Incorporation of Bromo-octadecane into Long-Chain Ester Monolayers at the Air/Water Interface

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ABSTRACT: Surface compatibility of 2-methoxy ethyl stearate and oleate esters with 1-bromo-octadecane (RBr) has been investigated at the air/water interface with a Langmuir film balance. The methoxy ethyl head group in the esters promotes flat conformation at the air/water interface as observed from its higher surface area (stearate, 22.41 Å^2/molecule; oleate, 57.20 Å^2/molecule) in comparison to the corresponding acids. The stearate ester forms a homogeneous mixed monolayer with maximal incorporation of 0.5 mole fraction of RBr. This is indicated by the retention of liquid condensed and solid condensed phases of stearate ester, and the positive deviation of the mean molecular area of the mixed film from the calculated additive areas. When the mole fraction of RBr (x_2) exceeds 0.5, the onset of formation of heterogeneous mixed film is indicated by the appearance of initial and final collapse pressures. On the contrary, oleate ester shows the least compatibility with RBr, which is indicated by the progressive decrease in mean molecular area with x_2. The more liquid expanded-phase structure of oleate ester probably does not promote compatibility with RBr at the air/water interface.

Paper no. J9738 in *JAOCS 78,* 503–507 (May 2001).

KEY WORDS: 1-Bromo-octadecane, collapse pressure, Langmuir film balance, mean molecular area, methoxy ethyl oleate, methoxy ethyl stearate, surface compatibility.

Amphiphilic molecules that exhibit a hydrophilic-lipophilic balance (HLB) in the range of 3–6 (1) tend to form insoluble monolayers at the air/water interface (2,3). The fatty acid series of C_{16}–C_{22} alkyl chain length provide classic examples for insoluble monolayer systems. Extensive studies on the monolayer characteristics of fatty acids as a function of chemical structure, pH, and soap-forming cations such as Cd^{2+} and Mg^{2+} have been well documented (4–6). The profound influence of double bonds on the conformation of fatty acids at the air/water interface can be recognized from the comparison of monolayer characteristics of saturated and unsaturated fatty acids. For example, stearic acid forms a condensed monolayer with a minimum area of closest packing (A_0) of 20 Å^2/molecule, in contrast to oleic acid which tends to form an expanded monolayer, resulting in A_0 of 41 Å^2/molecule (7). The presence of a *cis* double bond at the 9:10 position in oleic acid plays a significant role in promoting expanded conformation at the air/water interface. Considerable changes in packing density, electrical characteristics, and collapse pressure occur in fatty acid monolayer films in the presence of different cations (8–10). For example, stearic acid tends to form a more condensed monolayer with a greater degree of packing, especially in the presence of Cd^{2+}. This has been attributed to factors such as larger nuclear sites and greater adhesion between monolayers of fatty acid soaps. The influence of carboxyl and conjugate ions over the monolayer characteristics of fatty acids at the air/water interface suggests that chemical modification of the carboxyl functional site, as rendered for example by simple esterification, might influence monolayer characteristics at the air/water interface. Besides, the significance of surface and interfacial properties of fatty esters can be recognized from the influence of interfacial characteristics of some of these esters, such as for glyceryl esters in biological and technological systems. Short-chain alcohols with less than a C_4 alkyl chain, which do not contribute much to hydrophobicity, could be an ideal choice. Hence, 2-methoxy ethyl stearate and oleate esters have been selected and synthesized for detailed investigations for two-dimensional surface characteristics at the air/water interface.

