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Effects of Anions in Subphases on a Langmuir Monolayer of *N,N*-Dimethyl-1-octadecanamine

Shigeru Negi, Eri Futami, Hiroshi Tsukube,[†] and Koji Kano*

Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University,
Kyotanabe, Kyoto 610-0321

†Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-0022

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The surface pressure–area (π–A) and surface potential–area (ΔV–A) isotherms of *N,N*-dimethyl-1-octadecanamine ($C18NMe_2$) were measured on water subsolutions containing various sodium halides (NaX). The amine monolayer showed an expanded liquid (LE) to a condensed liquid (LC) phase transition on water at pH 7 containing 0.01 mol dm^{-3} NaF, while only the LE phase existed on a subsolution with NaI. The Langmuir monolayer (LM) regularly expanded and the A value at $\pi = 30$ mN m^{-1} increased in the order $F^- < Cl^- < Br^- < I^-$, while the ΔV value decreased in the order $F^- > Cl^- > Br^- > I^-$. The X^--dependent π–A isotherm of the $C18NMe_2$ LM is interpreted in terms of deprotonation from the protonated amine molecules at the LM surface upon compression. Similarly, the $C18NMe_2$ LM expanded regularly in the presence of AMP, ADP, and ATP. Such a phenomenon is understandable by assuming that a high-valent anion in subphase is bound to protonated amine molecules more strongly than a low-valent anion.

The effects of cations and anions in subsolutions on the behavior of monolayers have been widely studied.[1] It has been known that the surface pressure–area (π–A) and surface potential–area (ΔV–A) isotherms depend on the kind of ion dissolved in a subsolution.[2—5] Yazdanian et al. studied the effects of cations on Langmuir monolayer (LM) of dodecanoic acid (C19COOH) on water at pH 6, and found that the monolayer membrane condenses upon the addition of metal cations whose effects increase in the order $Na^+ < Ba^{2+} < Cd^{2+}$.[2] On the basis of the fact that ΔV of the monolayer formed on the water subsolution containing Co^{2+}, Cd^{2+}, or Pb^{2+} is smaller than that on the subsolution with Ba^{2+}, Ca^{2+}, or Mg^{2+}, it has been concluded that C19COOH is covalently bound to Co^{2+}, Cd^{2+}, or Pb^{2+}, while it is bound to Ba^{2+}, Ca^{2+}, or Mg^{2+} through Coulomb interactions. The difference in binding between these transition-metal ions and alkaline-earth metal ions has been ascribed to the difference in the degree of hydration to ions.[4]

In 1942, Hoffman et al. measured the π–A isotherms of 1-octadecanamine ($C18NH_2$) monolayers on water containing 0.01 mol dm^{-3} HCl, which shows a phase transition from a liquid expanded (LE) phase to a liquid condensed (LC) phase via a LE–LC coexistence phase.[6] Upon adjusting the pH by HBr or HI in place of HCl, LM expands. The degree of expansion increases in the order HCl < HBr < HI. The phase transition disappears in the case of HI. These results have been interpreted in terms of the difference in the sizes of the halogen ions, which are the counter anions of $C18NH_3^+$.[6] Similarly, LM of protonated 1-docosanamine ($C22NH_3^+$) on water containing NaBr and 1×10^{-3} mol dm^{-3} HCl is known to expand as compared with that on water containing NaCl.[7] However, LM of *N,N,N*-trimethyl-1-docosanaminium bromide ($C22NMe_3Br$) on water at pH 5.1—5.5 condenses upon the addition of sodium halides (NaX); also, the effect of X^- on LM condensation is remarkable in the order $F^- < Cl^- < Br^- < I^-$.[7] Essentially the same results concerning the effect of X^- were reported with LM of *N,N*-dimetyl-*N*-octadecyl-1-octadecanaminium bromide ($2C18NMe_2Br$).[8—10] The effects of X^- on the $C22NMe_3^+$ monolayer as well as the $2C18NMe_2^+$ one are opposite to those on the $C22NH_3^+$ monolayer. The difference in the effects of X^- on LMs between the quaternary ammonium salts and the protonated primary amine has not been clarified. Several reports on the amine monolayers lack studies concerning the effects of pH as well as a consideration of deprotonation from protonated amine monolayers upon compression. The present study fills such a lack, and reports on the deprotonation from the protonated amine head groups, which depend on the lipophilicity of X^-.

Experimental

Materials. *N,N*-Dimethyl-1-octadecanamine ($C18NMe_2$) was prepared according to procedures described in the literature.[11] An ultrapure analytical grade of chloroform (Wako) was used as a spreading solvent. Reagent grades of inorganic salts, sodium hydroxide, and hydrochloric acid were purchased (Nacalai). Reagent grades of the disodium salts of adenosine-5′-mono- (AMP), -di- (ADP), and -triphosphates (ATP) were commercially obtained (Kowa). Sodium tetraphenylborate (analytical grade, Tokyo Kasei), sodium 2,4,6-trinitrophenolate (chemical grade, Wako), and ammonium hexafluorophosphate (reagent grade, Nacalai) were used as received. Water was deionized by a Yamato Autostill WG220 system and further purified (> 18 MΩ cm) using a Milli-Q system

(Millipore).

