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Monolayers of Alkylammonium Alkanesulfonates

Osamu Shibata,* Shoji Kaneshina, Makoto Nakamura, and Ryohei Matuura†
College of General Education, Kyushu University-01, Ropponmatsu, Fukuoka 810
† *Department of Chemistry, Faculty of Science, Kyushu University-33, Higashi-ku, Fukuoka 812*

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The surface pressure-area (π-A) curves for monolayers of cation-anion double long-chain salts, alkylammonium alkanesulfonates, were determined at the air-water interface by the Langmuir method. When the total chain length of cation and anion was constant, the transition pressure from the expanded to the condensed state in the monolayer was lowered as the chain length of cation elongated, and the lowest pressure at the transition point was observed in the case of the equal chain length of cation and anion. The lower the pressure at the transition point, the larger the value of the mean area per molecule at that point. The apparent molar entropy, enthalpy, and energy of transition from the expanded to the condensed phase were calculated from the temperature dependence of the transition pressure on the π-A curve. All the values calculated were negative. The magnitude in the changes of the apparent molar quantities was greatest when both a cationic and an anionic chain had the same length. These results were interpreted in terms of the orientation of double long-chain salt in the condensed state of monolayer. The increase in the chain length of cation and anion tends to increase the values of apparent molar quantity changes. The contributions of long-chain anion and cation to the phase transition of monolayer are not equivalent; the condensing effect of long-chain cation is larger than that of long-chain anion.

There are numerous studies on the adsorbed films from the mixture of cationic and anionic surfactant solutions at the air-water interfaces.[1-7] With respect to the mixed monolayers of cationic and anionic surfactants, a few studies have been reported.[8-12] Our previous investigation[13] has been made on the insoluble monolayers of double long-chain salts, which are composed of a long-chain cation and a long-chain anion, and has shown unique behavior with a series of alkyltrimethylammonium alkanesulfonates. The surface pressure-area curves of these salts exhibited the transition from an expanded to a condensed film, in such a manner as to depend upon the combination of the anion and cation chain-lengths. To elucidate this phenomenon in more detail, it is necessary to extend the study so as to include the double long-chain salts with a different polar group.

In the present study, alkylammonium alkanesulfonates were prepared, and the surface pressure of monolayers of these salts has been measured as a function of molecular area at various temperatures. The thermodynamic quantities on the phase transition from the expanded to the condensed state were determined.

Experimental

The double long-chain salts, that is, alkylammonium alkanesulfonates, were prepared by mixing equimolar solutions of alkylammonium chlorides and sodium alkanesulfonates (Tokyo Kasei Kogyo Co., Ltd.). The precipitates formed were purified by recrystallization from an acetone/ethanol mixture (3:1, v/v). In this study 16 salts of different hydrocarbon chain length shown in Table 1 were used. These salts are abbreviated as C*m*–C*n*, in which m is the number of carbon atoms in the cationic long chain and n is that in the anionic long chain. The purity of these salts was checked by elemental analyses, which gave correct results.

Table 1. Materials

Double long-chain salt		Abbreviation	
$C_mH_{2m+1}N^+H_3 \cdot C_nH_{2n+1}SO_3^-$		C*m*–C*n*	
m = 12, 14, 16, 18		(cationic long-chain)	
n = 12, 14, 16, 18		(anionic long-chain)	
Salt used for monolayers			
C12-C12	C12-C14	C12-C16	C12-C18
C14-C12	C14-C14	C14-C16	C14-C18
C16-C12	C16-C14	C16-C16	C16-C18
C18-C12	C18-C14	C18-C16	C18-C18

Each double long-chain salt was spread from a chloroform/methanol (4:1, v/v) mixture (both Merck, Uvasol) at the air-water interface. The substrate solution of 0.1 M (1 M = 1 mol dm^{-3}) sodium chloride was prepared by thrice-distilled water. Here the sodium chloride was roasted at 973 K to remove any surface active material.

