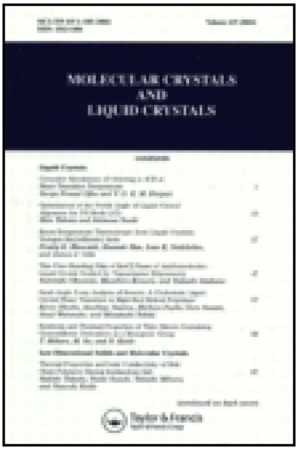

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Interaction Between Carboxylic Salt and Alcohol from Long Chained Molecules in Mixed Langmuir Monolayers. Relations with Nematic Aggregate Formation in Lyotropic Solutions

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The effect of octadecanol on Langmuir films of potassium docosanoate has been studied. The mixture was chosen in order to modelize the amphiphile interaction in the well known nematic potassium dodecanoate-decanol-water solution. The film study discloses an association between one molecule of the alcohol and one molecule of the soap. The results have been compared with results from the literature. The consequences on the amphiphile packing at the micellar interface are discussed.

INTRODUCTION

The nature of micellar aggregates in soap-water solutions is often considerably changed when aliphatic alcohol is added: New mesomorphic phases appear when aliphatic alcohol is introduced into lyotropic soap-water systems.[1,2] Fatty alcohol is a necessary co-surfactant in microemulsions.[3] The presence of alcohols leads to a decrease of the c.m.c. in soap solutions.[4]

Our study covers the effect of long chained alcohol on a monomolecular film of fatty acid alcali salt on a water surface. The situation of the amphiphilic molecules in such a compressed film is conceivably similar to their situation in micellar aggregates where the average position of the aliphatic tails is perpendicular to the interface and the polar heads are located in the interfacial aqueous region.

Our purpose has been to establish a monolayer system as close as possible to the ternary nematic lyophase composed of potassium dodecanoate-water-decanol.[1]

Two lyotropic phases exist in the binary soap-water system: one lamellar phase and one hexagonal phase as seen in the phase diagram.[5] A nematic domain appears when the aliphatic alcohol is added to the system. The nematic phase domain likely exists over a small concentration range, but the ternary phase diagram at constant or room temperature has not been established. The studies and applications of this nematic phase deal with compositions varying only slightly from that of the most frequently encountered mixture[6]: 26% potassium dodecanoate, 67.8% water, 6.2% decanol (percentages by weight) which represents a molar ratio alcohol/total amphiphile of 0.26.

EXPERIMENTAL PART

The amphiphilic compounds used for the film preparation were the following: docosanoic acid C22AC (Aldrich) recrystallized from acetone (mp. 80–82°C), octadecanol C18OH (Merck) recrystallized twice from acetone (mp. 59°).

The following stock solutions were prepared for the film spreading: C22AC 848.8 $g \cdot l^{-1}$, C18OH 674.0 $g \cdot l^{-1}$, both compounds in the solvent mixture hexane 90%—ethanol 10% (by volume). The stock solutions were spread on an aqueous subphase containing hydrochloric acid at pH 2, pure water at pH 5.7 and potassium hydroxyde at pH 10,11 and 12.

The water was purified in a four cartridge system ORC-U3-R3-M3 from Bioblock.

The solvents, potassium hydroxyde and hydrochloric acid were Prolabo analytical grade products.

The isotherms were measured on a Krüss film balance. 50 μl of stock solution were spread on the subphase with a Hamilton CR-200 syringe. The spread quantities were in agreement with an area of $20 Å^2$ $molecule^{-1}$ at a surface of 150 cm^2 within the balance frame. The 15 cm width piston advanced at a speed of 1.5 $cm \cdot min^{-1}$ during all the runs. The working temperature was 22°C.

EXPERIMENTAL RESULTS

Potassium docosanoate C22K has been chosen as representative of the soap amphiphile in our study of mixed Langmuir films because of its good film stability. Films from shorter chained soaps up to carbon chains of 18 atoms were more or less soluble in the subphase at high pH values.

