as platinum⁸⁾ (Natarajan and Iwasaki, 1973) and mercury⁹⁾ (Usui and Iwasaki, 1970), sulfides as Ag_2S ^{10,11)} (Iwasaki and DeBruyn, 1963, 1971), using the technique of redox potentials, double layer capacitance, and cyclicvoltammetry. It is postulated that metals, metallic oxides and sulfides would chemisorb free amines in affecting the contact angle and floatability, if the respective cations could react with the amine molecules without interference. On oxide minerals such as quartz and hematite, the aminium ion and the amine molecule formed in solution through hydrolysis in alkaline pH would chemisorb at the interface¹²⁾ (Natarajan and Iwasaki, 1982),

However, definite evidence has not been sufficient with regard to this point, e. g., the nature and/or the difference of the aminium ion and the amine molecule binding to the surface due to the difficulty of analyzing their roles independently in the amine adsorption.

The objective of this paper is theoretically to elucidate the electronic and binding states of the silica-amine system by the application of a molecular orbital method.

METHOD OF CALCULATION

A linear combination of the atomic orbital molecular orbital (LCAO MO) method used here is the CNDO (complete neglect of differential overlap) / 2 method which Pople¹³⁻¹⁵⁾ (1965, 1966), Santry and Segal^{16,17)} (1967, 1968) originally developed. It is, however, modified to calculate a large adsorption system, and its exactness of SCF (self-consistent field) calculation is programmed to be 10^{-6} in terms of electron density. The method will be simply repeated here. Roothan¹⁸⁾ (1951) expressed the Hartree-Fock equation in a matrix form as Eq. (1),

$$FC = C\epsilon \quad (1)$$

In a molecular orbital treatment, one takes a linear combination of atomic orbital (X_i) for each of the valence-shell molecular orbitals (Ψ_i) as Eq. (2) and then writes the Hartree-Fock equation in Eq. (3) :

$$\Psi_i = \sum_{\mu} C_{\mu i} X_{\mu} \quad (2)$$

$$\sum_{\nu} (F_{\mu\nu} - \epsilon_i S_{\mu\nu}) C_{\nu_i} = 0 \quad (3)$$

C_{ν_i} , ϵ_i and $S_{\mu\nu}$ are LCAO coefficients, energies, and overlap integrals expressed in Eq. (4), respectively:

$$S_{\mu\nu} = \int X_{\mu} X_{\nu} d\tau \quad (4)$$

The CNDO approximation gives Eqs. (5) and (6) for the matrix elements in Eq. (3):

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \frac{1}{2} P_{\mu\mu}) T_{AA} + \sum_{B \neq A} (P_{BB} T_{AB} - Z_B T_{AB}) \quad (5)$$

$$F_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu} - \frac{1}{2} P_{\mu\nu} T_{AB} \quad \mu \neq \nu \quad (6)$$

where $U_{\mu\mu}$ is the one-electron energy of the atomic orbital, X_{μ} in the isolated atom, $P_{\mu\mu}$ is the total electron density on the atomic orbital, X_{μ} , Z_B is the core charge on atom B, and β_{AB}^0 is an empirical bonding parameter. $P_{\mu\nu}$, P_{AA} , and T_{AB} are respectively elements of the bond order-electron density, a total density of an atom A, and a two-electron integral between an electron on atom A and an electron on atom B given in Eqs. (7), (8), and (9),

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu_i} C_{\nu_i} \quad (7)$$

$$P_{AA} = \sum_{\mu}^A P_{\mu\mu} \quad (8)$$

$$T_{AB} = \int \int X_A(1) X_A(1) \frac{1}{12} X_B(2) X_B(2) d\tau_1 d\tau_2 \quad (9)$$

the summation being over all occupied molecular orbitals. Solving Eq. (3), the total energy of a molecule is expressed in terms of matrix elements over atomic orbitals as Eq. (10):

$$E = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) + \sum_{A < B} Z_A Z_B / R_{AB} \quad (10)$$

The first term in Eq. (10) is the electron energy, and the second is the nuclear repulsion. R_{AB} is the internuclear distance. $H_{\mu\nu}$ is the one-electron matrix element between the atomic orbitals X_{μ} and X_{ν} , containing the kinetic energy and electron-nuclear attraction. $F_{\mu\nu}$ is a matrix element of the two-electron operator, including contributions from the coulomb and exchange interaction. Using the

CNDO approximation, one may derive a convenient expression in which the total energy is separated into a sum of one- and two-center terms,

$$E = \sum_A E_A + \sum_{A < B} \sum E_{AB} \quad (11)$$

whose detailed expressions are given in Eqs. (12) and (13).

$$E_A = \sum_{\mu}^A P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_{\mu}^A \sum_{\nu}^A (P_{\mu\mu} P_{\nu\nu} - \frac{1}{2} P_{\mu\nu}^2) T_{AA} \quad (12)$$

$$E_{AB} = \sum_{\mu}^A \sum_{\nu}^B (2 P_{\mu\nu} S_{\mu\nu} \beta_{AB}^2 - \frac{1}{2} P_{\mu\nu} T_{AB}) + (Z_A Z_B R_{AB}^{-1} + P_{AA} P_{BB} T_{AB} - P_{AA} Z_B T_{AB} - P_{BB} Z_A T_{AB}) \quad (13)$$

