Molecular Interactions in Mixed Monolayers: Existence of a 1:2 Molecular Association between Stearic Acid and Stearyl Alcohol in Mixed Monolayers

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Surface pressures and surface potentials of mixed monolayers of stearic acid and stearyl alcohol were determined on the following subsolutions: HCl or HCl + CaCl$_2$ at pH 2.0 and NaCl or CaCl$_2$ at pH 6.0.

Average area and average potential per molecule for the mixed monolayers follow the simple additivity rule at pH 2.0 in the presence or absence of CaCl$_2$ in the subsolution.

At pH 6.0, the average area per molecule follows the additivity rule for subsolutions of NaCl, but shows a considerable expansion of monolayers (except for 1:1 molar ratio) for subsolutions of CaCl$_2$. At the same pH, the average potential per molecule shows a deviation from the additivity rule for both NaCl and CaCl$_2$ subsolutions. The deviation for subsolutions of NaCl suggests an ion-dipole interaction between the hydroxyl and ionic carboxyl groups in the mixed monolayers whereas that on subsolutions of CaCl$_2$ suggests a molecular association in a molar ratio 1:2 between stearic acid and stearyl alcohol.

INTRODUCTION

Molecular interactions in mixed monolayers have been of great interest to surface chemists, and biologists who have been investigating molecular aspects of foam stability, emulsion formation, retardation of evaporation by films, and reactions occurring at the cell surface (1-12). Earlier studies on mixed monolayers of acids, amines, alcohols, ethers, and triglycerides were reported by Schulman and his co-workers (13-15). Similar studies were also reported by Harkins and his group (16,17). Ries and Cook (18) have reported their studies on mixed monolayers of stearic acid with isostearic acid.

Various investigators have studied the effect of di- and trivalent cations on fatty acid monolayers the ionic structure of which depends mainly on the pH of the subsolution (19-29). The present paper attempts to answer the following questions regarding interactions in mixed monolayers: Firstly, what is the influence of pH and hence of ionization of the carboxyl group on the interaction of stearic acid with stearyl alcohol? Secondly, how do pH and surface dilution by stearyl alcohol influence the interaction of calcium ions with stearic acid in monolayers?

EXPERIMENTAL

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deionized water of electrical resistance 1.2 \times 10^4 \text{ ohms/cm} were used in all experiments.

Methods. The surface pressure was measured by a modified Wilhelmy plate method, and the surface potential was determined by using a radioactive electrode as described previously (30,31). The surface measurements were taken on the following subsolutions: 0.02 M HCl and 0.02 M HCl in 0.01 M CaCl$_2$ solution at pH 2.0 and 0.02 M NaCl and 0.01 M CaCl$_2$ at pH 6.0. Although the expected pH of 0.02 M HCl solution is 1.7, the measured value was 2.0, presumably owing to insensitivity of the electrodes in the extreme pH region.

Theory. The average area per molecule in a mixed monolayer is calculated by dividing the total area by the total number of molecules of both components in the mixed monolayer. If the molecules of both components occupy the same molecular areas as in their individual monolayers, the points for the average area per molecule of the mixed monolayers would follow the additivity rule which is represented by a straight line joining the two points for the pure components at the same state of compression (see Fig. 1). A deviation from this "additivity rule" indicates condensation of the mixed monolayers due either to an interaction or to an intermolecular cavity effect in the mixed monolayers (12,32,33).

Surface potential ($\Delta V$) of a monolayer can be expressed as $\Delta V = K \eta \mu$, where $K$ is a constant, $\eta$ is the number of molecules per square centimeter of the film (i.e., $\eta = 10^4$/area per molecule in square Angstroms), and $\mu$ is the resultant vertical component of the surface dipole moment of the molecule. Thus, $\Delta V/\eta = K \mu$, where the term on the left-hand side of the equation, representing the average potential per molecule (millivolts/molecule), is proportional to the surface dipole moment $\mu$ of the molecule. Hence, $\Delta V/\eta = \Delta V \times 10^{-14} \times$ area per molecule in square Angstroms, where the term on the right-hand side can be used for calculations.

The advantages of using $\Delta V/\eta$ instead of $\Delta V$ alone are the following: firstly, the average potential per molecule ($\Delta V/\eta$) is a parameter which is a characteristic of the molecule, and is analogous to average area per molecule; and secondly, it eliminates changes in surface potentials caused by expansion or condensation of the mixed monolayers. Conclusive evidence for ionic interaction can be obtained from surface potential measurements only when $\Delta V/\eta$ is plotted against mole fraction of the components in mixed monolayers at the same state of compression. In this case a deviation from the additivity line indicates ion-ion or ion-dipole interaction between the two components in mixed monolayers (12,33).