The surface pressure was measured by an automatic Langmuir film balance, which was constructed in our laboratory, within an accuracy of ±0.1 mN m^{-1}.[13] The temperature of the substrate was controlled within ±0.1 K at the desired temperature by circulating thermostated water. The monolayer was compressed continuously with a constant velocity of 2.93×10^{-2} nm^2 molecule^{-1} min^{-1}.

Results and Discussion

The surface pressure-area (π-A) curve of C12–C12 was affected by the NaCl concentration of substrate, and showed a reasonable limiting area on the 4 M NaCl solution. Except for a C12–C12 system, the concentration of NaCl did not affect the π-A curves only if it is above 0.1 M; that is, the π-A curves coincide with each other. Considering this, the concentration of NaCl was held at 0.1 M except for the C12–C12 system.

The π-A curves of C12–C12, C14–C14, C16–C16, and C18–C18 salts, which have equal numbers of carbon atoms in the long-chain cation and anion, that is, m=n, are depicted in Fig. 1. The π-A curve of C12–C12 salt had a transition point from an expanded to a condensed state at 298.2 K under the high concentration of sodium chloride (4 M). The π-A curve of C14–C14 had also a transition point, while the curves of C16–C16 and C18–C18 exhibited only the condensed film. It is of interest to compare the monolayer of a double long-chain salt with that of the corresponding single long-chain salt, but the

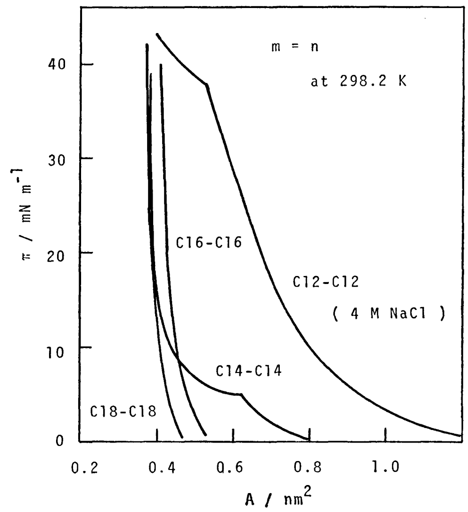

Fig. 1. The π-*A* curves of double long-chain salts on 0.1 M NaCl at 298.2 K. Except for C12–C12 on 4 M NaCl.

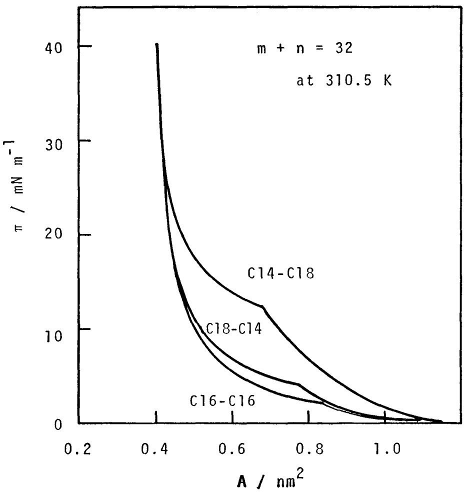

Fig. 2. The π-*A* curves in the case of total carbon number of long-chain cation and anion equal to 32. Substrate: 0.1 M NaCl at 310.5 K.

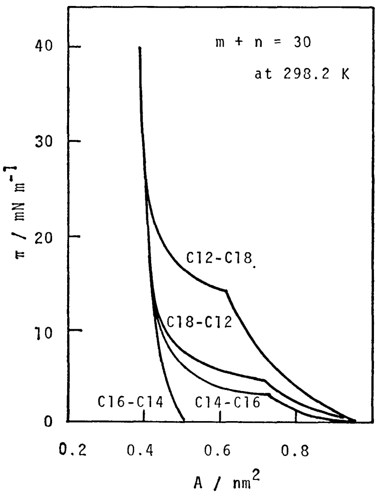

Fig. 3. The π-*A* curves in the case of total carbon number of long-chain cation and anion equal to 30. Substrate: 0.1 M NaCl at 298.2 K.

