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Two-Dimensional Arrangements of Adsorbed Alkylammonium Halides on Cleaved Mica Surface

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The adsorbed films of alkylammonium halides, $1C_nTAX$ and $2C_nDAX$ with alkyl chain lengths of $n = 1, 6, 8, 10, 12, 14, 16$, and 18 , on cleaved mica surfaces was analyzed by atomic force microscopy for their two-dimensional arrangement and molecular area. The stable hydrophobic surface was obtained by cleaving mica in an adsorption bath and stands for prolonged adsorption time of 72 h at 5 °C. The adsorbed molecules are stable and do not desorb easily when put in distilled water. The occupied area of double-chained alkylammonium bromides, $2C_nDAB$, on a mica surface was found to range from 0.45 to 0.47 nm², which is equivalent to the density of a potassium ion (1/0.47 nm⁻²), while the single-chained alkylammonium halides, $1C_nTAX$, showed the area ranging from 0.23 to 0.24 nm² per molecule, which is half the density of a potassium ion (1/0.47 nm⁻²) on a mica surface. The symmetry of the two-dimensional arrangement of adsorbed molecules agreed with the lattice structure of a cleaved mica surface despite the numbers and the lengths of alkyl chains.

Introduction

Layered silicate crystals including mica have been attracting the interest of surface scientists for their ease of obtaining clean single-crystal surfaces having relatively large areas.^{1–11} Muscovite mica, a typical layered silicate mineral,³ is thus exclusively used as the standard surface of surface force apparatus (SFA)¹² and is often used as a reference surface for atomic force microscopy (AFM).¹³ Potassium ions in laminar crystal of mica are known to play a role in binding two neighboring surfaces together^{1,2} and are equally shared to each plane on cleavage. The surface density of K⁺ ions accordingly is 50% of that expected from the bulk crystallographic data. These K⁺ ions should be responsible for the adsorption of both inorganic^{3,7} and organic^{8–11} cations in solution by ion exchange. The modification of a mica surface could offer various model surfaces well defined for their compositions^{4–7} and hydrophobicity as well as hydrophilicity.^{14–16} The process of adsorption of ions or molecules

may be one of the easiest ways to modify a mica surface; however, the method to characterize the compact plane surface has been rather limited.

Electron spectroscopy for chemical analysis (ESCA) is one of the available tools to determine the number of cations adsorbed on the mica surface at an accuracy of 10%.¹⁷ Chen et al. have estimated the occupied area of dihexadecyldimethylammonium ($2C_{16}DA^+$) adsorbed on a cleaved mica surface to be 0.75 nm²/molecule by dipping a mica specimen in an adsorption bath of 25 °C for 30 min¹⁶ while other researchers have found the molecular area of dioctadecyldimethylammonium ($2C_{18}DA^+$) to be 0.5 nm²/molecule when the Langmuir–Blodgett (LB) film was transferred to a mica surface.¹⁴ In our previous studies,¹⁸ we have reported that the occupied areas of $2C_{18}DA^+$, $1C_{18}TA^+$, and $4C_1A^+$ on mica were 0.43, 0.24, and 0.27 nm², respectively, for their saturated films adsorbed in solution at 5 °C for 72 h.

AFM is an outstanding tool to analyze the two-dimensional arrangement of the surface molecules with atomic resolution.^{19–23} Tsao et al.²⁴ have studied the

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adsorption of double-chained cationic surfactants on a mica surface by AFM and showed that the adsorption was by ion-exchange mechanism. The AFM images were resolved up to the individual alkyl chain from which they have estimated the molecular areas for $2C_{16}DA^+$, $2C_{18}DA^+$, and $2C_{20}DA^+$ to be 0.52, 0.51, and 0.47 nm², respectively. The dependency of the chain length for the occupied area is explained that the two-dimensional arrangement of adsorbed surfactant molecules is solely determined by the packing of alkyl chains rather than by the ion-exchange process of the headgroups.

The purpose of the present studies is to estimate the packing density and two-dimensional arrangement of adsorbed alkylammonium ions by AFM and to analyze the effect of chain length and the number of chains on the hydrophobic nature of adsorbed film.