In quantum-chemical calculations of molecular interactions, the total adsorption system is considered as a supermolecule, for which the CNDO/2 calculation is carried out. The interaction energy (ΔE) is determined as the difference between the energy of the supermolecule ($E^{P,Q}$) and the sum of the energy of the isolated solid and collector (E^P , E^Q) in their equilibrium geometry in Eq. (14) :

$$\Delta E = E^{P,Q} - (E^P + E^Q) \quad (14)$$

RESULTS AND DISCUSSION

Silica possesses a tetrahedral structure in the unit of which a silicon locates in the center of four tetrahedrally coordinating oxygen atoms. Charge distributions, bond energies, and transition energies of quartz, cristobalite, tridymite, and symmetrical silica as a form, $\text{Si}_2\text{O}_7^{6-}$, consisting of two SiO_4 tetrahedral sharing a bridge oxygen atom are almost the same in the CNDO/2 calculations. Furthermore, their calculated band gaps are well coincident with the experimental value of quartz¹⁹⁾ (Takahashi, 1982). Calculations for a model of the silica-amine adsorption system were done for amine on symmetrical silica with the distance $\text{Si}-\text{O} = 1.61 \text{ \AA}$, the angle $\text{OSiO} = 109.47^\circ$ in a tetrahedral structure, the angle $\text{SiOSi} = 141.06^\circ$ in a bridge structure. The surface of silica immersed in water has an equilibrium with H^+ and OH^- functioning as potential-determining ions illustrated schematically in Fig. 1. The surface of silica is covered with silanols round PZC, while the surface exposes oxygen because of detaching protons from the surface silanols in alkaline ranges. Figures 2-4 show the molecular diagram of three silica without a proton ($\text{Si}_2\text{O}_7^{6-}$), with one proton ($\text{Si}_2\text{O}_7^{5-}\text{H}^+$), and two protons ($\text{Si}_2\text{O}_7^{4-}2\text{H}^+$) in their most stable state obtained

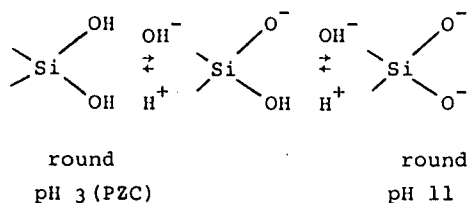
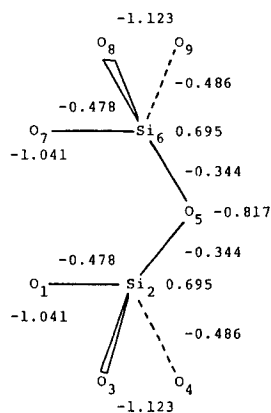
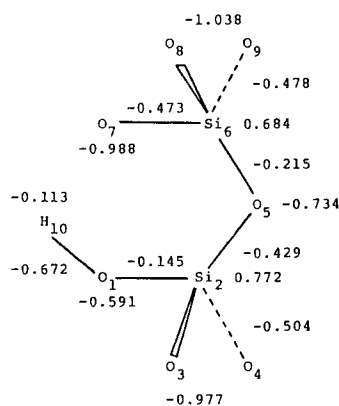


Fig.1 Silica surfaces at different pH values.

Fig.2 Charge distributions and bond energy (atomic units) in the system, $\text{Si}_2\text{O}_7^{6-}$ Fig.3 Charge distributions and bond energy (atomic units) in the system, $\text{Si}_2\text{O}_7^{6-}\text{H}^+$

energetically at a bond length $\text{O}-\text{H}=1.06$ Å slightly longer than the normal bond length of $\text{O}-\text{H}=0.96$ Å. The angle, $\text{SiOH}=137.5^\circ$, is a little greater than the angle $\text{SiOH}=113^\circ$ determined from infrared spectroscopy²⁰⁾ (Peri, 1966). However, the difference of the electron densities and bond energies in both silica with the angle 137.5° and with the angle 113° is as small as 10^{-2} orders in magnitude by the CNDO/2 calculation¹⁹⁾ (Takahashi, 1982).