Measurements of Surface Pressure-Area and Surface Potential–Area Isotherms. Surface pressure–area (π–A) isotherms were measured with a USI FSD-110 computer-controlled film balance system. The monolayers were prepared at the air–water interface of a rectangular Teflon® trough with an inner dimension of 100×175 mm^2 and a depth of 5.5 mm, which was enclosed in a dark plastic cabinet. The surface pressures were measured by a Wilhelmy plate (a 10 mm wide filter paper) which was calibrated using the pressure at the kink point (π = 24 mN m^{-1}) of the octadecanoic acid monolayer. All measurements were carried out at 293 K. The quality of the aqueous subsolution was checked by compressing the surface without any amphiphiles (π < 0.4 mN m^{-1}). The monolayer was obtained by spreading 8.8 µL of a chloroform solution of C18NMe$_2$ (4.8×10^{-3} mol dm^{-3}) using a microsyringe on the subphase surface. After 10 min, the monolayer was compressed at a rate of 30 mm min^{-1}. The pH values of the subsolutions were adjusted by adding HCl or NaOH. The reproducibility of the π–A isotherm measurements was checked by repeating the experiments several times for each system.

Surface Potential Measurements. The ΔV values of the monolayers at the air–water interface were measured by an ionizing electrode using an ^{241}Am α radiation source connected to a digital electrometer (Advantest) and a standard electrode (Ag/AgCl) dipped into a subsolution. The ionizing electrode was suspended 2 mm above the surface of the subsolution to provide sufficient conductivity and to prevent leakage to other surfaces of the system. The experiment involved the measurements of the electromotive force (EMF) of the cell after preparing a pure-water subphase (V_0) and EMF after spreading a monolayer on the surface (V). The difference V–V_0 is the surface potential (ΔV). All ΔV–A isotherms were reproducible.

Results and Discussion

Surface Pressure–Area and Surface Potential–Area Isotherms of C18NMe$_2$ Monolayers at Various pHs. Figure 1 shows the π–A and ΔV–A isotherms of the C18NMe$_2$ monolayers on water whose pH values were adjusted by a small amount of HCl or NaOH. Since a buffer solution could not be used in this study, the pH values before and after measurements of the isotherms were checked. A remarkable reduction in the pH was detected with a subsolution at pH 9. We eliminated the data obtained for the subsolutions at pH > 7.

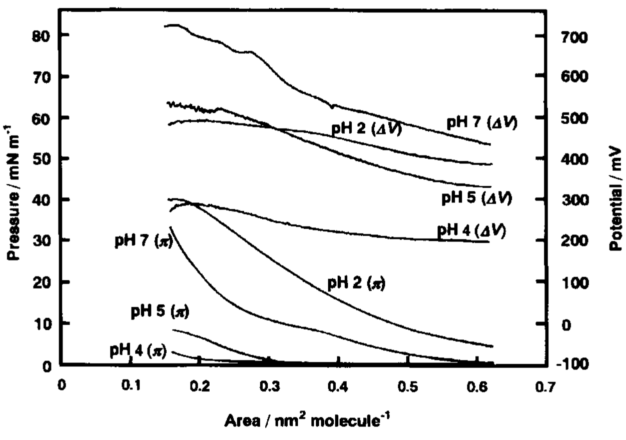

Fig. 1. Surface pressure–area and surface potential–area isotherms of the C18NMe$_2$ monolayers on water without inorganic salt.

The behavior of LM on the subsolution of HCl (pH = 2) is the simplest. At large area/molecule (A), most C18NMe$_2$ molecules should be protonated at pH 2. An electrostatic repulsion between the charged head groups causes the formation of a largely expanded monolayer in the LE phase. In this case, no phase transition of LM exists and the monolayer collapses directly from the LE phase at A = 0.2 nm^2 molecule^{-1} and π = 40 mN m^{-1}. ΔV is nonzero at the LE phase (ΔV = 400 mV at A = 0.6 nm^2 molecule^{-1}), indicating that C18NMe$_2$ is protonated and forms an electric double layer. The ΔV value monotonously increases upon the compression of LM.

At pH 4, no π–A isotherm was measured, and the ΔV value at large A was considerably smaller than that at pH 2. Presumably, although most C18NMe$_2$ molecules are protonated, the amounts of anions in the subphase are not enough to construct a stable electric double layer. Therefore, considerably large amounts of the protonated C18NMe$_2$ molecules might dissolve in the subsolution. Essentially, the same phenomenon was observed at pH 5, though the ΔV values were larger than those at pH 4.