Functionalization of insoluble monolayers of amphiphilic molecules, such as fatty acids and their respective esters, is of immense significance in view of biological and industrial applications, e.g., surface modifications. Basically, this process is afforded by three approaches: (i) incorporation of molecules such as lipids and amphiphilic proteins capable of forming insoluble monolayers by themselves; (ii) employing amphiphilic molecules of high HLB (>8.0), e.g., emulsifiers, as penetrants; and (iii) incorporation of long-chain molecules, e.g., alkanes and haloalkanes, that are incapable of forming monolayer films by themselves at the air/water interface (11,12). Modifications in monolayer characteristics of arachidic acid in the presence of cationic amphiphiles, namely, octadecyl dimethyl amine oxide and dioctyl dimethyl ammonium chloride, have been established through infrared spectroscopic investigations on mixed monolayers (13). Paraffins and their halogen derivatives are preferred in surface modification systems in view of some of their desirable characteristics, such as photo and thermal stability. These materials are incapable of forming monolayers at the air/water interface. The successful incorporation of long-chain alkanes and alkyl halides into long-chain fatty acid matrices, which is due to lateral attraction between alkyl chains, has been well documented (14–16). Fatty acid monolayers in general exhibit limited compatibility, <0.3 mole fraction with haloalkanes at an ambient temperature of 25°C. It is

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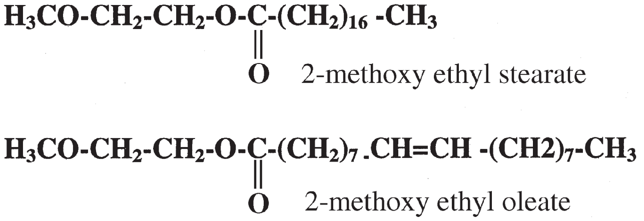
of interest to examine the scope for promotion of surface compatibility of fatty acids with haloalkanes after modification into esters. In this investigation, a detailed study has been carried out to examine the surface compatibility of 2-methoxy ethyl stearate and oleate esters with bromo-octadecane (RBr) at the air/water interface.

EXPERIMENTAL PROCEDURES

Materials. 2-Methoxy ethyl stearate and oleate esters with purity >98% have been synthesized in this laboratory. The chemical structures of stearate and oleate esters are presented in Scheme 1. For details regarding synthesis and characterization of the esters, see References 17 and 18. Chloroform and methanol used in the Langmuir film balance (LFB) experiments were of high-performance liquid chromatography (HPLC) grade. RBr (Sisco Chemical Industries Ltd., Mumbai, India) for compatibility studies was of analyzed reagent grade. Double-distilled water was filtered through a Milli Q system (Millipore, Bedford, MA) and showed a surface tension of 72.0 dyn cm^{-1} at 25°C.

Measurements with LFB. The surface pressure–area (π-A) isotherm experiments were performed at 25°C on a water subphase in a Teflon-coated Langmuir trough (model no. 6015); Nima Technology Ltd., Warwick, United Kingdom). A Wilhelmy plate with a microprocessor-controlled film balance with a precision of 0.01 mN·m^{-1} was employed to measure surface pressures. Separate stock solutions (3 mM) of materials under investigation were prepared. HPLC-grade chloroform was employed for preparation of oleate ester and RBr solutions. Because the stearate ester exhibited limited solubility in chloroform, a mixture of chloroform and methanol (1:1, vol/vol) was employed to prepare stock solutions of the stearate ester. Mixed solutions containing different mole fractions of RBr (x_2, 0.0–1.0) were made from calculated volumes of respective stock solutions. Typically, 50 µL of the solution was slowly spread on the water subphase with a Hamilton microliter syringe and allowed to stand for 10 min for evaporation of the solvent. Afterward, the floating layer was compressed with a barrier speed of 50 cm^2/s. All isotherms were repeated three times to check reproducibility. The trough was washed thoroughly with mild alkaline solution and hot water before starting each experiment. The water surface was cleaned by aspiration after each isotherm experiment, and the purity of the surface was confirmed by sweeping the surface. The absence of surface-active impurities in the solvent was confirmed by conducting a blank run with the solvent. To check the purity of the surface, the stearic acid isotherm was measured, and was found to compare well with literature data, within the limits of experimental error.