![Fig. 1. Average area per molecule of stearic acid-stearyl alcohol monolayers at different surface pressures on subsolutions of 0.02 M HCl or 0.02 M HCl + 0.01 M CaCl$_2$, pH 2.0, at 22°C. The broken lines indicate the additivity rule of molecular areas.](image)

RESULTS

Figures 1 and 2 show average area and average potential per molecule plotted against mole fraction of stearic acid and stearyl alcohol in mixed monolayers at 5, 10, and 20 dynes/cm of surface pressure on subsolutions of 0.02 M HCl at pH 2.0. Three of these surface pressure values were selected in order to investigate the influence of low, medium, and high surface pressures on the interaction in mixed monolayers. Both average areas and potentials per molecule.
approximately follow the additivity rule, which is indicated by the broken lines (Figs. 1, 2). Similar results were obtained on sub- 
solutions of 0.02 M HCl in the presence of 0.01 M CaCl₂ at pH 2.0.

Average molecular areas and potentials of the mixed monolayers on sub-solutions of 0.02 M NaCl at pH 6.0 are shown in Figs. 3 and 4. The expansion of the mixed monolayers of 1:9 molar ratio, as shown by the dotted line in Fig. 3, was consistently reproducible. The rest of the mixed monolayers follow the additivity rule of molecular areas. Average potentials per molecule for mixed monolayers show deviation from the additivity rule at all surface pressures (Fig. 4). This deviation is greater for monolayers which contain larger proportions of stearyl alcohol.

Figures 5 and 6 show average molecular areas and potentials on sub-solutions of 0.01 M CaCl₂ at pH 6.0. Average molecular areas are greater than those predicted by the additivity rule except for the molar ratios close to 1:1. The expansion of the mixed monolayers becomes less pronounced at higher surface pressures. Average potentials per molecule show both positive and negative deviations from the additivity rule (Fig. 6). The minimum in average potential occurs at a 1:2 molar ratio of stearic acid to stearyl alcohol.

**DISCUSSION**

It is evident from Fig. 1 that there is no interaction or "intermolecular cavity effect" in the mixed monolayers since the molecular areas approximately follow the additivity rule at all surface pressures. Figure 2 shows that the average potentials follow the additivity rule at pH 2.0 in the presence or absence of calcium ions, suggesting that there is no ionic interaction in these mixed monolayers. It has been suggested that

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Fig. 4. Average potential per molecule of stearic acid-stearyl alcohol monolayers at different surface pressures on subsolutions of 0.02 M NaCl, pH 6.0, at 22°C. The broken lines indicate the additivity rule of average potentials.

Fig. 5. Average area per molecule of stearic acid-stearyl alcohol monolayers at different surface pressures on subsolutions of 0.01 M CaCl₂, pH 6.0, at 22°C. The broken lines indicate the additivity rule of molecular areas.

Fig. 6. Average potential per molecule of stearic acid-stearyl alcohol monolayers at different surface pressures on subsolutions of 0.01 M CaCl₂, pH 6.0, at 22°C. The broken lines indicate the additivity rule of average potentials. Molecular association occurs at a 1:2 molar ratio.

Hydrogen bonding occurs in fatty acid monolayers (34); however, if this is actually the case then the presence of varying amounts of stearyl alcohol should change the distribution of polar groups in the mixed monolayers, which should change the extent of hydrogen bonding, and hence show a deviation in average potentials from the additivity rule. But the absence of such a deviation suggests that there is no interaction or hydrogen bonding between carboxyl groups in stearic acid monolayers at pH 2.0 in the presence or absence of calcium ions.

The average molecular areas follow the additivity rule on subsolutions of 0.02 M NaCl at pH 6.0, except for the molar ratio 1:9 between stearic acid and stearyl alcohol (Fig. 3). This deviation, which was consistently reproducible, suggests that the presence of a small fraction (≈10 mole %) of stearic acid is more effective in disordering the lattice structure of stearyl alcohol monolayers than the presence of a larger fraction.
of stearic acid. This conclusion is further supported by molecular areas of the mixed monolayers on subsolutions of 0.01 M CaCl₂ at pH 6.0 (Fig. 5).

Figure 4 shows the deviation in average potentials from the additivity rule on subsolutions of 0.01 M NaCl at pH 6.0. This deviation suggests an ion-dipole interaction between the hydroxyl and ionic carboxyl groups in mixed monolayers (12,33). The mixed monolayers which contain greater proportions of stearic acid show larger deviations in the average potential.