The π–A and ΔV–A isotherms at pH 7 are quite different from those at pH 2, 4, and 5. The predominant species at pH 7 might be C18NHMe$_2^+$OH$^-$. The π value at large A (ca. 0 mN m^{-1} at A = 0.6 nm^2 molecule^{-1}) is smaller than that at pH 2 (8 mN m^{-1} at A = 0.6 nm^2 molecule^{-1}), suggesting that the protonated and free C18NMe$_2$ molecules coexist at this pH where the electrostatic repulsion between the protonated head groups is negligible at large A. Upon compression, the monolayer shows a phase transition from the LE phase to the LC phase via the LE–LC coexistence phase. Fox reported the π–A and ΔV–A isotherms of the C18NH$_2$ monolayer at pH 8.2.[12] The lift-off area of the C18NH$_2$ monolayer is ca. 0.3 nm^2 molecule^{-1} and the kink point due to the LE–LC phase transition is 0.2 nm^2 molecule^{-1}. The C18NH$_2$ monolayer does not show the LE–LC coexistence phase. At pH 2.5, the lift-off area of the C18NH$_2$ monolayer was observed at > 0.6 nm^2 molecule^{-1}.[12] These findings suggest that most of the C18NH$_2$ molecules are not protonated at pH 8.2. We could not measure the reliable π–A isotherms at pH > 7 because of a rapid decrease in pH due to the dissolution of CO$_2$ and carbamate formation at higher pH.[13,14] It is clear, however, that, at least, some amounts of the C18NMe$_2$ molecules are protonated on water at pH 7 where electrostatic repulsion accounts for the formation of the expanded LM at large A. The ΔV values at large A (for example, 430 mV at A = 0.6 nm^2 molecule^{-1}) also indicate the formation of the electric double layer due to protonated amine. The ΔV value gradually increases upon the compression of LM, and a steep increase in ΔV occurs at the LE–LC coexistence phase (A = 0.4—0.3 nm^2 molecule^{-1}). ΔV of LM is expressed as[9,15—18]

$$\Delta V = [1/(\varepsilon_0 A)][\mu_h/\varepsilon_h + \mu_t/\varepsilon_t] + \Psi_0, \qquad (1)$$

$$\Psi_0 = (2kT/e)\sinh^{-1}\{e\alpha/[A(8\varepsilon_0\varepsilon kTC_b)^{1/2}]\}, \qquad (2)$$

where μ_h is the head-group dipole moment including a contribution of the polarization of the water molecules induced by the presence of LM, μ_t is the dipole moment of the tail CH_3 group, ε_0 is the dielectric constant of the vacuum, ε_h is the dielectric constant of the water surface, ε_t is the dielectric constant in the vicinity of tail groups, A is the area per amphiphilic molecule, Ψ_0 is the interfacial potential, k is the Boltzmann's constant, T is the absolute temperature, e is the electric charge, α is the degree of dissociation, ε is the dielectric constant of water, and C_b is the bulk concentration of univalent electrolyte in the subsolution. The increase in ΔV at the LE–LC coexistence phase can be explained by the increase in the mean local dipole moment of the tails of LM (μ_t) due to a reorientation of the alkyl chains to the vertical position in this phase.[9,16,17] If the density of the charged head groups increases upon compression, the electrostatic repulsion between the head groups should become remarkable. The monolayer should expand if no avoidance from electrostatic repulsion takes place. This is the case of LM at pH 2. However, the monolayer at pH 7 shows the LE–LC coexistence phase where the electrostatic repulsion is cancelled via some process. It is plausible that deprotonation from the ammonium head groups is a process by which it is possible to avoid the electrostatic repulsion. If this is true, LM at pH 7 should be markedly affected by the counter anion of the $C18NHMe_2^+$, because the deprotonation is always accompanied by simultaneous release of a counter anion from the electrical double layer. We then studied the effects of sodium halides (NaX) in subsolutions on LM of $C18NMe_2$.

$C18NMe_2$ Monolayers in the Presence of Halogen Anions. The effects of halogen ions on the π–A and ΔV–A isotherms of the monolayer on water at pH 7 are exhibited in Fig. 2. In each case, the addition of NaX (0.01 M, 1 M = 1 mol dm^{-3}) causes an expansion of the monolayer. The A value at $\pi = 30$ mN m^{-1} increases in the order $F^- < Cl^- < Br^- < I^-$ and the phase transition from LE to LC phase disappears in the case of I^-. The effects of the halogen anions on the monolayers of the quaternary ammonium cations are completely opposite to those for the present system.[7—10] Namely, LM of $C22NMe_3^+$ or $2C18NMe_2^+$ markedly expands in the presence of F^-, while it condenses on water containing I^-. The degree of expansion of the quaternary ammonium monolayers increases in the order $I^- < Br^- < Cl^- < F^-$. These results are explained as follows. The I^- and F^- ions form the contact and loose ion-pairs with the quaternary ammonium cation, respectively. Since the electrostatic repulsion between the ammonium groups of the loose ion-pairs is stronger than that of the contact ion-pairs, the monolayer in the presence of F^- expands more extensively than that in the presence of I^-. However, the same explanation cannot be applied for the effects of X^- on the $C18NMe_2$ LM. As shown in Fig. 2, the ΔV value of LM before collapse decreases regularly in the order $F^- > Cl^- > Br^- > I^-$, suggesting that the most hydrophilic F^- ion forms a loose ion-pair with $C18NHMe_2^+$, while the most lipophilic I^- ion affords a contact ion-pair. Neutralization of the positive charge of the ammonium head group by X^- reduces ΔV in LM on water containing I^-. The fact that the π values at $A > 0.5$ nm^2 molecule^{-1} in the presence of I^- are smaller than those of other halogen ions is explained by the formation of a contact ion-pair, $C18NHMe_2I$. The electrostatic repulsion between the head groups of the contact ion-pairs should be weaker than that of the loose ion-pairs at large A. The formation of a contact ion-pair is likely to occur because the ε_h value (6.4—7.6) is known to be much lower than the dielectric constant of bulk water.[15,17] The $C18NHMe_2I$ monolayer shows only the LE phase, similar to the case of LM at pH 2 (HCl) in the absence of NaX. The area (A_c) where LM of $C18NHMe_2I$ collapses is 0.33 nm^2 molecule^{-1}, which is much larger than the cross-section area of I^- (0.152 nm^2, see Table 1), indicating that the expansion of the $C18NHMe_2I$ monolayer can be ascribed to a dipole–dipole interaction at the air–water interface, not to the large size of I^-. At the air–water interface, the microscopic dipoles due to the NH–I bonds are arranged regularly. Two-dimensionally well-arranged dipoles yield a strong electrostatic-repulsion between the head groups in the lateral direction upon compression of the monolayer. Such a dipole–dipole repulsive interaction seems to cause a significant expansion of the $C18NHMe_2I$ monolayer. In the case of the quaternary ammonium cation $2C18NMe_2^+$, however, the LC phase appears directly on water containing I^- upon compression, though only the LE phase is formed in water containing F^-.[9] The difference in the effects of I^- between the quaternary and protonated tertiary amine LMs may be ascribed to the density of the positive charges when LM is compressed. The dipole–dipole repulsion in the case of $C18NHMe_2I$ having one positive charge per alkyl chain should be stronger than that of $2C18NMe_2I$ having one positive charge per two alkyl chains when the LMs are maximally compressed. Probably, the van der Waals interactions between the $2C18NMe_2I$ molecules overcome the dipole–dipole repulsive force, resulting in the formation of the LC phase. Meanwhile, the dipole–dipole repulsive force