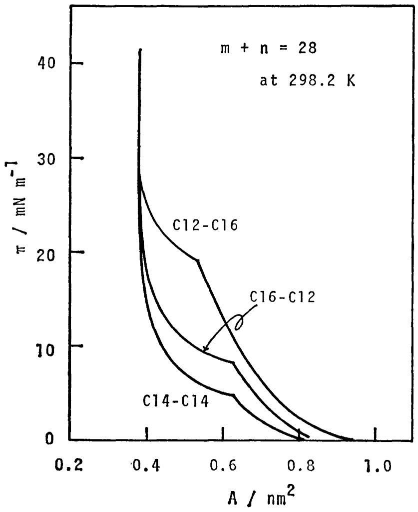

Fig. 4. The π-*A* curves in the case of total carbon number of long-chain cation and anion equal to 28. Substrate: 0.1 M NaCl at 298.2 K.

latter is soluble in water. So we compared the former with the monolayer of single long-chain fatty acid. For example, the π-*A* curve of tetradecanoic acid is of an expanded type, which has a transition from the expanded to the condensed state at 298.2 K. The π-*A* curve of C14–C14 in the present work has also a transition point under this condition. When the alkyl chain of double long-chain salt is longer, *i.e.*, m $(=n)\geq 16$, the monolayer shows only a condensed type film at 298.2 K. The same trend is shown for the monolayers of a single long-chain fatty acid. This result is different from the previous data of alkyltrimethylammonium alkanesulfonates.[13]

Figure 2 shows the π-*A* curves at 310.5 K for three double long-chain cation and anion when $m+n$ is equal to 32. At this temperature the C16–C16 salt shows phase transition and it has the lowest transition pressure among three compounds as seen in Fig. 2. It is noteworthy that in the case of the equal length of cation and anion, the condensing effect is most pronounced. This condensing effect seems to be due to the increase in the molecular interaction between the alkyl chains.

Figures 3—5 show the π-*A* curves for sets of double long-chain salts with the total carbon numbers of long-chain cation and anion, that is, $m+n$, equal to 30, 28, and 26, respectively. When the carbon number difference between a long-chain cation and anion is large as in the case of C12–C18 and C18–C12, the transition pressure is higher than that of C14–C16 and C16–C14. As is seen from Figs. 2—5, when the chain length of the cation is longer than that of the anion, the transition pressure is lower. The π-*A* curve of C16–C14, in this case, shows only a condensed type of film at 298.2 K. It can be concluded that when the chain length of the cation is longer than that of the anion, the monolayer is apt to be more condensed.

The π-*A* curves of alkylammonium alkanesulfonates studied in this paper, as shown in Figs. 1—5, show

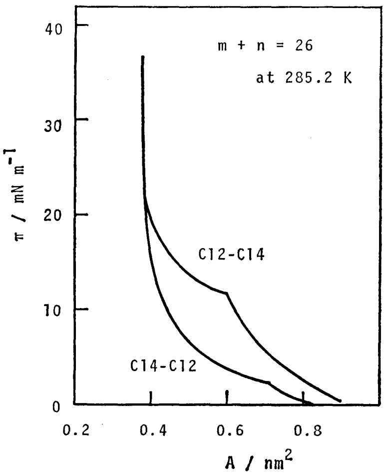

Fig. 5. The π-A curves in the case of total carbon number of long-chain cation and anion equal to 26. Substrate: 0.1 M NaCl at 285.2 K.

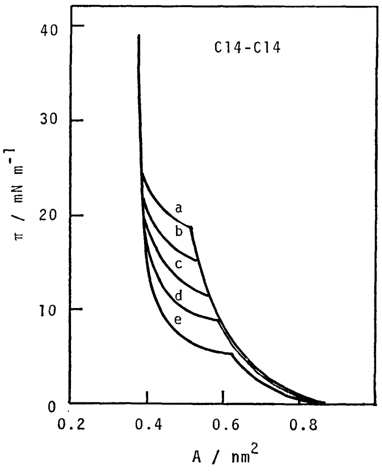

Fig. 6. Temperature dependence of π-A curves of C14–C14 salt. Substrate: 0.1 M NaCl. Temperature: (a) 308.4 K, (b) 306.4 K, (c) 303.2 K, (d) 300.9 K, (e) 298.2 K.