Since ionic carboxyl groups interact with hydroxyl groups in mixed monolayers, it is evident that they will also interact with un-ionized carboxyl groups in stearic acid monolayers. In the mixed monolayers, a hydroxyl group replaces an un-ionized carboxyl group, and, therefore, causes a deviation of average potentials. Since at pH 6.0 a small fraction of stearic acid is ionized in mixed monolayers (35-37), increasing amounts of stearic alcohol replace the un-ionized carboxyl with hydroxyl groups adjacent to ionic carboxyl groups. Hence, a greater deviation in average potentials is observed for mixed monolayers containing larger proportions of stearic alcohol.

Figures 5 and 6 show average molecular areas and potentials for the mixed monolayers on subsolutions of 0.01 M NaCl at pH 6.0. The mixed monolayers are more expanded when one of the components is present as a small fraction. However, mixed monolayers in molar ratios close to 1:1 follow the additivity rule of molecular areas. With increasing surface pressures, the deviation from the additivity rule becomes smaller. This can be explained as follows:

The stability of the monolayers on these subsolutions was measured by compressing the monolayers maintained at a constant pressure of 10 dynes/cm for 10 min, which was approximately the time interval for compression of a monolayer in our studies. The change in the area per molecule was 0.02-0.05 Å² for these monolayers on subsolutions of 0.02 M NaCl or 0.01 M CaCl₂ at pH 6.0. Since the surface potential data at 5, 10, and 20 dynes/cm are similar and since the change in area at a constant pressure is very small (0.02-0.05 Å²) compared to the deviations from the additivity rule (Fig. 5), the monolayers should be considered stable on these subsolutions.
stearic acid and stearyl alcohol monolayers are, respectively, in the solid and viscous liquid state on subliquid solutions of 0.01 M CaCl₂ at pH 6.0. This suggests that the hydrocarbon chains are in the crystalline state in stearic acid monolayers but not in stearyl alcohol monolayers (Fig. 7a, b). In both stearic acid and stearyl alcohol monolayers, the polar groups presumably form crystalline lattices. The presence of a small fraction of stearyl alcohol in stearic acid monolayers seems to reduce the crystallinity of the lattice, producing a greater disorder and hence, causing a larger area per molecule. Therefore, the mixed monolayers containing a small fraction of either stearic acid or stearyl alcohol are considerably expanded (Fig. 5).

The area per molecule of 19.0–19.5 for stearic acid found on subliquid solutions of both 0.02 N NaCl and 0.01 M CaCl₂ at pH 6.0 in this work is close to that found by Spink and Sanders (38). Harkins and Anderson (39) have reported a value of 18.4 Å² per molecule as the limiting area for stearic acid monolayers at pH 8.2. Sobottka et al. (40) have found 19.7 Å², 17.8 Å², and 17.5 Å² for the area per molecule at a surface pressure of 25 dynes/cm for stearic acid, behenic acid, and lignoceric acid, respectively, on subliquid solutions containing Ba⁺⁺ at pH 6.6.

In contrast to average potentials on subliquid solutions of NaCl (Fig. 4), the average potentials on subliquid solutions of CaCl₂ show a minimum at a 1:2 molar ratio of stearic acid to stearyl alcohol in mixed monolayers (Fig. 6), suggesting that there is a maximum charge interaction between molecules at this ratio. Figure 7a and b represents schematically the monolayers of stearic acid and stearyl alcohol on subliquid solutions of CaCl₂ at pH 6.0. The ionized stearic acid molecules presumably form calcium distearate in which the two remaining oxygen atoms interact with adjacent un-ionized carboxyl groups; this is indicated by broken lines (Fig. 7a). Figure 7c and d represents a proposed arrangement of molecules (2 molecules of stearic acid, a calcium ion, and 4 molecules of stearyl alcohol), which will permit a maximum charge interaction at a 1:2 molar ratio in the mixed monolayers. It should be emphasized that all molecules in mixed monolayers are not arranged in such repeating units, since stearic acid is not fully ionized at pH 6.0 (35–37). However, the ionized stearic acid molecules would form calcium distearate, which, in turn, when surrounded by four stearyl alcohol molecules would cause maximum charge interaction among them as shown in Fig. 7d. Here a calcium ion is surrounded by two anionic and two negatively polarized oxygen atoms. Calcium ions are known to interact in a similar fashion with phosphate groups in dicetyl phosphate and lecithin monolayers (30,41).

In summary, average molecular areas and potentials of the mixed monolayers of stearic acid:stearyl alcohol show characteristic changes depending upon the pH of the subliquid and the presence or absence of calcium ions.

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