Figure 2 indicates that the oxygen atom and the silicon atom have a negative charge and a positive charge respectively. When protons are added to oxygen atoms, as shown in Figs. 3 and 4, electrons of the oxygen atoms flow to the protons so that the oxygen atoms may decrease in their negative charge, and the hydrogen atoms have a negative charge due to the excess flow of electrons from the oxygen to the proton. Consequently, the silicon atom transfers its electrons on the silicon-oxygen bond to decrease electron densities on itself, that is, to increase positive charges on itself. New silanol bonds are

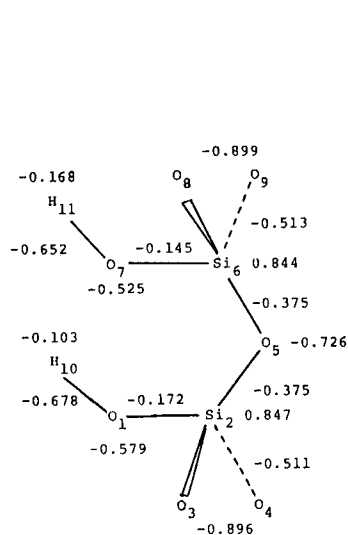


Fig.4 Charge distributions and bond energy (atomic units) in the system, $\text{si}_2 \text{o}_7^{-6} 2\text{H}^+$

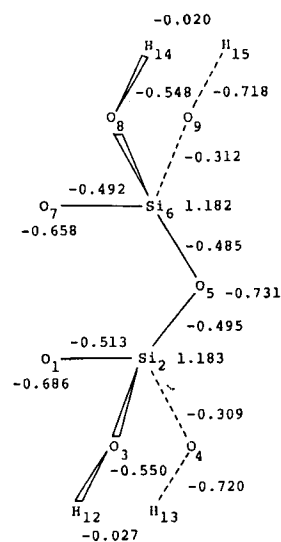


Fig.5 Charge distributions and bond energy (atomic units) in the system, $\text{si}_2 \text{o}_7^{-6} 4\text{H}^+$

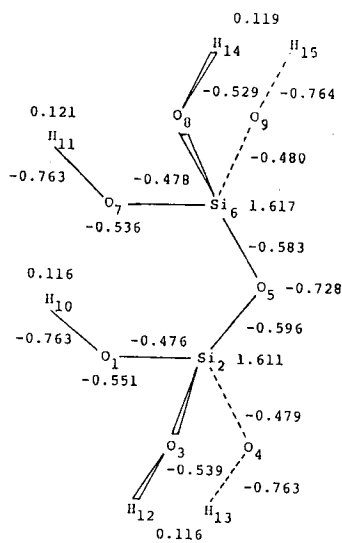


Fig.6 Charge distributions and bond energy (atomic units) in the system, $\text{si}_2 \text{o}_7^{-6} 5\text{H}^+$

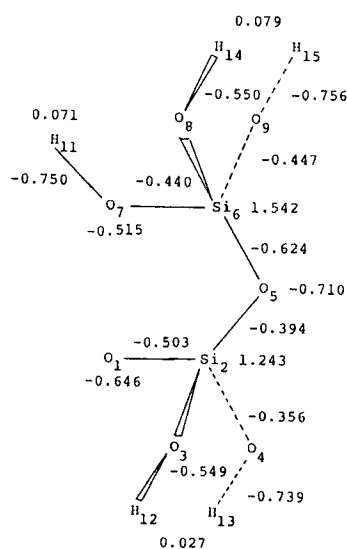


Fig.7 Charge distributions and bond energy (atomic units) in the system, $\text{si}_2 \text{o}_7^{-6} 6\text{H}^+$

formed between the protons and the surface oxygen atoms with the result that the adjacent bonds of silicon and oxygen to silanols slightly decrease in their strength. Successive calculations were carried out for silica with four protons ($\text{Si}_2\text{O}_7^{6-} 4\text{H}^+$), five protons ($\text{Si}_2\text{O}_7^{6-} 5\text{H}^+$), and six protons ($\text{Si}_2\text{O}_7^{6-} 6\text{H}^+$) to obtain a positive charge on a surface proton. Figures 5–7 give the calculated results of the charge distributions and the bond strengths of silica with protons in their most stable state. Hydrogen atoms present their positive charges in silica with surface silanols ($\text{O}_1\text{—H}_{10}$, $\text{O}_7\text{—H}_{11}$) in Figs. 6 and 7, in spite of having their negative charges in silica without surface silanols in Fig. 5, due to electron migration from oxygen to surface proton. It is recognized from these figures that the negative charges of the surface oxygen atom without protons is greater than those of the oxygen atom with protons. The silica surface covered with silanols round PZC in Fig. 7 has positive charges of protons of about 0.12. The surface without silanols round $\text{pH}=11$ in Fig. 5 has negative charges of oxygen atoms of about $-0.66 \sim -0.69$. The surface partially covered with silanols in middle pH ranges in Fig. 6 has positive charges of protons of about 0.07 and negative charges of oxygen atoms of about -0.65 .