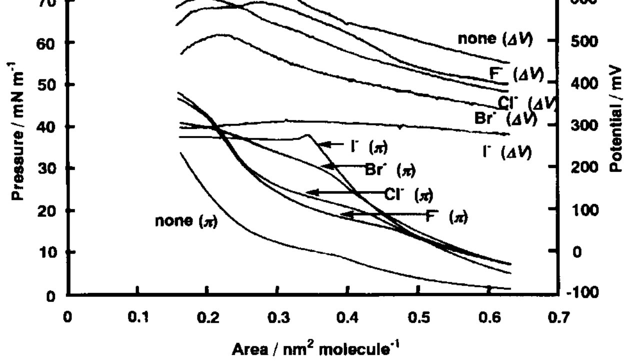

Fig. 2. Surface pressure–area and surface potential–area isotherms of the $C18NMe_2$ monolayers on water at pH 7 in the presence of various sodium halides (0.01 mol dm^{-3}).

Table 1. Physical Parameters of Anions Used in This Study[a)]

Anion	Ionic radius/nm	Cross-section area of ion/nm^2	$\Delta G_{\rm hyd}$/kJ mol^{-1}
F$^-$	0.130	0.053	−465
Cl$^-$	0.181	0.103	−340
Br$^-$	0.196	0.121	−315
I$^-$	0.220	0.152	−275
OH$^-$	0.137	0.059	−430
PIC$^-$	0.329	0.340	−190
TPB$^-$	0.421	0.557	+50

a) B. A. Moyer and P. V. Bonnesen, in "Supramolecular Chemistry of Anions, ed by A. Bianchi, K. Bowman-James, and E. García-España, Wiley-VCH, New York (1997), Chap. 1.

may be stronger than the van der Waals interactions in the case of C18NHMe$_2$I to prevent the formation of the LC phase. In the case of F$^-$, the loose ion-pair, C18NHMe$_2^+$F$^-$, is formed because F$^-$ is extensively hydrated (see negative and large $\Delta G_{\rm hyd}$ in Table 1). In such a case, a large Ψ_0 is expected because of a large α (see Eq. 2), which causes a large ΔV (see Eq. 1). Indeed, F$^-$ causes the largest ΔV value among the halogen ions. Upon compression of the C18NHMe$_2^+$F$^-$ monolayer, the electrostatic repulsion between the head groups becomes remarkable. Judging from the results obtained for LMs of the quaternary ammonium cations,[7—10] it is expected that the expansion of the C18NHMe$_2^+$F$^-$ monolayer is more remarkable than that of the C18NHMe$_2$I monolayer unless the electrostatic repulsion is not avoided by some process. However, the experimental result is opposite to this expectation. We then assumed deprotonation from C18NHMe$_2^+$F$^-$ as a process to avoid electrostatic repulsion. Deprotonation accompanied by simultaneous release of F$^-$ from the interface might occur in the LE–LC coexistence phase. The electrostatic repulsion between the ammonium head groups at the air–water interface becomes significant upon the compression of LM. In the case of quaternary ammonium ions, because an increase in the electrostatic repulsion upon compression cannot be avoided, LM expands most extensively in the case of F$^-$ because F$^-$ is strongly hydrated to form a loose ion-pair. On the other hand, an electrostatic repulsion can be avoided in the case of protonated amine LM by the deprotonation from the ammonium groups, which is accompanied by simultaneous release of strongly hydrated X$^-$. The ease of deprotonation from the protonated amino group depends upon $\Delta G_{\rm hyd}$ of the counter anion, X$^-$. The effects of X$^-$ on the π–A and ΔV–A isotherms of the C18NMe$_2$ monolayer shown in Fig. 2 are clearly explained by the $\Delta G_{\rm hyd}$-dependent elimination of HX from the monolayer–water interface upon compression.