Experimental Section

Materials and Sample Preparation. Muscovite mica produced in India was used as a substrate. The homologues and the analogues of cationic amphiphiles dialkyldimethylammonium bromides ($2C_nDAB$), alkyltrimethylammonium bromides ($1C_nTAB$), and tetramethylammonium chloride ($4C_1AC$) were purchased from Tokyo Kasei Kogyo Co., Ltd., Japan, all having 98% purity. These reagents were used without further purification. The water used was purified by a Milli-Q system of the Millipore Corp. Two different processes of adsorption were compared. In the first process, mica was cleaved in air immediately before immersing into adsorptive solution, and in the second process, it was cleaved in the solution. The optimal concentration of the surfactant was chosen to give saturation adsorption, which is uniquely determined by the property of surfactant chosen. The optimal concentrations as determined for each surfactant used are 500 mM for $4C_1AC$, 1 mM for $2C_{10}DAB$, 0.4 mM for $2C_{12}DAB$, 0.2 mM for $2C_{14}DAB$, 0.2 mM for $2C_{16}DAB$, 0.1 mM for $2C_{18}DAB$, 30 mM for $1C_6TAB$, 30 mM for $1C_8TAB$, 20 mM for $1C_{10}TAB$, 5 mM for $1C_{12}TAB$, 1 mM for $1C_{14}TAB$, 0.3 mM for $1C_{16}TAB$, and 0.1 mM for $1C_{18}TAB$.¹⁸ All the adsorptive solutions were kept in glass weighing bottles, each containing mica specimens at 5 °C. The mica was withdrawn from the solution at proper intervals of time, rinsed thoroughly with flowing Milli-Q water of about 1 L, enough to remove excess surfactant and leaving those molecules which are chemically adsorbed. Finally the modified mica surface was dried under the stream of dry nitrogen for AFM observation.

Atomic Force Microscopy. The structure of the mica surface was measured both in air and in water by using AFM (NanoScope-II, Digital Instruments, USA). A microfabricated stylus made of Si_3N_4 and a cantilever having an elastic modulus 0.38 N/m coupled with a 0.7 μ m scanner were used. A mica specimen was mounted on a stainless steel disk using glue. All AFM images were taken in constant force mode. We have paid special precautions in judging whether the AFM images obtained are not the artifact but representing the real structure of the surface. For this purpose, the measurements were made repeatedly for the same specimen with different scanning directions until the reproducibility of the images was confirmed. Any computer process of filtering or smoothing was not applied at this stage. Only those images reliable in this sense were accepted as data for further analysis. The occupied area of adsorbed surfactant molecule on mica was estimated from the two-dimensional Fourier transformed (FT) pattern for ca. 40 original AFM images.

Results and Discussion

Adsorption of Double-Chained Cations. The typical AFM images obtained for those mica surfaces cleaved and modified in aqueous solutions of several adsorptives,

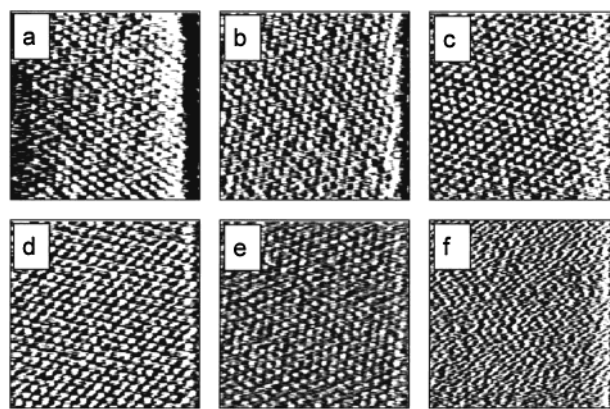


Figure 1. AFM micrographs of the surfaces modified with (a) $2C_{12}DAB$, (b) $2C_{18}DAB$, (d) $1C_6TAB$, (e) $1C_{18}TAB$, and (f) $4C_1AC$ and (c) a freshly cleaved bare mica surface. The images were taken in water under constant force mode with a cantilever having an elastic modulus of 0.38 N/m. The scan area was set at 10 nm \times 10 nm.