The bond lengths and bond angles of a methylamine molecule and a met-

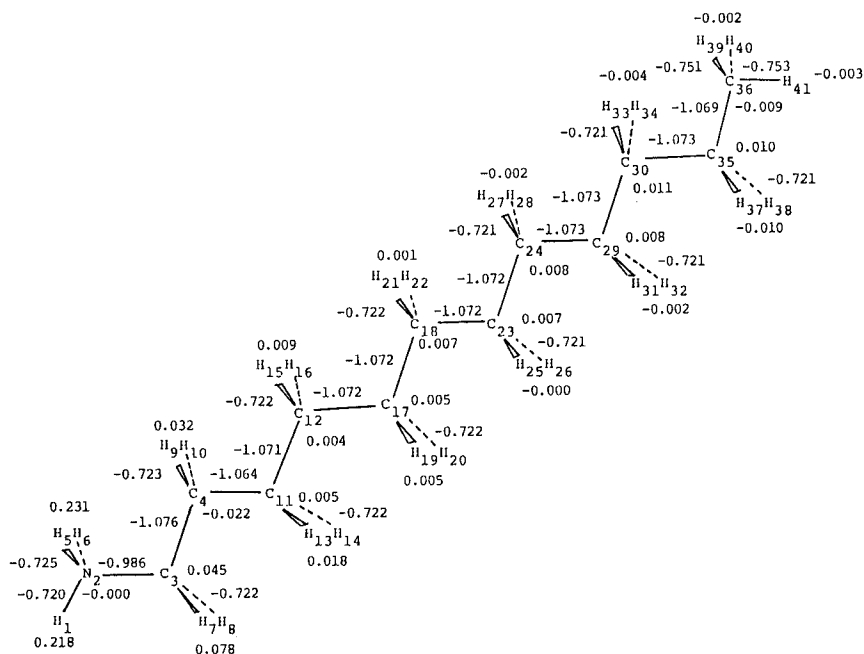


Fig.8 Charge distributions and bond energy (atomic units) of dodecylaminium ion.

hylaminium ion have been determined by microwave spectroscopy^{21,22)} (Lide, 1957, Kivelson and Lide, 1957). Calculations for a series of alkyl-amine molecules and alkylaminium ions have been done to look into the difference of their electronic states and binding states after the structures of both were determined in reference to the mentioned spectroscopic data. Figures 8 and 9 show the charge distributions and the bond strengths of the dodecylaminium ion as well as the dodecylamine molecule, the characteristics of which are as follows: 1. The charge of nitrogen in the dodecylamine molecule is negative, -0.19 , while it is almost neutral in the dodecylaminium ion. 2. The positive charge (0.23) of hydrogen connecting nitrogen in the dodecylaminium ion is greater than that (0.08) in the dodecylamine molecule. 3. The electron density of carbon adjacent to nitrogen is slightly greater in the dodecylaminium ion than in the dodecylamine molecule. 4. The bonds of N-H and N-C in the dodecylamine molecule are a little stronger in their strength than those in the dodecylaminium ion. The charge distributions of a series of alkylaminium ions and alkylamine molecules, illustrated in Fig. 10, indicate that the positive property of hydrogen and carbon atoms or the negative property of nitrogen atoms tends to increase in the order of $10^{-4} \sim 10^{-5}$ as the chain length of the alkyl group becomes longer.

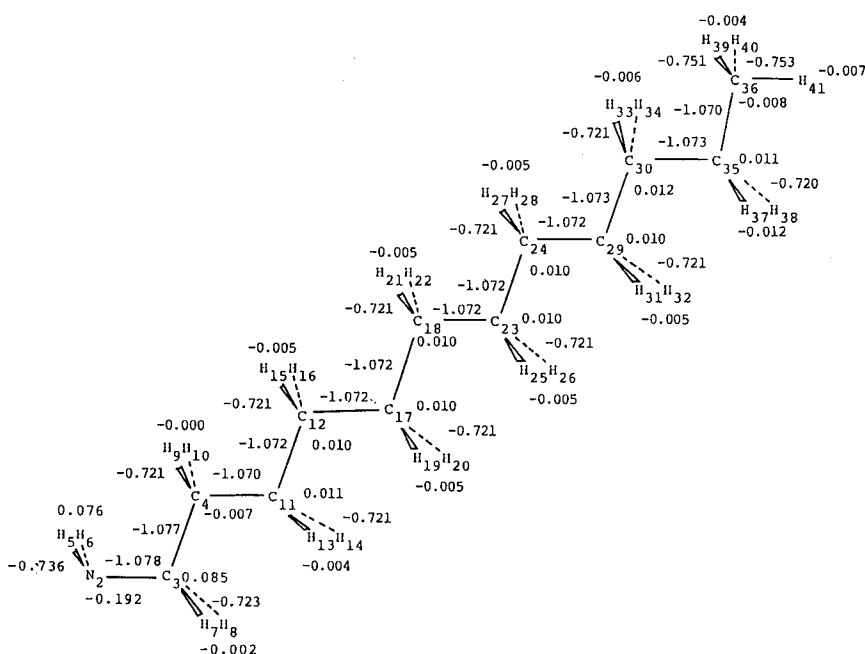


Fig.9 Charge distributions and bond energy of dodecylamine molecule.