The C22K monolayer was prepared through spreading of C22AC stock solution on an aqueous subphase buffered with potassium hydroxyde. It is well known that the Π-A isotherms of the acid depend strongly on the pH.[7,8] The curves we have obtained for C22AC at pH 2, 5.7, 10, 11 and 12 are shown in Figure 1. The "smooth" curve, characteristic for the completely dissociated acid[7] as (C22K), was obtained only at pH 12.

We have chosen C18OH as alcohol amphiphile in our mixed films, we could thus compare our study with results in the literature on mixed films from another soap amphiphile with the same chain as ours but with a different head group: sodium docosylsulfate and alcohols with 16 and 18 carbon atoms.[9,10]

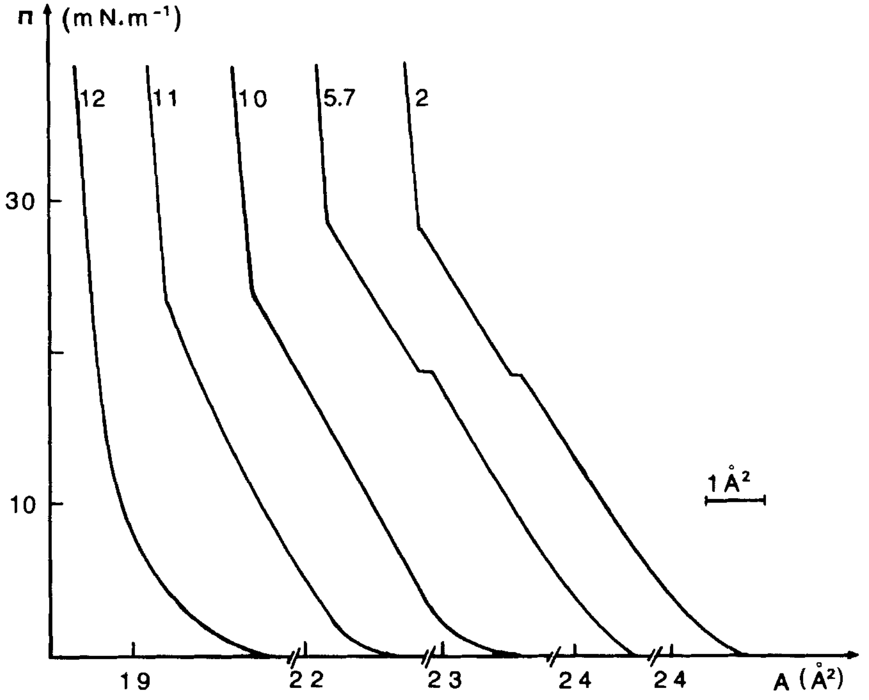

FIGURE 1 Π-A isotherms of docosanoic acid at the different pH-values indicated on the curves. Subphases: HCl 10^{-2} M, pure water, KOH 10^{-4} M, KOH 10^{-3} M, KOH 10^{-2} M. Temperature 22°C.

The Π-A isotherms at pH 12 for C22K and C18OH at the following molar ratios alcohol/total amphiphile: 0.02, 0.1, 0.2, 0.3, 0.5, 0.7 and 0.9 together with the curves for the pure compounds are shown in Figure 2.

Several series of curves have been plotted in order to suppress experimental uncertainty. As the maximum difference between the compared molecular areas is small (about 1, 5 Å^2), it is necessary that the curves have a good reproducibility and it is important to always operate with equally treated stock solutions, to prepare the amphiphile mixture just prior to use and to operate with a microsyringe allowing constant volume setting and elimination of any air bubbles.

The results indicate that the mixture is not ideal.[9] An abnormal increase in molecular area is produced through alcohol addition to the film mixture.