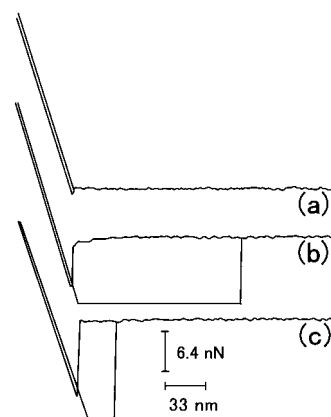


Figure 2. Force curves measured in water for (a) freshly cleaved mica, (b) $2C_{18}DAB$ adsorbed surface, and (c) $1C_{18}TAB$ adsorbed surface.

namely, $2C_{12}DAB$ and $2C_{18}DAB$, are shown in panels a and b of Figure 1. Figure 1c is the image for a bare mica surface cleaved in pure water for comparison. The appearance of the images was almost the same despite the cleavage and the imaging conditions whether the surface was observed in air or in water. All of the AFM images presented here were taken in water. The bright spots in the images are arranged hexagonally for all images obtained for $2C_nDAB$ ($n = 10, 12, 14, 16, 18$). The distance between the two neighboring spots is about 0.5 nm, irrespective of the alkyl chain length. The symmetry and the spacing of the spots pattern resemble those observed for the bare mica surface shown in Figure 1c.

To check the surface coverage, we measured a force–distance relationship, referred here after as force curve, for the bare and the modified mica surfaces in pure water. The force curve for the mica surfaces with adsorbed film of $2C_{18}DAB$, Figure 2b, is entirely different from that observed for the bare mica surface, Figure 2a. Adsorbed surfaces show an attractive force on approaching and a large adhesive force on leaving compared with that for bare mica surfaces. Since the surface of freshly cleaved mica has only potassium and/or hydronium ions in water, electrostatic repulsion should be the one main attribute to the surface force in water. On the other hand, the modified mica surface with adsorbed alkylammonium ions attracts or adheres with AFM probe by hydrophobic interaction. The appearance of the large attraction or adhesion is regarded to be the evidence that the mica

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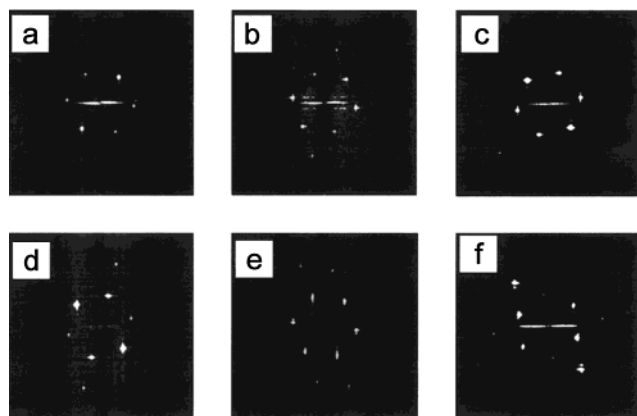


Figure 3. Fourier transform (FT) patterns derived from Figure 1. The distorted regions at the right margin of each image in Figure 1 were cut off before the FT process. The effective pattern areas are thus reduced to $9 \text{ nm} \times 9 \text{ nm}$. Horizontal lines indicate the presence of random noise in each scan. Tiny extra FT-spots observed should indicate the high regularity of the original pattern in that direction. The bright spots of satellites at top left and bottom right in pattern f should represent the double spot in the original real pattern suggesting a closer arrangement of the spots.

Table 1. Two-Dimensional Lattice Parameters for Modified and Clean Surfaces As Estimated from the Fourier Transform Patterns of AFM Images^a

	<i>a</i> /nm	<i>b</i> /nm	<i>c</i> /nm	θ_1 /deg	θ_2 /deg
mica	0.46	0.46	0.45	58.1	61.0
2C ₁₀ DAB	0.47	0.46	0.45	60.3	62.0
2C ₁₂ DAB	0.45	0.46	0.45	61.8	60.3
2C ₁₄ DAB	0.45	0.46	0.46	60.0	59.1
2C ₁₆ DAB	0.53	0.46	0.45	61.6	52.4
2C ₁₈ DAB	0.47	0.46	0.47	57.6	62.6
1C ₆ TAB	0.46	0.46	0.47	61.0	59.5
1C ₈ TAB	0.45	0.48	0.47	59.1	62.4
1C ₁₀ TAB	0.47	0.43	0.46	61.1	57.5
1C ₁₂ TAB	0.46	0.46	0.46	60.1	59.3
1C ₁₄ TAB	0.47	0.47	0.47	62.3	59.8
1C ₁₆ TAB	0.46	0.46	0.46	60.8	60.6
1C ₁₈ TAB	0.47	0.45	0.47	61.7	58.3
4C ₁ AC	0.46	0.45	0.45	61.0	59.1

^a The parameters *a*, *b*, and *c* each express the distance of the spot from symmetry center, *o*, and θ the angle of neighboring symmetry axes: θ_1 , $\angle aob$; θ_2 , $\angle boc$.

surface was modified with alkyl chains. Therefore, we may reasonably ascribe the observed spots in panels a and b of Figure 1 to represent the terminal methyl groups of individual alkyl chains adsorbed instead of the oxygen atoms in the lattice structure of bare mica.