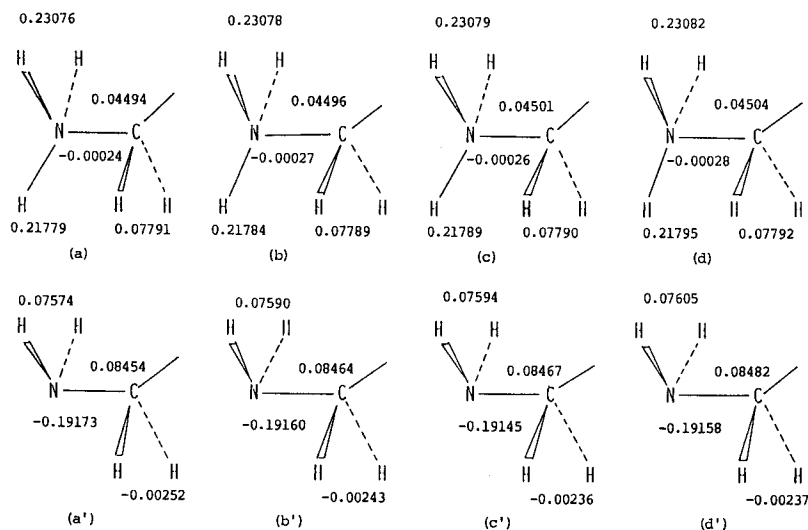


Fig.10 Charge distributions of a series of aminium ions and amine molecules, (a), (a') : hexyl, (b), (b') : octyl, (c), (c') : decyl, (d), (d') : dodecyl.

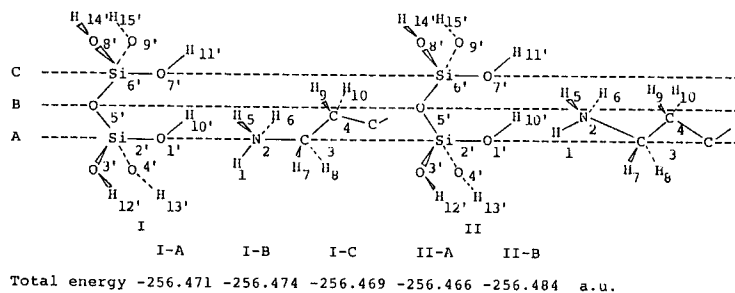


Fig.11 Configurations of dodecylaminium ion on silica with their total energy.

The schematic figure of adsorption of the dodecylaminium ion on silica round PZC is given with the numbering of constituent atoms in Fig. 11. The axis of the N-C line is the same as the axis of the $\text{Si}_2\text{-O}_1$ line in I-A, and the aminium ion in II-B or II-C parallelly moves to the upper lines B and C. In II-A, the C-C axis is coincident with the $\text{Si}_2\text{-O}_1$ axis. Figure 11 shows the total energy of each adsorption system of the dodecylaminium ion on silica at a distance $\text{C}_3\text{-O}_1 = 3.8 \text{ \AA}$. The stability of these adsorption systems becomes in order as $\text{II-B} > \text{I-B} > \text{I-A} > \text{I-C} > \text{II-A}$, where the axis of the dodecylaminium ion in the most stable state of case II-B lies between $\text{Si}_2\text{-O}_1$ and $\text{Si}_6\text{-O}_7$. The total energy of the adsorption system of case II-B is illustrated as a function of the distances between H_1 and O_1 in Fig. 12. The total energy

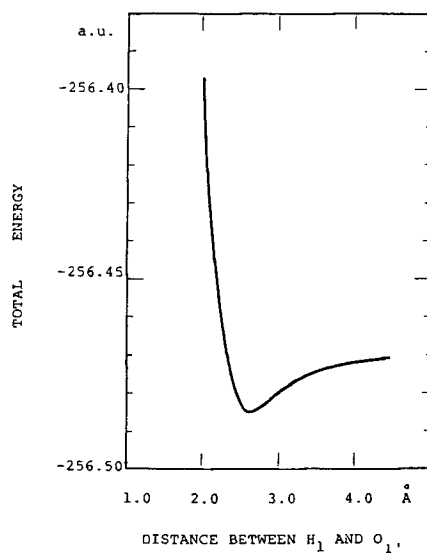


Fig.12 Total energy of adsorption system as a function of distances from silica surface.

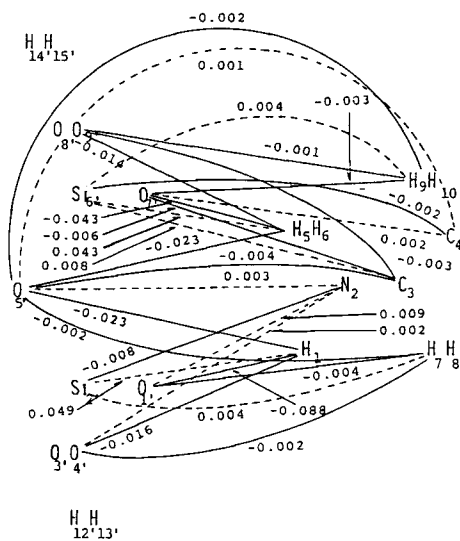


Fig.13 Bond energy (atomic units) between dodecylaminium ion and silica round pH=11.