Another explanation for the results shown in Fig. 2 is possible. The electrostatic repulsion can also be avoided by dissolution of C18NHMe$_2^+$X$^-$ into the subsolution. Since it is likely that C18NHMe$_2^+$F$^-$ tends to move to the subsolution more easily than the iodide salt upon compression, the fluoride salt might apparently form a denser LM, as compared with the iodide salt. In order to examine this point, we studied the hysteresis in the π–A isotherms (Fig. 3). As Fig. 3 shows, LM formed on water containing NaF at pH 7 becomes slightly dense after a compression/expansion cycle. No hysteresis was observed in the π–A isotherm of LM on water containing NaI. If protonated amine dissolves into the subsolution upon compression, a large hysteresis should be measured. We also examined the effects of the compression rate on the π–A isotherm. The Teflon bar was moved with rates of 10, 30, 60, and 90 mm min^{-1}. No remarkable effect of the compression rate was measured for the π–A isotherm of the C18NMe$_2$ monolayer on water at pH 7 in the presence of NaF or NaI. These results indicate that the dissolution of the amphiphile salts is not the mechanism for the X$^-$-dependent π–A isotherms at pH 7. It is concluded, therefore, that deprotonation from the ammonium head groups is the reason for the appearance of the LE–LC coexistence phase as well as for the X$^-$-dependent π–A isotherms in the C18NMe$_2$ monolayer system.

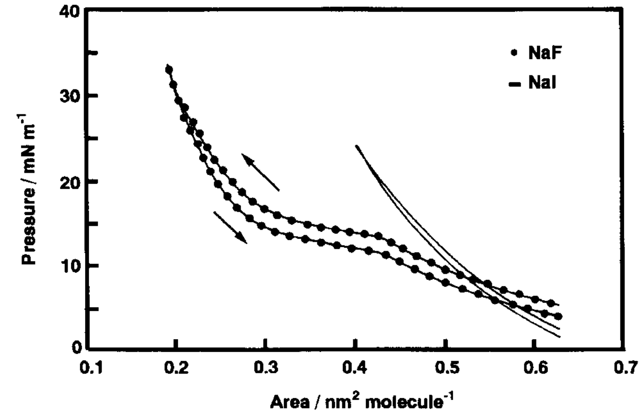

Fig. 3. Surface pressure–area isotherms for compression/expansion cycles of the C18NMe$_2$ monolayers on water at pH 7 in the presence of NaF and NaI (0.01 mol dm^{-3}).

Figure 4 shows the π–A and ΔV–A isotherms of the C18NMe$_2$ monolayers on water at pH 4 in both the absence and presence of sodium halides. No LM was formed in the absence of NaX. It has been known that a primary amine amphiphile, C18NH$_2$, forms unstable LM on an acidic subsolution because of the dissolution of C18NH$_3^+$X$^-$.[19] A similar dissolution of protonated C18NMe$_2$ into water at pH 4 seems to account for the unstable LM of this amphiphile. The addition of NaX salts, however, provides expanded monolayers. Large amounts of X$^-$ in the subsolution might cause the formation of an electric double layer to stabilize LM. In

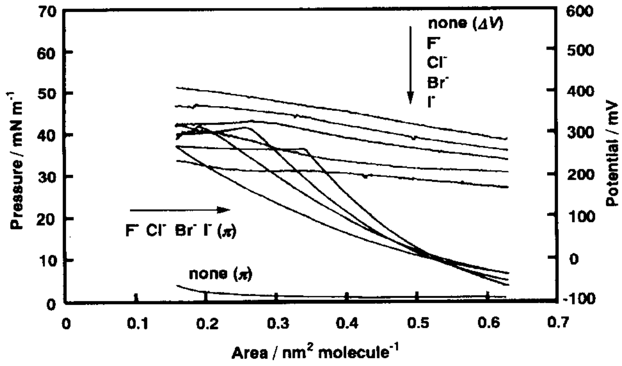

Fig. 4. Surface pressure–area and surface potential–area isotherms of the C18NMe$_2$ monolayers on water at pH 4 in the presence of various sodium halides (0.01 mol dm^{-3}).

all cases, no phase transition was observed. The degree of expansion increased in the order $F^- < Cl^- < Br^- < I^-$ at $A < 0.45$ nm^2 molecule^{-1}. Since the A_c value is much larger than the cross-section area of X^- (see Table 1) in each case, the expansion of the monolayer might be ascribed to an electrostatic repulsion between the head groups. If no deprotonation from the ammonium head groups and/or no dissolution of the charged amphiphile molecules occur at pH 4, the effects of the halogen ions on the expansion of LM should be the same as in the case of the quaternary ammonium salt monolayers, which expand in the order $I^- < Br^- < Cl^- < F^-$.[7—10] We then studied the possibility for the dissolution of C18NHMe$_2{}^+$X$^-$ on water at pH 4.0 upon compression. Figure 5 shows the hysteresis loops of the π–A isotherms of the C18NMe$_2$ monolayers on water at pH 4 containing various NaX salts (0.01 M). Remarkable hysteresis was observed with NaF. The effect of X^- on the hysteresis becomes remarkable in the order $I^- < Br^- < Cl^- < F^-$. The hysteresis in the π–A isotherms can be interpreted in terms of dissolution of the protonated amine amphiphile molecules into the subsolution. Strictly speaking, therefore, we cannot discuss the effect of deprotonation on the π–A isotherms of the amine LM formed on water at pH 4 unless the degree of dissolution upon compression is quantitatively measured. Both dissolution of the protonated amine molecules and the deprotonation from the LM surface upon compression should be considered for the X^--dependent π–A isotherms at pH 4.0.