For the statistical treatment of the AFM images of adsorbed molecular layers, each AFM image was subjected to two-dimensional Fourier transformation to give a pattern by employing the device equipped in NanoScope-II software. Figures Panels a–c of Figure 3 show the FT patterns as derived from panels a–c of Figure 1, respectively. All FT patterns showed a common hexagonal symmetry with the central angle of 60° . The spotted pattern of the AFM images can be well characterized by the distance and the angle of spots in the FT patterns, Table 1. The parameters *a*, *b* and *c* each express the distance of the spot from the symmetry center, *o*, and θ , the angle of neighboring symmetry axes: θ_1 , $\angle aob$; θ_2 , $\angle boc$. From these parameters, the average occupied area of the spots, *A*, which corresponds to the terminal methyl group, can be calculated, $A = ab \sin \theta$.

The average occupied area of the terminal methyl group is enlisted in Table 2 under different cleavage conditions,

Table 2. The Average Occupied Area of Unit Spot for Double-Chained Cations

cation	<i>A</i> /(nm ² /spot) ^a		
	I ^b	II ^c	III ^d
2C ₁₀ DAB	0.231 ± 0.006	0.235 ± 0.009	0.228 ± 0.006
2C ₁₂ DAB	0.232 ± 0.003	0.230 ± 0.005	0.226 ± 0.007
2C ₁₄ DAB	0.227 ± 0.004	0.233 ± 0.004	0.227 ± 0.005
2C ₁₆ DAB	0.233 ± 0.006	0.239 ± 0.005	0.229 ± 0.007
2C ₁₈ DAB	0.224 ± 0.005	0.236 ± 0.002	0.233 ± 0.002
mica		0.234 ± 0.005	0.232 ± 0.004

^a Area *A* was calculated from the parameters in Table 1 by following $A = ab \sin \theta$. ^b I: mica cleaved in solution/imaged in air.

^c II: mica cleaved in solution/imaged in water. ^d III: mica cleaved in air/imaged in air.

Table 3. Average Occupied Area of Unit Spot for Single-Chained Cations

cation	<i>A</i> /(nm ² /spot)	
	I ^a	II ^b
1C ₆ TAB	0.233 ± 0.009	0.235 ± 0.005
1C ₈ TAB	0.235 ± 0.013	0.236 ± 0.006
1C ₁₀ TAB	0.231 ± 0.005	0.227 ± 0.004
1C ₁₂ TAB	0.240 ± 0.009	0.240 ± 0.003
1C ₁₄ TAB	0.233 ± 0.006	0.237 ± 0.004
1C ₁₆ TAB	0.234 ± 0.005	0.239 ± 0.006
1C ₁₈ TAB	0.241 ± 0.011	0.238 ± 0.004
4C ₁ AC	0.118 ± 0.003	0.119 ± 0.004

^a I: mica cleaved in solution/imaged in air. ^b II: mica cleaved in solution/imaged in water.

either in air or in aqueous surfactant solutions, and different imaging conditions, in air and in water. For double-chained cations, the occupied areas of the spots correspond to the area for each alkyl chain of adsorbed 2C_{*n*}DAB molecules. Thus, the molecular area for 2C_{*n*}DAB is twice the area of the spot and ranges from 0.45 to 0.47 nm², irrespective of the alkyl chain length. This value coincides with the area of ion-exchangeable site on a cleaved mica surface, 0.47 nm². The agreements of the molecular area and the array patterns of the spots support the fact that the 2C_{*n*}DAB molecules are epitaxially adsorbed by exchanging all of the ion-exchangeable cations (K⁺ or H₃O⁺ ions, etc.) originally present on a cleaved mica surface after a long adsorption time more than 72 h at 5 °C.