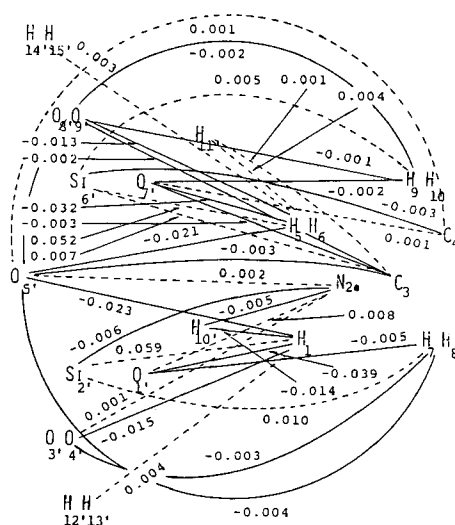


Fig.14 Bond energy (atomic units) between dodecylaminium ion and silica round PZC.

becomes lower as the distances are closer from 4 Å. It becomes the lowest energy state at a distance 2.6 Å, rising up and becoming unstable as the distance is closer than 2.6 Å. Therefore, the configuration of the dodecylaminium ion on silica is assumed at the distance $H_I-O_I = 2.6$ Å ($H_I-H_{10} = 1.5$ Å).

It is very interesting that this bond length is longer than the usual chemical bond length (0.96 Å) between oxygen and hydrogen, close to the sum of the Van der Waals radius of oxygen (1.4 Å) and hydrogen (1.2 Å). This means that the bond is much weaker than the chemical bond. As a calculation of the adsorption system in which a dodecylaminium ion adsorbs on silica round pH=11 by fixing H_I-O_I as 2.6 Å couldn't be self-consistent, it was carried out for the next stable configuration of the adsorption system, I-B, by fixing H_I-O_I as 2.6 Å, as seen in Fig. 13. Figure 14 illustrates a calculation result for the adsorption system of the dodecylaminium ion on silica round PZC. The bonds between the dodecylaminium ion and silica are relatively strong in H_I-O_I , $H_5(H_6)-O_7$, H_I-O_5 , $H_5(H_6)-O_5$ round pH=11, and in H_I-O_I , $H_5(H_6)-O_7$, H_I-O_5 , $H_5(H_6)-O_5$ round PZC. However, they are about one-tenth or one-twentieth of the silanol bond, being almost the same as, or less than the hydrogen bond of the water dimer calculated (-0.068 a.u.)¹⁹⁾ (Takahashi, 1982). On the other hand, the bonds of H_I-Si_2 and $H_5(H_6)-Si_6$ are relatively large antibonding. The bond strengths of H_I-O_I and $H_5(H_6)-O_7$

Table I Bond energy dodecylamine (dodecylaminium ion and amine molecule) and silica round PZC.

Bond*	Bond energy a. u.	
	DA ⁺	DA
H ₅ –O ₇	– 0.032	– 0.013
H ₅ –Si ₆	0.052	0.019
H ₅ –O ₅	– 0.021	– 0.008
H ₅ –H ₁₁	0.004	0.001
N ₂ –O ₁	0.008	0.022
N ₂ –Si ₂	– 0.006	– 0.039
N ₂ –O ₅	0.002	0.017
N ₂ –H ₁₀	– 0.005	– 0.053
C ₃ –O ₅	– 0.003	– 0.006
C ₃ –Si ₆	0.007	0.013
C ₃ –O ₇	– 0.003	– 0.006
C ₃ –H ₁₁	0.001	0.001
Atom	Charge	
H ₅	0.231	0.076
N ₂	– 0.000	– 0.192
C ₃	0.045	0.085
	Energy a. u.	
	Total	– 256.474
	E _A	– 255.976
	E _{AB}	– 216.074
		– 40.3965
		– 39.9058
	Difference	
	E _A	0.004
	E _{AB}	0.4907

* See Fig. 11 for atomic numbering.

round pH= 11 become twice those round PZC, while the antibonding strengths of H₁–Si₂ and H₅(H₆)–Si₆ round pH= 11 become a little weaker than those round PZC, due to the lack of silanols on the silica surface round pH= 11. Therefore, the bonds to bind a dodecylaminium ion to silica are stronger round pH= 11 than those round PZC.

Table I shows the bond energies, the atomic charges, the total energies, the one-center and two-center energies, and their differences in the adsorption system round PZC. The bond between hydrogen and oxygen whose hydrogen charge is more positive in the dodecylaminium ion becomes stronger than the

Table II Stability by adsorption of dodecyl amine on silica.