The expansion of the monolayer at pH 1 in the presence of highly concentrated Cl^- (0.1 mol dm^{-3}) is more remarkable than that in the presence of I^- (Fig. 6). Under such conditions, deprotonation upon compression should hardly occur. Therefore, it is expected that the results obtained for C18NMe$_2$ at pH 1 should become similar to those of the quaternary ammonium cations. Indeed, LM of C18NMe$_2$ at pH 1 in the presence of Cl^- expands more extensively than LM in the presence of I^-, which is consistent with the results for the 2C18NMe$_2$ cation.[7—10] The difference from the 2C18NMe$_2$X LM is the absence of the LC phase for the C18NHMe$_2$X LM. The absence of the LC phase in the C18NHMe$_2$X LM is attributed to the higher density of the positive charge upon compression (vide supra).

Interactions of C18NMe$_2$ Monolayer Membrane with Very Lipophilic Anions. The effects of lipophilic anions, such as $PF_6{}^-$, picrate (PIC$^-$), and tetraphenylborate (TPB$^-$), on the π–A and ΔV–A isotherms of the C18NMe$_2$ monolayer are shown in Fig. 7. The monolayers formed on water at pH 7.0 expand extremely upon the addition of these lipophilic anions, and the degree of expansion increases in the order $PF_6{}^- <$ PIC$^- <$ TPB$^-$, which is the same order of the lipophilicity of the anions.[10] No LE–LC phase transition was observed in each case. In the presence of the least lipophilic anion, $PF_6{}^-$, the system shows a ΔV of 200 mV at large A, indicating the formation of an electric double layer in the LE phase. The ΔV values are very small and almost zero in the cases of more lipophilic PIC$^-$ and TPB$^-$, respectively. Because ΔG_{hyd} value of TPB$^-$ is positive and small (+50 kJ mol^{-1}), the ion pair C18NHMe$_2$TBP scarcely dissociates into the ions. From the results of ΔV measurements, Shapovalov and Tronin[11] concluded that TPB$^-$ as well as PIC$^-$ is incorporated into the monolayer membrane of 2C18NMe$_2{}^+$, while $PF_6{}^-$ adsorbs on the surface of the membrane. The A_c values of the C18NMe$_2$ monolayer in the presence of PIC$^-$ and TPB$^-$ are 0.38 and 0.58

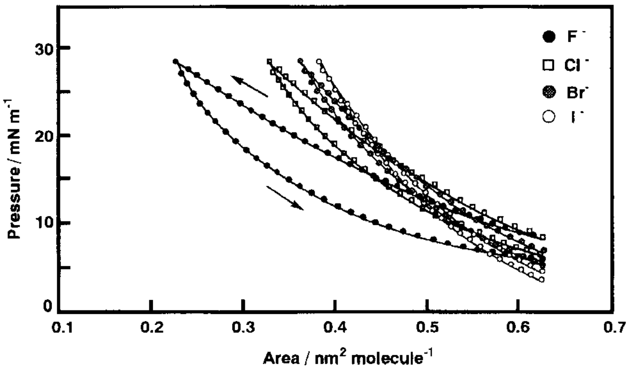

Fig. 5. Surface pressure–area isotherms for compression/expansion cycles of the C18NMe$_2$ monolayers on water at pH 4 in the presence of various sodium halides (0.01 mol dm^{-3}).

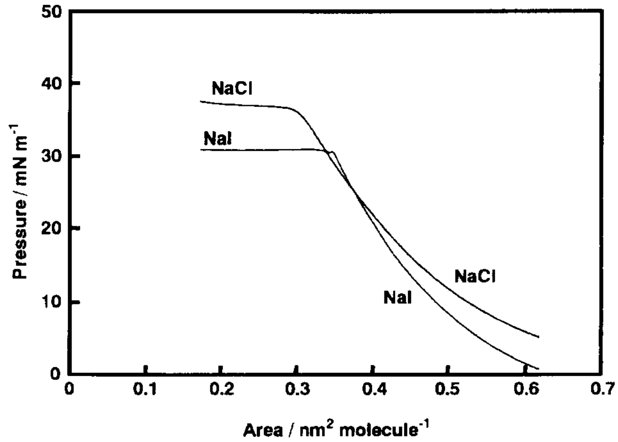

Fig. 6. Surface pressure–area and surface potential–area isotherms of the C18NMe$_2$ monolayers on water at pH 1 (HCl) in the presence of NaCl and NaI (0.1 mol dm^{-3}).