Adsorption of Single-Chained Cations. The AFM images of the single-chained cations adsorbed on the mica surfaces observed in water are shown in panels d and e of Figure 1 for 1C₆TAB and 1C₁₈TAB, respectively. The appearance of the images obtained is almost the same irrespective of the imaging conditions, whether it was observed in air or in water. Much like the double-chained cations (Figure 1a,b), the two-dimensional arrangements of the observed spots in all AFM images are hexagonal, and the distance between the two neighboring spots is also 0.5 nm. The arrangements also resemble that of the mica substrate (Figure 1c). The force curve for the modified mica surface in water also shows attractive and adhesive forces (Figure 2c). The behavior of the force curve apparently indicates that the surface is covered with a hydrophobic species. These results also suggest that the observed spots are reasonably regarded to represent the terminal methyl group of alkylammonium adsorbed.

Panels d and e of Figure 3 show the FT patterns as derived from panels d and e of Figure 1, respectively; The parameters of FT patterns are listed in Table 1. The average occupied areas of each spot, *A*, are listed in Table 3, and areas estimated under various imaging conditions are also listed. Since 1C_{*n*}TAB has only one alkyl chain for

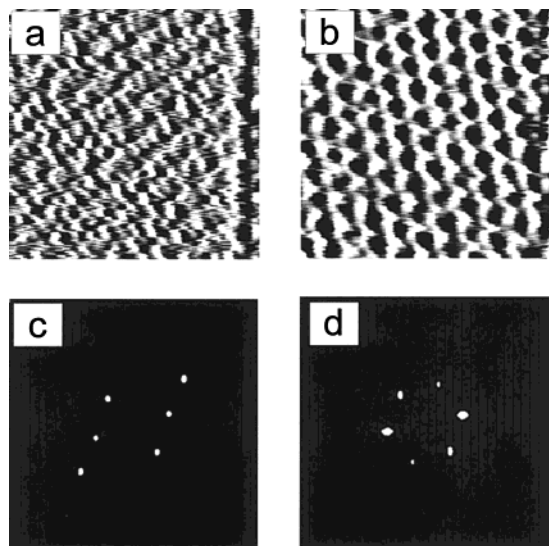


Figure 4. In situ AFM micrographs of $4C_1AB$ adsorbed surface (a) before and (b) after the injection of aqueous 1 N HCl to the AFM fluid cell, $5\text{ nm} \times 5\text{ nm}$. Panels c and d are Fourier transform (FT) patterns derived from (a) and (b), respectively. The effective pattern areas are reduced to $4.5\text{ nm} \times 4.5\text{ nm}$. The top right and bottom left spots in pattern c are indicating the presence of double spots, which are not seen in pattern d due to the desorption of $4C_1AB$ in acidic environment.

each molecule, the occupied area for one $1C_nTAB$ molecule ranges from 0.23 to 0.24 nm^2 . This area is half the area of ion-exchangeable cations, 0.47 nm^2 , on a cleaved mica surface. That is, the adsorption density of single-chained cationic surfactant on a cleaved mica surface is twice as large as that expected from the electrical neutrality of the ion-exchangeable cations originally present on mica surface.

Adsorption of Tetramethylammonium Chloride.

The molecular shape of $4C_1AC$ is different from other analogues $2C_nDAB$ and $1C_nTAB$, for not having long alkyl chains. The AFM images observed in water for a mica surface modified with $4C_1AC$ (Figure 1f) show considerably different appearance with respect to the arrangement of spots. Although the spots are aligned in three directions similar to the double- and single-chained cations, the spots are aligned closer in one particular direction than other two. In fact, the FT pattern of Figure 3f transformed from Figure 1f shows that the spots correspond to a shorter periodicity of 0.27 nm along the direction of closer alignment. The period along this direction is comparable to the calculated spacing of 0.248 nm between two methyl groups of $4C_1AC$ as computed by the MM2 simulation program of molecular structure. The periods along the other two directions remained to be 0.45 nm . Accordingly, the observed spots in Figure 1f should reasonably be assigned to each protruding methyl group of $4C_1AC$.