$H_3CO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_{16}\text{-}CH_3$ 2-methoxy ethyl stearate

$H_3CO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_7.CH{=}CH\text{-}(CH2)_7\text{-}CH_3$ 2-methoxy ethyl oleate

SCHEME 1

RESULTS AND DISCUSSION

π-A Isotherm characteristics of 2-methoxy ethyl stearate and oleate esters. The reproducibility of π-A isotherm experiments for stearate and oleate esters at 25°C was checked and found to be acceptable. The surface area was reproducible within the limits of experimental error of 0.5 Å^2/molecule at a given surface pressure. The π-A isotherm curves of stearate and oleate esters are presented in Figures 1 and 2. The shapes of the isotherms of the esters resemble their respective parent acids. Thus, stearate ester (a in Fig. 1) exhibits distinct regions that correspond to liquid condensed (LC) and solid condensed (SC) phases, in contrast to oleate ester, which forms a liquid expanded (LE) phase up to the maximum surface pressure of 26.2 mN m^{-1} (a in Fig. 2). The larger areas [stearate ester, 22.41; stearic acid, 20 (19); oleate ester, 57.20 (17); oleic acid, 41 Å^2/molecule (7)] exhibited by the esters in comparison to the respective acids suggest more expanded conformation of the esters at the air/water interface. This probably arises from the flat conformation provided by the extended polar methoxy ethyl group in the head group region. Presence of the ester group also brings about changes in collapse pressure (π_c) and maximum surface pressure of the parent acids, the effect being more pronounced for oleic acid (π_c oleic acid = 30 mN/m; oleate ester = 25.0 mN/m; stearic acid = 40.8 mN/m; stearate ester = 40.5 mN/m).

π-A isotherms of mixed systems of esters and RBr. Pure RBr does not form a monolayer on the aqueous subphase at 25°C. The surface pressure does not rise significantly on compression, and in fact, the formation of drops or lens-like structures

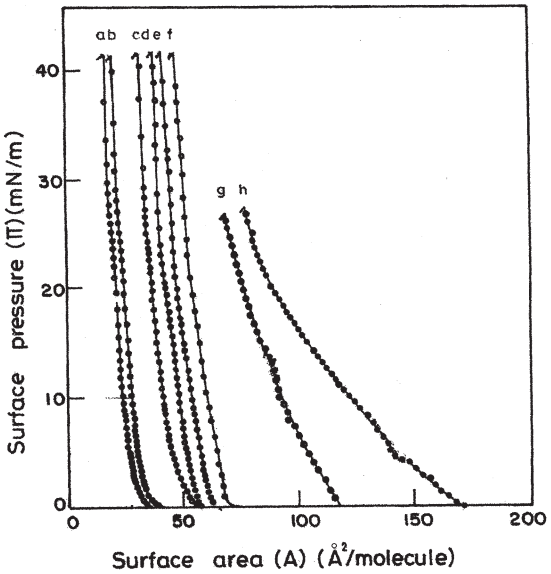


FIG. 1. Surface pressure-area (π-A) isotherms at the air/water interface of stearate ester in presence of various mole fractions of bromo-octadecane (RBr), a–h: 0.0, 0.1, 0.2, 0.3, 0.4 , 0.5, 0.6, and 0.8, at 25°C.

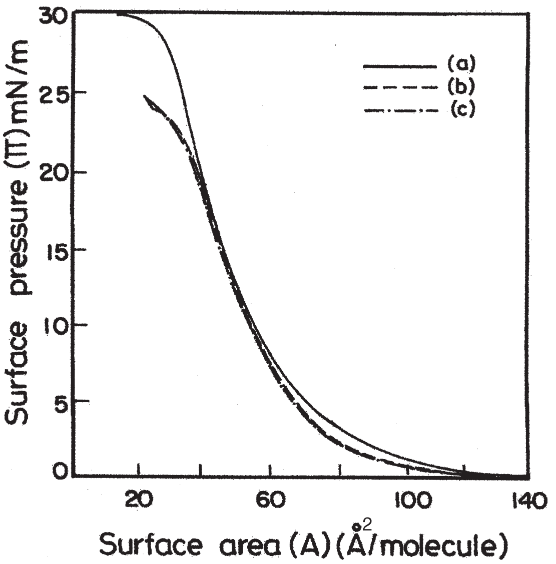


FIG. 2. Surface pressure-area (π-A) isotherms at the air/water interface of oleate ester in presence of various mole fractions of RBr (a–c): 0.0, 0.1, and 0.2, 25°C. For abbreviation see Figure 1.