	Adsorption	Difference of energies a. u.
(1)	$\text{Si}_2\text{O}_7 \cdot 6\text{H} + \text{C}_{12}\text{H}_{25}\text{NH}_3^+ \rightarrow \text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_3^+$	$\Delta E = -0.004$ (-2.51 Kcal/Mol)
(2)	$\text{Si}_2\text{O}_7 \cdot 4\text{H}^{-2} + \text{C}_{12}\text{H}_{25}\text{NH}_3^+ \rightarrow \text{Si}_2\text{O}_7 \cdot 4\text{H}^{-2} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_3^+$	$\Delta E = -0.287$
(3)	$\text{Si}_2\text{O}_7 \cdot 6\text{H} + \text{C}_{12}\text{H}_{25}\text{NH}_2 \rightarrow \text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_2$	$\Delta E = -0.006$ (-4.08 Kcal/Mol)
(4)	$\text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{H}_2\text{O} + \text{C}_{12}\text{H}_{25}\text{NH}_3^+ \rightarrow \text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_3^+ + \text{H}_2\text{O}$	$\Delta E = -0.058$ (-36.58 Kcal/Mol)
(5)	$\text{Si}_2\text{O}_7 \cdot 4\text{H}^{-2} \cdot \text{H}_2\text{O} + \text{C}_{12}\text{H}_{25}\text{NH}_3^+ \rightarrow \text{Si}_2\text{O}_7 \cdot 4\text{H}^{-2} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_3^+ + \text{H}_2\text{O}$	$\Delta E = -0.274$ (-172.11 Kcal/Mol)
(6)	$\text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{H}_2\text{O} + \text{C}_{12}\text{H}_{25}\text{NH}_2 \rightarrow \text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_2 + \text{H}_2\text{O}$	$\Delta E = -0.065$ (-40.97 Kcal/Mol)
(7)	$\text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{Na}^+ + \text{C}_{12}\text{H}_{25}\text{NH}_3^+ \rightarrow \text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_3^+ + \text{Na}^+$	$\Delta E = -0.085$ (-53.27 Kcal/Mol)
(8)	$\text{Si}_2\text{O}_7 \cdot 4\text{H}^{-2} \cdot \text{Na}^+ + \text{C}_{12}\text{H}_{25}\text{NH}_3^+ \rightarrow \text{Si}_2\text{O}_7 \cdot 4\text{H}^{-2} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_3^+ + \text{Na}^+$	$\Delta E = -49.11$
(9)	$\text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{Na}^+ + \text{C}_{12}\text{H}_{25}\text{NH}_2 \rightarrow \text{Si}_2\text{O}_7 \cdot 6\text{H} \cdot \text{C}_{12}\text{H}_{25}\text{NH}_2 + \text{Na}^+$	$\Delta E = -0.092$ (-57.66 Kcal/Mol)

Table III Bond energy between aminium ions and silicaround PZC

Bond	Bond energies (e. V.)		
	Dodecyl	Decyl	Octyl
H_1-O_1	-1.0558	-1.0557	-1.0552
H_1-Si_2	1.6041	1.6038	1.6032
H_1-O_3	-0.4177	-0.4176	-0.4175
H_1-O_5	-0.6124	-0.6121	-0.6120
H_1-H_{10}	-0.3916	-0.3918	-0.3915
H_1-H_{11}	0.0975	0.0975	0.0976
H_1-H_{12}	0.1007	0.1007	0.1007
N_2-O_1	0.2076	0.2075	0.2075
N_2-Si_2	-0.1521	-0.1519	-0.1518
N_2-O_3	0.0338	0.0338	0.0337
N_2-O_5	0.0543	0.0543	0.0542
N_2-H_{10}	-0.1480	-0.1480	-0.1483
N_2-H_{11}	-0.0044	-0.0044	-0.0044
N_2-H_{12}	-0.0082	-0.0082	-0.0082

bond whose hydrogen charge is less positive in the dodecylamine molecule. The bond between nitrogen and silicon whose nitrogen charge is more negative in the dodecyl-amine molecule becomes stronger than the bond whose nitrogen charge is almost neutral in the dodecylaminium ion. Concerning antibonding property, the bond between hydrogen hydrogen and silicon whose hydrogen charge is more positive in the dodecylaminium ion becomes greater than the bond whose hydrogen charge is less positive in the dodecylamine molecule.

Table IV Bond energy between aminium ions and silica round pH= 11

Bond	Bond energy (e. V.)			
	Dodecyl	Decyl	Octyl	Hexyl
H ₁ -O ₁	- 2.3945	- 2.39322	- 2.3912	- 2.3878
H ₁ -Si ₂	1.3234	1.3231	1.3226	1.3219
H ₁ -O ₃	- 0.4398	- 0.4397	- 0.4396	- 0.4395
H ₁ -O ₅	- 0.6251	- 0.6250	- 0.6249	- 0.6247
N ₂ -O ₁	0.2429	0.2428	0.2426	0.2423
N ₂ -Si ₂	- 0.2104	- 0.2102	- 0.2099	- 0.2095
N ₂ -O ₃	0.0459	0.0459	0.0458	0.0457
N ₂ -O ₅	0.0709	0.0709	0.0708	0.0707

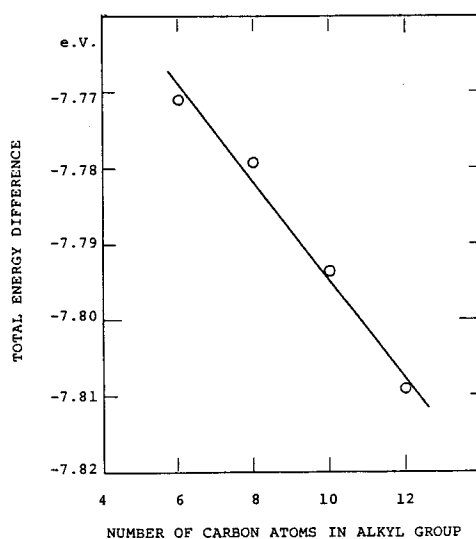


Fig.15 Total energy difference of adsorption system, a series of aminium ions on silica, as a function of the number of carbon atoms of the alkyl group, round pH=11.