To see the correspondence of the array of spots for modified and clean surfaces, the mica surface with adsorbed $4C_1AC$ was exposed to 1 N HCl for 4 h and then rinsed with water in an AFM fluid cell. The treatment makes the adsorbed $4C_1AC$ molecules completely wash off the surface according to the condition determined by the preliminary experiments of both contact angle and ESCA measurements. The in situ images of AFM obtained for mica surface with adsorbed $4C_1AC$ before and after the treatment with 1 N HCl solution are shown in panels a and b of Figure 4, respectively. The FT patterns corresponding to panels a and b of Figure 4 are also shown in panels c and d of Figure 4, respectively. These FT patterns show that the closely packed array of spots in (c),

top right and bottom left spots, diminished by acid treatment and the hexagonally arranged spots of base mica surface appeared instead. The arrays of the spots in other two directions in Figure 4d are the same as those seen in Figure 4c. The two methyl groups of adsorbed $4C_1AC$ molecules should explain the observed double-spots hexagonally arranged. The pattern of the arrangement is akin to the array of spots observed for a clean mica surface.

Similar arrangement of adsorbed $4C_1AC$ molecules was also reported by Shindo et al.²⁵ for cleaved a $K_4NbO_{17} \cdot 3H_2O$ surface. They explained the observed molecular packing as formed by the orientation of $4C_1AC$ two methyl groups protruding upward and the rest downward. The two methyl groups of adsorbed $4C_1AC$ were observed as a double-spot with a separation of 0.25 nm whose periodicity agrees with that of K^+ ions in a cleaved niobate crystal.

The molecular area of $4C_1AC$ adsorbed on mica corresponds to the occupied area of the double-spot which is about 0.23 nm^2 , the value close to that of $1C_nTAB$. The occupied area of methyl groups of adsorbed $4C_1AC$ in our case is smaller than that of the ion-exchangeable site on the mica surface by a factor of 0.5 which means that the number of adsorbed $4C_1AC$ molecules is twice as large as that expected from the electrical neutrality of surface sites.

Effect of Two-Dimensional Number Density of Adsorbed Carbon Atoms on Hydrophobicity of Surface. The analysis of the AFM images shows that a $2C_nDAB$ molecule adsorbed on a mica surface occupies an area of 0.46 nm^2 , which corresponds to that of ion-exchangeable sites on mica surface, while $1C_nTAB$ and $4C_1AC$ occupy 0.23 nm^2 . It means that the amount of $1C_nTAB$ and $4C_1AC$ adsorption is twice as large as that of $2C_nDAB$. In previous studies the authors have estimated the ratio of nitrogen atoms in adsorbed $2C_{18}DAB$, $1C_{18}TAB$, and $4C_1AC$ to that of ion-exchangeable potassium atoms on a clean mica surface by using ESCA.¹⁸ Those ratios found for $2C_{18}DAB$, $1C_{18}TAB$, and $4C_1AC$ to the K atoms on mica surfaces are 1.1, 1.9, and 1.7, respectively. Since the atomic area of K^+ ions on a mica surface is known as 0.47 nm^2 , the occupied areas for $2C_{18}DAB$, $1C_{18}TAB$, and $4C_1AC$ should be 0.43 , 0.25 , and 0.28 nm^2 , respectively. These values agree with our AFM observations within experimental error.

The studies of Tsao et al. showed that the occupied area of $2C_nDA^+$ decreased with the increase of chain length as mentioned in the previous section. The smallest area obtained was 0.24 nm^2 per chain for $2C_{20}DA^+$. In the present studies, the occupied area of the alkyl chain found was 0.23 to 0.24 nm^2 regardless of both lengths and numbers of alkyl chain. The lower temperature, and the longer time for the adsorption treatment should be the cause of difference, which made the adsorbed film of closer packing with better arrangement of molecules.

To compare the hydrophobicity of adsorbed mica surface modified with various homologues and analogues of single- and double-chained cations, we have measured the contact angle of water drops placed on modified surfaces. Figure 5 shows the dependence of the contact angle on a two-dimensional number density of total carbon atom in adsorbed alkylammonium, which was estimated from the values of the occupied areas listed in Table 2 and Table 3. The contact angle of the surface modified with $1C_nTAB$ was found to be dependent on the two-dimensional number density of total carbon atoms in adsorbed alkylammonium. For a density of more than $60\text{ carbon atoms nm}^{-2}$, the contact angle of the surface with $1C_nTAB$ is similar to