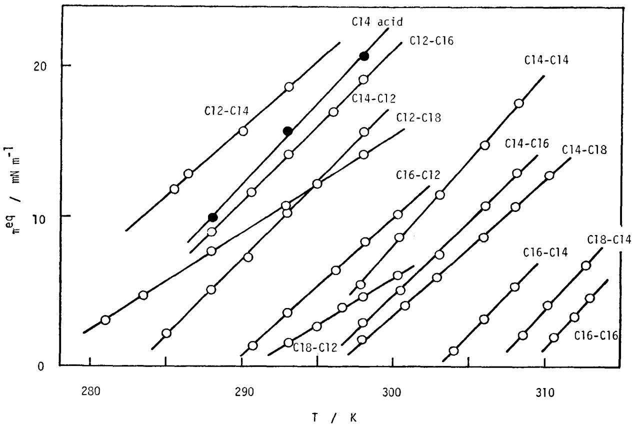

Fig. 7. Transition pressure (π^{eq}) as a function of temperature. Substrate: 0.1 M NaCl, C14 acid: tetradecanoic acid.

the same limiting area of about 0.4 nm^2. This value is in good agreement with twice area of corresponding single long-chain fatty acid.[17,19–21] The double long-chains of these salts are probably aligned perpendicular to the water surface when the film is fully compressed. We have reported previously the value of 0.6 nm^2 for alkyltrimethylammonium alkanesulfonate.[13] Corkill *et al.* reported also the value of 0.6 nm^2 for alkyltrimethylammonium alkyl sulfate.[8] The replacement of sulfate for sulfonate hardly causes the difference in the limiting area. It is evident, on the contrary, that the substitution of cationic ammonium group for trimethylammonium group leads to the appreciable increase in the limiting area. Compared with alkylammonium ion, the bulky head of alkyltrimethylammonium ion may be responsible for the larger limiting area in the π-A curve of the double long-chain salt containing alkyltrimethylammonium ion.

The studies of the temperature effect on the transition pressure in the monolayer are of much interest, since it provides us with thermodynamic information about the state of the monolayers. Figure 6 shows the π-A isotherms of C14–C14 at various temperatures. All the curves have break points, showing the phase transition from the expanded to the condensed state. As was expected, the transition pressure increased with an increase in the temperature. The π-A curves of other salts Cm–Cn with a transition pressure were also measured at various temperatures. In Fig. 7, the transition pressure (π^{eq}) is shown as a function of temperature for various double long-chain salts. The curves are almost linear. This figure includes the temperature effect of π^{eq} of tetradecanoic acid (C14 acid) in order to compare with that of double long-chain salts. The slopes of these lines were determined in order to calculate the apparent molar entropy change on the phase transition.

Exact thermodynamic equations for the multicomponent monolayers were recently derived by Motomura *et al.*[14–18] The thermodynamic quantities on the transition from the expanded to the condensed film can be determined by this thermodynamic treatment, which takes account of contribution of water in a monolayer. When a substance exists in the monolayer state, the apparent molar entropy change is evaluated by applying the relation

$$\Delta s^{r} = (a^{c}-a^{e})\left[\left(\frac{\partial \pi^{eq}}{\partial T}\right)_{p}-\left(\frac{\partial \gamma^{0}}{\partial T}\right)_{p}\right], \tag{1}$$

which corresponds to Eq. 29 of Ref. 17. In this equation, Δs^{r} is the apparent molar entropy change, a^c and a^e are the molecular area (nm^2) (superscripts c and e refer to the condensed and expanded state, respectively), π^{eq} is the transition pressure from the expanded to the condensed state, and γ^0 is the surface tension of pure water. a^c and a^e are estimated as follows. a^e is the area at the point where the film begins to change from the expanded to the condensed state. a^c is determined in the following way: when the point (π^{eq}, a^e) is shifted parallel to the area axis, it comes into contact with the elongated line of the π-A curve in the condensed state to the lower surface pressures. This point of intersection gives the a^c value. The right side of Eq. 1 is calculated numerically from the results given in Figs. 6 and 7. Moreover, the apparent molar enthalpy change is calculated by the relation