could be observed visually. π-A Isotherms of binary systems composed of different mole fractions of RBr (x_2) with stearate and oleate esters are shown in Figures 1 (curves b–h) and 2 (curves b,c), respectively. For mixed films of stearate ester with RBr, ($x_2 \leq 0.5$), π-A isotherms consist of distinct regions of LC and SC phases, similar to those of simple ester (Fig. 1, curves a–f). The retention of LC and SC phases in stearate ester film in the presence of RBr ($x_2 \leq 0.5$), as well as the small expansion of isotherms to larger areas in this compositional range, suggests formation of homogeneous mixed film. However, when $x_2 > 0.5$, the final collapse pressure of the mixed film shows a sharp decrease from about 40.5 to 26 mN/m, and the more expanded isotherms mainly consist of LE and LC phase structures (Fig. 1, curves g,h). Such a trend is suggestive of formation of an unstable mixed film. For oleate ester, formation of such an unstable mixed film with RBr occurs even when x_2 is as low as 0.1. This is indicated by a negligible modification in oleate ester film in the presence of RBr ester except for a small decrease in surface area/molecule at lower surface pressures (Fig. 2, curves a–c). The important characteristics of the mixed film with respect of homogeneity and stability require comparative analysis of mean molecular areas and collapse pressure as a function of x_2. We will first analyze the π-A isotherms of the mixed system of stearate ester and RBr in terms of these significant parameters.

Mean molecular areas. The plot of mean molecular areas of the mixed monolayers of stearate ester and RBr vs. mole fraction of RBr (x_2) at different surface pressures (π = 0, 5, 10, 20 and 25 mN/m) is presented in Figure 3. The additive areas of the mixtures with x_2 = 0.0–1.0 has been calculated from Equation 1:

$$XA = x_1a_1 + x_2a_2 \qquad [1]$$

$$X = x_1 + x_2 = 1 \qquad [2]$$

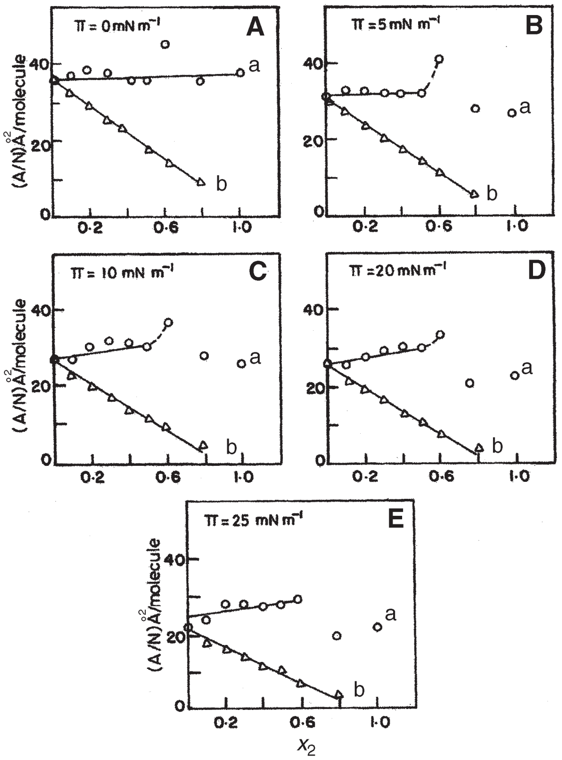


FIG. 3. Plot of mean molecular area of 2-methoxy ethyl stearate ester-RBr mixtures vs. mole fraction of RBr on the aqueous subphase at selected pressures, A–E, π = 0, 5, 10, 20, and 25 mN/m, at 25°C. Curves a represent experimental mean molecular areas, and curves b, calculated additive mean molecular areas. For abbreviation see Figure 1.

where x_1 = mole fraction of stearate ester, x_2 = mole fraction of RBr, a_1 = area of neat stearate ester for the respective mole fraction x_1, and a_2 = area of RBr = 0 (as RBr exhibits negligible area at all surface pressures).