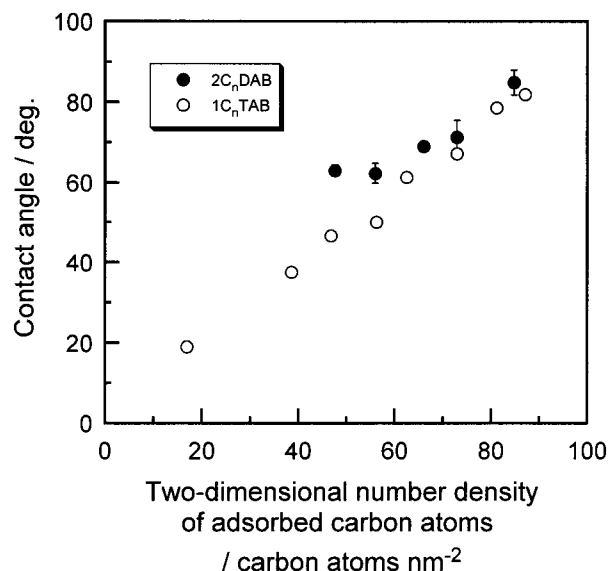


Figure 5. The contact angle of water drop on a mica surface modified with adsorbed alkylammonium homologues. The contact angle was plotted against the two-dimensional number density of adsorbed carbon atoms. Filled circles (●) represent the results for $2C_nDAB$ and open circles (○) are results for $1C_nTAB$.

that with $2C_nDAB$. Therefore, the hydrophobicity of a mica surface modified with adsorbed alkylammonium is solely determined by the two-dimensional number density of total carbon atoms despite the numbers of alkyl chains of adsorbed alkylammonium at the range of the density. In the lower density region, the contact angle of the surface with $1C_nTAB$ is lower than that with $2C_nDAB$. The difference of the dependency may come from the difference of the adsorption manner between $1C_nTAB$ and $2C_nDAB$ on the mica.

The molecular area of $2C_nDA^+$ agrees with that of K^+ ions on bare mica surface, and suggests that the $2C_nDA^+$ ion was adsorbed on mica surface by an ion-exchange mechanism. On the other hand, the surface density of adsorbed $1C_nTAB$ is twice as large as that of $2C_nDAB$. Fifty percent of the $1C_nTA^+$ ions may be adsorbed by the ion-exchange mechanism; however, it is not known by which

force the rest of molecules are bound. For the electrical neutrality, the other half of the $1C_nTA^+$ ions should be accompanied with their counteranions on adsorption. We have tried to detect the signal of bromine for the adsorbed film of $1C_nTAB$ and the signal of chlorine for adsorbed $4C_1AC$ by ESCA; however, no signal was detected within the experimental error.¹⁸ The nature of the interaction that binds these molecules of $1C_nTAB$ and $4C_1AC$ to the mica surface other than the K^+ ion-exchange mechanism is not clear at this moment. The interaction probably causes the difference of the contact angle between $2C_nDAB$ and $1C_nTAB$ especially in the lower density region.

Conclusion

Two-dimensional arrangements and occupied areas of adsorbed cationic amphiphiles “*dialkyldimethylammonium bromides*” ($2C_nDAB$, $n = 10, 12, 14, 16, 18$), “*alkyltrimethylammonium bromides*” ($1C_nTAB$, $n = 6, 8, 10, 12, 14, 16, 18$), and “*tetramethylammonium chloride*” ($4C_1AC$) stably adsorbed (those adsorbed molecules remained after the rinse with water) on freshly cleaved mica surfaces were directly observed and analyzed by atomic force microscopy (AFM). The occupied area of $2C_nDAB$ ranging from 0.45 to 0.47 nm² per molecule, is almost the same as that (0.468 nm²) of the ion-exchangeable cations (K^+ or H_3O^+ ions, etc.) on cleaved mica surface and is independent of the chain length of $2C_nDAB$, suggesting that the epitaxial ion-exchange adsorption has occurred. On the other hand, the occupied area of $1C_nTAB$ and $4C_1AC$ ranging from 0.23 to 0.24 nm² per molecule is half the area (0.47 nm²) of the ion-exchangeable cations (K^+ or H_3O^+ ions, etc.) on cleaved mica surface and is also independent of the alkyl chain length. The observed spots in the AFM image are representing methyl groups of adsorbed $4C_1AC$ molecules. The spots align toward the particular directions which agree with the lattice structure of cleaved mica surface and suggest that the cationic surfactant molecules are epitaxially adsorbed on cleaved mica surface. Those molecules of $1C_nTAB$ and $4C_1AC$ are adsorbed on cleaved mica not only by ion-exchange with K^+ or H_3O^+ ions at adsorption sites but also by any other special forces.

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