$$\Delta h^r = T\Delta s^r. \tag{2}$$

Now the apparent molar energy change Δu^r is related to Δs^r by

$$\Delta u^r = -(\pi^{eq}-\gamma^{o})(a^{c}-a^{e}) + T\Delta s^r, \tag{3}$$

which corresponds to Eq. 32 of Ref. 17. Thus we can determine Δu^r by use of the above experimental results.

The apparent molar quantity changes on the phase transition calculated by using these equations are given in Table 2. In Table 2, the column represents the cation chain length and the row represents the anion chain length. The element of any column or row shows the value of the apparent molar quantity change on the phase transition of the salt combined. It is seen from Table 2 that for the apparent molar enthalpy changes, all the values are negative as expected. That is, the transition from the expanded to the condensed state is exothermic. These values for the double long-chain salts may be expected to be close to twice the values for corresponding fatty acid. In the C14(+) system, however, the values were about four-fold that of tetradecanoic acid, ($\Delta h^r = -14$ kJ mol^{-1}),[17,19–21] Since the double long-chain salts of the type of alkylammonium alkanesulfonates are composed of a long-chain anion and a long-chain cation, the transition from the expanded to the condensed state causes the cohesion of alkyl chains as well as the formation of ionic pairs between ionic head groups. Therefore, the large exothermic change on the transition may be attributable to the combined effects of the cohesive interaction between the alkyl chains, and the electrostatic attraction between the charged head groups. Similar results are reflected upon the values of other apparent molar quantities, which are likely to be characteristic of the monolayers of these salts.

TABLE 2. THE APPARENT MOLAR QUANTITY CHANGES ON THE PHASE TRANSITION OF DOUBLE LONG-CHAIN SALTS $C_mH_{2m+1}N^+H_3\cdot C_nH_{2n+1}SO_3^-$ AT 298.2 K

Cation	Anion C 12(−)	 C 14(−)	 C 16(−)	 C 18(−)
Entropy change ($-10^{-2}\Delta s^r$/J K^{-1} mol^{-1})				
C 12(+)	—	0.6[a)]	0.9	1.1
C 14(+)	1.9[a)]	1.8	2.2	2.3 1.8[c)]
C 16(+)	1.5	— 2.7[b)]	— 2.9[c)]	— —
C 18(+)	1.5	— 2.7[c)]	— —	— —
Enthalpy change ($-\Delta h^r$/kJ mol^{-1})				
C 12(+)	—	17[a)]	28	31
C 14(+)	55[a)]	54	65	69 57[c)]
C 16(+)	44	— 82[b)]	— 89[c)]	— —
C 18(+)	45	— 85[c)]	— —	— —
Energy change ($-\Delta u^r$/kJ mol^{-1})				
C 12(+)	—	20[a)]	32	39
C 14(+)	66[a)]	64	78	84 67[c)]
C 16(+)	53	— 98[b)]	— 106[c)]	— —
C 18(+)	58	— 99[c)]	— —	— —

a) 285.5 K. b) 304.4 K. c) 310.4 K.
Thermodynamic quantities for tetradecanoic acid (C14 acid): $\Delta s^r = -0.47\times10^{-2}$ J K^{-1} mol^{-1}, $\Delta h^r = -14$ kJ mol^{-1}, $\Delta u^r = -17$ kJ mol^{-1}.

The longer the chain length of cation and anion, the larger the apparent molar entropy change (Δs^r) on the transition from the expanded to the condensed state. Holding the total carbon number of long-chain cation and anion constant, the salts with a small difference in the chain length or with the equal-chain-length cation and anion such as C14–C14, C16–C14, and C16–C16 tend to increase the value of the entropy change. The apparent molar enthalpy change (Δh^r) and the apparent molar energy change (Δu^r) follow similar trends.