Therefore, those bonding and antibonding properties in main come from the coulombic interaction between atoms. Though each bond in the silica-amine system is as weak as the hydrogen bond, the atoms making the main bonds between both are different in the dodecylaminium ion and the dodecylamine molecule. They are hydrogen in the former and nitrogen in the latter. The energy difference of the one center term (0.004 a. u.) and the two center term (0.4907 a. u.) leads to the conclusion that this stabilization energy in the silica-amine adsorption system results from the interaction between the silica atoms and the amine atoms rather than from the energy change of the constituent atoms themselves.

The calculation as seen in table II exceeds the stbilization energy of the adsorption system where the dodecylaminium ion and the dodecylamine molecule adsorb on silica round PZC or $\text{pH}=11$. Therefore, these results seem only to indicate qualitative suggeststions. The dodecylaminium ion is ready to adsorb on silica in alkaline ranges rather than in acidic ranges, comparing case (1) with case (2). This theoretical remark in addition to the calculated result that the bond strength between the dodecylaminium ion and silica is stronger in alkaline ranges than round PZC, as seen Figs. 13 and 14, proves the empirical fact that the dodecylamine is easy to adsorb on silica in alkaline ranges rather than in acidic ranges. Judging from the difference of energy in cases (1) and (3), the adsorption of both the dodecylaminium ion and the dodecylamine molecule on silica round PZC differs little, though their small stabilization energy could be obtained. It is impossible to compare the dodecylaminium ion on silica with the dodecylamine molecule on silica round $\text{pH}=11$, because the CNDO/2 calculation for the adsorption of the dodecylamine molecule (even the decylamine molecule) on silica is not self-consistent. The stabilization energies of the adsorption process in cases (4) - (9) suggest that both the dodecylaminium ion and the dodecylamine molecule have a possibility to exchange a sodium ion and a water molecule in the diffuse layer, or on the double layer. Even in this exchanging adsorption process, the dodecylaminium ion is easier to adsorb on silica round $\text{pH}=11$ rather than round PZC from the comparison of cases (4) and (5). The stabilization energies of the two cases (4) and (6) indicates that the adsorption of the dodecylaminium ion and the dodecylamine molecule on silica round PZC tend to be almost the same in their adsorptive easiness.

The main bond energies between a series of aminium ions and silica round PZC and $\text{pH}=11$ are given in Tables III and IV. The bond energies tend to increase in order to bind the aminium ions to the silica surface more tightly as the chain length of the alkyl group becomes longer. However, their increase is

as small as 10^{-4} e. V. in order per CH_2 . Figure 15 explains that the increase of the chain length of the alkyl group enhances the stabilization energy between aminium ions and silica. The slope of the straight line amounts to 0.25 kT per CH_2 group, which is almost one-fourth of the Van der Waals potential, kT, per CH_2 group. The other adsorption energy supposedly comes from the Van der Waals interaction between long chain amines when they adsorb on silica.

CONCLUSIONS

A series of alkylaminium ions and alkylamine molecules on silica have been theoretically studied to reveal their electronic states and binding states by the CNDO/2 method. Silica surface covered with silanols round PZC has positive charges of proton, and negative charges of oxygen, while the silica surface detaching protons from its surface in alkaline ranges increases the negative charges of oxygen. The difference between charge distributions of aminium ions and amine molecules concerning their polar groups consists in the calculated result that the nitrogen of aminium ions is almost neutral in charge, and that of amine molecules is negative. On the other hand, the positive charge of hydrogen is greater in aminium ions than in amine molecules. The dodecylaminium ion is ready to adsorb on silica in alkaline ranges rather than in acidic ranges. The adsorption of the dodecylaminium ion and the dodecylamine molecule on silica is mainly by due to the coulombic interaction between the constituent atoms of amine and silica. The bonds formed between amine and silica are almost the same, or less in strength than the hydrogen bond of a water dimer. The adsorption process of the dodecylaminium ion and the dodecylamine molecule is energetically preferential by exchanging a water molecule and a sodium ion in a diffuse layer, or on a double layer. A series of aminium ions is easier to adsorb on silica as the chain length of the alkyl group becomes longer. However, the stabilization energy of the adsorption of a series of aminium ions is evaluated to be 0.25 kT by every CH_2 group, which is only one-fourth of the Van der Waals potential per CH_2 group.

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