Area a_1 has been estimated for various mole fractions at different surface pressures from simple stearate ester isotherms for the corresponding π, and a_2 is taken as zero because RBr does not form a monolayer on its own. The additive plots of calculated mean molecular areas are shown in Figure 3A–E (curve b). The actual experimental mean molecular areas (Fig. 3A–E, curve a) for the mixtures have been estimated from mixed isotherm curves of stearate ester in the presence of x_2 (Fig. 1). The positive deviation of experimental mean molecular area of the mixed film from the additive area suggests the incorporation of RBr into the ester host monolayer. The mean molecular areas of the mixtures show progressive and small changes in comparison to stearate ester at all π values. The retention of LC and SC phase structures of stearate ester in mixed films with $x_2 < 0.5$ and the positive deviation of the mean surface area in this compositional range further suggest the formation of homogeneous mixed film at all π. However, when x_2 = 0.6, an unforeseen increase in mean surface area occurs, especially at π = 5 and 10 mN/m. This probably suggests the onset of formation of heterogeneous mixed film and multilayers, leading to instability of the mixed film. The behavior of the stearate ester/RBr mixed film is in sharp contrast to fatty acids hitherto investigated. For example, heptadecanoic acid (HPA) is reported to exhibit almost negligible miscibility with either RBr or RCl at 25°C . The miscibility range of HPA has been improved considerably at 15°C in the absence and presence of $CdSO_4$ (16). In analyzing the compositional range of miscibility between HPA and RBr, in particular at 15°C, it has been inferred that HPA enables incorporation of RBr to an extent of 0.3–0.2 mole fraction in the presence of $CdSO_4$ and 0.6–0.3 mole fraction in the absence of $CdSO_4$ in the pressure range of 10–20 mN/m, whereas the synthesized stearate ester enables incorporation of about 0.5 parts of RBr at 25°C and forms homogeneous mixed monolayers in the pressure range 0–25 mN/m with retention of typical SC phase structures in the high-pressure regions. The greater surface area of stearate ester afforded from flat conformation of the methoxy ethyl ester group probably promotes incorporation of RBr to a greater extent.

Collapse pressure. Collapse pressure (π_c), identified by the change in the slope of the π-A isotherm, serves as definite proof for the miscibility of components at the air/water interface. The appearance of only one collapse pressure in the mixed system is a clear indication of formation of a homogeneous mixture at the interface. On the other hand, two distinct (initial and final) collapse pressures are observed for insoluble mixtures. The π-A isotherms of mixtures of stearate ester and RBr exhibit only one collapse pressure ($\pi_c > 40$ mN m^{-1}) when $x_2 < 0.5$. This indicates the formation of a homogeneous mixed film, in agreement with the conclusions drawn from mean molecular area estimations. But when $x_2 > 0.5$, two collapse pressures, corresponding to initial and final collapse pressures, π_{ic} and π_{fc}, appear. Thus, π_{ic} appears at 11 and 4.5 mN/m when $x_2 = 0.6$ and 0.8, respectively. However, π_{fc} remains constant at 27 mN/m in this compositional range. The decrease in π_{ic} with increase in x_2 further suggests that the initial collapse of the mixed monolayer film arises from squeezing of excess RBr from the interface. The final collapse pressure probably arises from the collapse of the mixed monolayer film. When $x_2 = 0.6$, at $\pi < \pi_{ic}$, i.e., at 5 and 10 mN/m, complete squeezing of RBr from the mixed monolayer at the interface does not occur, and this results in formation of an unstable and heterogeneous mixed film and a large increase in molecular area (Fig. 3, curves A–C). When $\pi = 20$ and 25 mN/m ($\pi > \pi_{ic}$), formation of a mixed film with maximum possible incorporation of RBr (after initial complete squeezing of RBr) occurs, and the resulting mixed isotherm mainly exhibits LC phase structures with the mean molecular area falling on the linear curve. When x_2 is increased to 0.8, π_{ic} occurs at a low π of 4.5 mN/m, and therefore, at $\pi > 4.5$ mN/m (5, 10, 20 and 25 mN/m), the formation of mixed film consisting of stearate ester saturated with RBr molecules after the complete squeezing of excess RBr occurs. Hence, the mean molecular areas of the mixed film do not deviate considerably at these surface pressures. The collapse pressure measurements thus suggest formation of a homogeneous mixed film of stearate ester with 0.5 mole fraction RBr, in agreement with the mean molecular area estimations.