In Fig. 8, the apparent molar entropy changes (Δs^r) are shown as a function of the carbon number of long-chain cation (m) or anion (n) when the total number ($m+n$) is equal to 28, 30, and 32 at a constant temperature. All the curves are convex upward. All the values of Δs^r are negative as mentioned before. In the case of total carbon number of long-chain cation and anion equal to 32 (the right side in Fig. 8), the magnitude of Δs^r for the C16–C16 salt is the greatest in three double long-chain salts. This means the C16–C16 salt has the most stable orientation in the condensed state of three salts. Similarly in the series of the salts with the total carbon number of long-chain cation and anion equal to 28, the magnitude of Δs^r is greatest for the C14–C14 salt. In the series of total carbon number of 30, the magnitude of Δs^r is the greatest for the C16–C14 salt. Con-

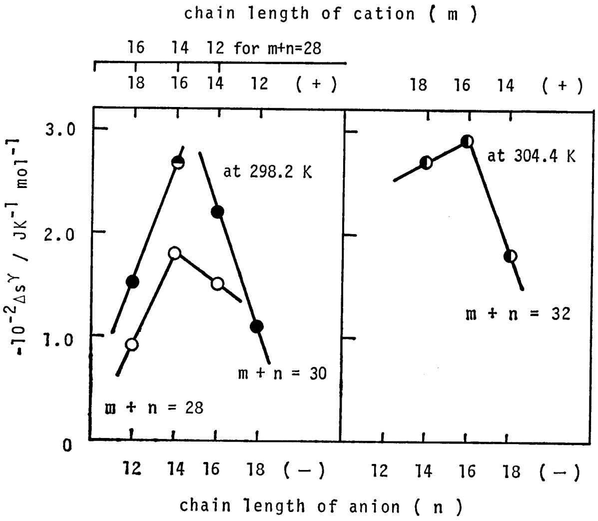

Fig. 8. The apparent molar entropy changes on the phase transition of double long-chain salts. m: cationic chain length, n: anionic chain length. ◓: C16–C14 salt at different temperature (304.4 K).

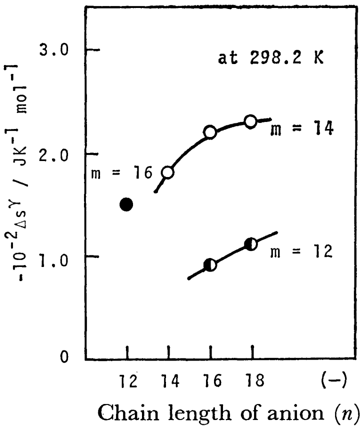

Fig. 9. Anionic chain length dependence of apparent molar entropy change at constant cationic chain length.

sidering above results, in the case of the total carbon number of long-chain cation and anion equal to 30, it is likely that the C15–C15 salt may have the most stable orientation in the condensed film. But the combination of odd carbon number was not treated in this study. This problem will be solved in the future. It is concluded from the above results that the change of apparent molar entropy on the transition tends to be greatest in its magnitude for the salts with the equal-chain-length cation and anion, and that the combination of the equal chain length of cation and anion makes the most stable arrangement in the monolayer of the condensed state.

Figure 9 shows the apparent molar entropy change as a function of the anion chain length at the constant length of the cationic chain. From Fig. 9, for the apparent molar entropy change (Δs^{r}), it may be concluded that the contribution of long-chain cation and anion to the phase transition of monolayer is not equivalent, the contribution of long-chain cation being slightly larger than that of long-chain anion.

Corkill *et al.*[2] studied solution properties of double long-chain salts (alkyltrimethylammonium alkyl sulfates). They showed that C8–C12, C10–C10, and a mixture of C12 and C8 (all total carbon number 20) gave the same values of cmc or free energy of micelle formation, no difference being present between the contribution of long-chain cation and anion. It is evident that the results we obtained in the present study are characteristic of monolayer properties.

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