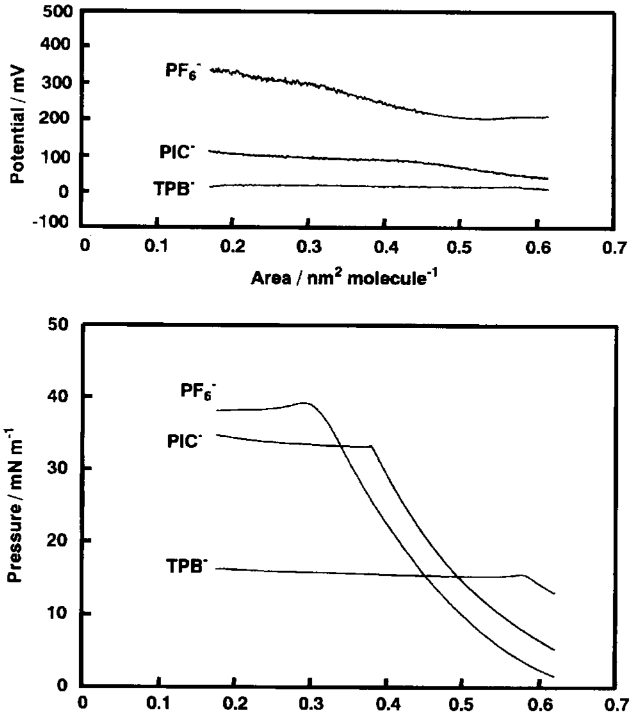

Fig. 7. Surface pressure–area and surface potential–area isotherms of the C18NMe$_2$ monolayers on water at pH 7 in the presence of NH$_4$PF$_6$, sodium picrate, and sodium tetraphenylborate (0.01 mol dm^{-3}).

nm^2 molecule^{-1}, respectively, which are close to the cross-section areas of these anions. Therefore, these anions seem to hang on to the ammonium head groups at the water surface. Judging from the very small ΔV values, the alkyl chains in the C18NHMe$_2$PIC or C18NHMe$_2$TPB monolayer should fluctuate extensively at any area in the LE phase. Even if a contact ion-pair is formed, ΔV should increase upon compression of LM if the alkyl chains are regularly ordered to the vertical position, because the CH$_3$ group in such an arrangement shows a positive microscopic dipole.[9,16] Meanwhile, the large fluctuation of the alkyl chains due to the large A dominated by the large size of the counter anion cancels the microscopic dipole moments of the CH$_3$ groups to reduce μ_t. The results of the effects of lipophilic anions also reveal that the deprotonation from the protonated amine head groups scarcely occur when C18NHMe$_2^+$ forms a contact ion pair with a hydrophobic anion.

C18NMe$_2$ Monolayers in the Presence of AMP, ADP, and ATP. We also studied the effects of AMP, ADP, and ATP on the C18NMe$_2$ monolayer. The acid–base equilibria of these phosphoric acids are summarized in Fig. 8. Figure 9 shows the π–A and ΔV–A isotherms of the C18NMe$_2$ monolayers on subsolutions at pH 7 containing AMP, ADP, and ATP (0.01 mol dm^{-3}). The predominant species in water at pH 7 are AMP^{2-}, ADP^{3-}, and ATP^{4-}. The monolayers expand in the presence of these anions and the degree of expansion increases in the order AMP^{2-} < ADP^{3-} < ATP^{4-}. The effects of AMP^{2-} resemble to those of F$^-$. The monolayer in the presence of AMP^{2-} expands more remarkable than that in the absence of this divalent anion, indicating that the AMP^{2-} anions are bound to the C18NHMe$_2^+$ cations. The LE-to-LC phase transition via the LE–LC coexistence phase was observed. The phase transition becomes obscure in the presence of ADP^{3-}, and no phase transition was detected in the case of ATP^{4-}. The effects of ATP^{4-} are similar to those of I$^-$. Since the lipophilicity of ATP^{4-} is not higher than that of AMP^{2-} or ADP^{3-}, the effects of these anions on the expansion of LM should be explained by a mechanism other than that applied for the effects of the halogen ions. It is quite reasonable to consider that an ion with a high ionic-valence is bound to C18NHMe$_2^+$ more strongly than an ion with a low ionic-valence.

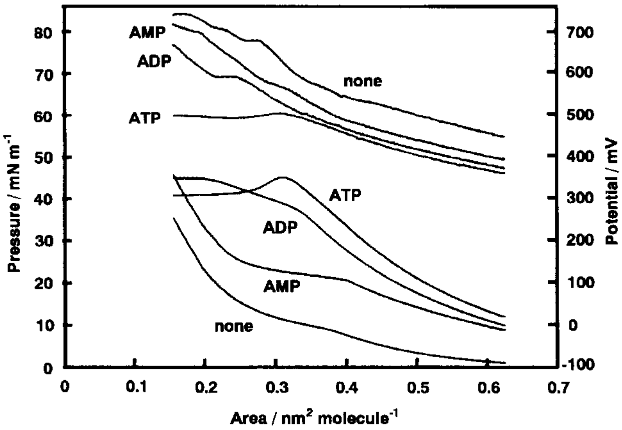

Fig. 9. Surface pressure–area and surface potential–area isotherms of the C18NMe$_2$ monolayers on water at pH 7 in the presence of AMP, ADP, and ATP (0.01 mol dm^{-3}).

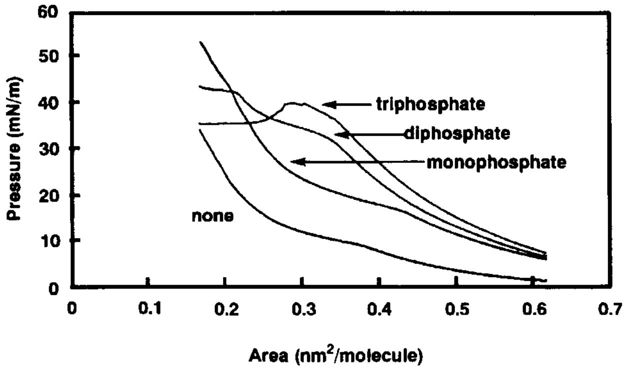

Fig. 10. Surface pressure–area isotherms of the C18NMe$_2$ monolayers on water at pH 7 in the presence of monophosphoric acid, diphosphoric acid, and triphosphoric acid (0.01 mol dm^{-3}).