π-A Isotherms of mixed system of oleate ester and RBr. Owing to the presence of a *cis* double bond, oleate ester exhibits different monolayer characteristics at the air/water interface than its saturated counterpart. The presence of only LE phase in oleate ester affects formation of mixed film to a considerable extent. The mean molecular areas plotted as a function of x_2 at two different surface pressures of 7.5 and 10 mN/m are shown in Figure 4**,** curves 1A and 2A, in comparison with the additive mean areas estimated from simple oleate ester isotherms (Eq. 1). The experimental molecular areas of the mixtures fall on a linear curve and show a progressive decrease with x_2, suggesting absence of RBr molecules at the interface. A close examination of the plot suggests that the experimental mean surface area lies close to the calculated area (shown by dotted lines, Fig. 4, curves 1B and 2B), thus suggesting almost total immiscibility between oleate ester and RBr at the air/water interface in a wide concentration range and at all surface pressures. Extrapolation of the linear experimental plot to $x_2 = 1.0$ leads to almost zero intercept at all surface pressures, indicating absence of RBr at the air/water interface in combination with the ester component. Alkyl bromide retains its typical behavior of forming lens-like structures at the air/water interface and provides no scope for compatibility with oleate ester.

The chemical modification of octadecanoic and octadecenoic acids into methoxy ethyl esters contributes to considerable alterations in the surface characteristics at the air/water interface. The stearate and oleate esters exhibit greater surface areas of 22.0 and 57.20 Å^2/molecule in comparison to parent acids. However, the various phase structures of acids are retained, even after esterification, suggesting similarity in packing behavior between acids and respective esters at the air/water interface. The stearate ester enables maximal incorporation of about 0.5 mole fraction of RBr at 25°C, and it forms a homogeneous mixed film at the air/water interface. Such a high surface compatibility has not been achieved with any similar fatty acid system under similar conditions. The expanded surface area provided by the methoxy ethyl functional site of the head group in the ester probably promotes

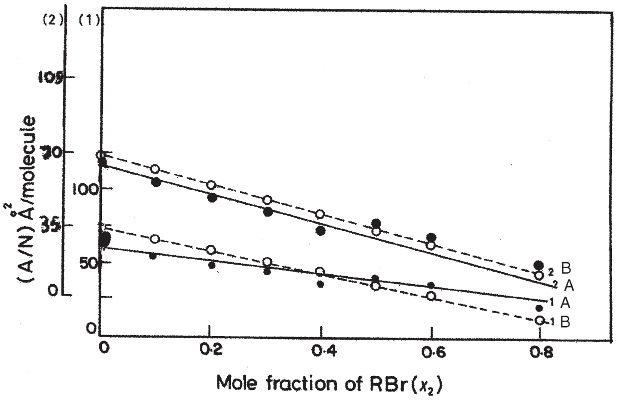


FIG. 4. Plot of mean molecular area of 2-methoxy ethyl stearate ester-RBr mixtures vs. mole fraction of RBr on the aqueous subphase at selected pressures 1, π = 7.5 and 2, π = 10 mN/m at 25°C. Curves A represent experimental mean molecular areas, and curves B, calculated additive mean molecular areas. For abbreviation see Figure 1.

incorporation of RBr in the stearate ester monolayer at the air/water interface. This property is significant, especially in technological systems that demand the benefits of RBr. The oleate ester monolayer, however, does not provide for incorporation of RBr, probably because of the availability of only LE phase structures in the ester film, which promote squeezing of RBr from the interface.

ACKNOWLEDGMENTS

The authors are thankful to Dr. Tirumalachari Ramasami, Director, Central Leather Research Institute, Chennai, for his constant encouragement and permission to submit this paper. The authors thank Dr. Aruna Dhathathreyan for her support in carrying out the LFB experiments. The constant support of Dr. Vajhala Syama Sundara Rao, is also acknowledged.

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[Received August 15, 2000; accepted February 9, 2001]