We then studied the effects of monophosphate (pK_a of MP$^-$ = 7.20), diphosphate (pK_a of DP^{2-} = 6.70) and triphosphate (pK_a of TP^{3-} = 6.50), which do not have the adenosyl group. The results are shown in Fig. 10. The monolayer in the presence of the phosphate anion without the adenosyl group is slightly denser than that in the presence of the corresponding adenosyl phosphate anion. Such a small effect of the adenosyl group suggests that the lipophilicity due to this group does not participate in the π–A and ΔV–A isotherms of

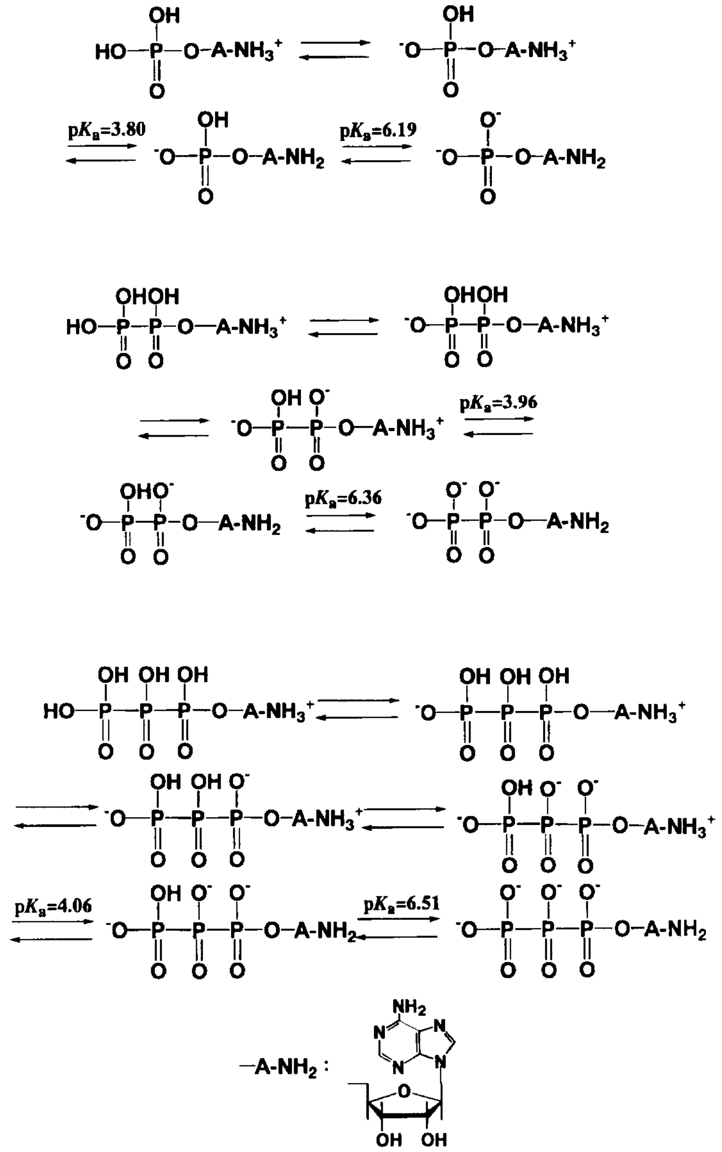

Fig. 8. Acid–base equilibria of AMP, ADP, and ATP.

the C18NMe$_2$ monolayer. Presumably, the high-valent anion such as ATP^{4-} is bound to C18NHMe$_2{}^+$ more strongly than the low-valent anon, such as AMP^{2-}. Deprotonation from the strongly bound ion-pair upon compression may hardly occur, as compared with the weakly bound ion-pair. The phase transition of the C18NMe$_2$ monolayer on water containing AMP^{2-} seems to be ascribed to deprotonation from the C18NHMe$_2$-AMP^{2-} loose ion-pair upon compression.

Another explanation for the effects of the adenosyl phosphate anions on the C18NMe$_2$ monolayer is possible by considering the cross-section areas of these anions. The monolayer formed on water containing ATP^{4-} having a large molecular size may expand more markedly than that on water in the presence of AMP^{2-} having a smaller size. However, the fact that the C18NHMe$_2$X monolayer forms only LM in the LE phase, unless deprotonation occurs, denies this mechanism for the present system.

Conclusions

It has been found that the π–A and ΔV–A isotherms of the C18NMe$_2$ monolayer are regularly affected by the halogen ions or the phosphate ions in the subsolutions. It might be said that the C18NMe$_2$ monolayer recognizes anions in subsolutions through its π–A and/or ΔV–A isotherms, though it is still very primitive. The new finding is deprotonation from the head groups of the protonated amine monolayer accompanied by a simultaneous release of the counter anion upon compression of the monolayer membrane. The present study should contribute to a systematic understanding of the behavior of amine monolayers.

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