THEORETICAL RESULTS

We have plotted the curve representing the mean molecular area A as a function of the alcohol molfraction x (Figure 3 curve a) and we have compared this curve with the theoretical straight line for the molecular area A_I as a function of x for an ideal soap-alcohol mixture (Figure 3 curve b). The molecular areas are those

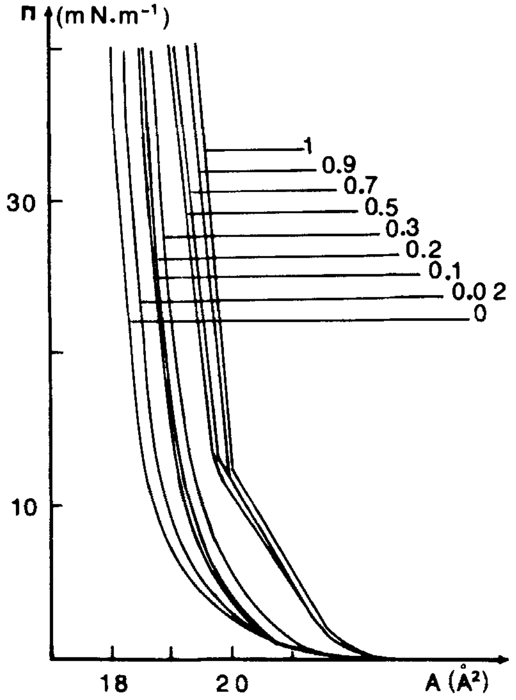

FIGURE 2 Π-A isotherms at pH 12 (subphase KOH 10^{-2} M) of docosanoic acid converted into potassium docosanoate, octadecanol and their mixtures. The different values of the alcohol molfraction x are indicated on the curves. Temperature 22°C.

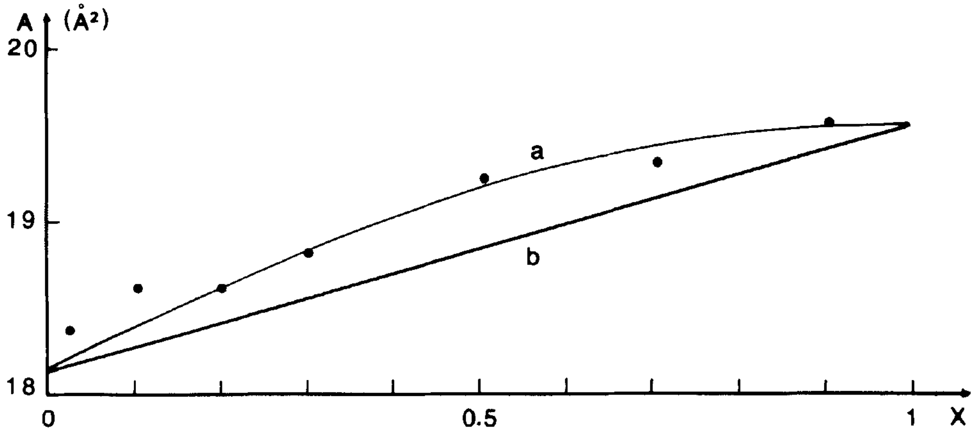

FIGURE 3 Mean molecular areas A as a function of octadecanol molfraction x for the mixed films of potassium docosanoate and octadecanol. Curve a: the experimental points. Curve b: ideal mixture. $\Pi = 30 \text{ mN} \cdot \text{m}^{-1}$.

measured at 30 $mN \cdot m^{-1}$, but the results are almost identical at all pressures in the interval between 10 and 40 $mN \cdot m^{-1}$.

The curve $A = f(x)$ contains the points from $x = 0.2$ to $x = 1$. The experimental points for smaller values of x are situated above this curve. The mixed films thus seem to behave differently depending on the alcohol content.

A maximum deviation of the experimental curve $A = f(x)$ from the theoretical curve for an ideal mixture is observed at $x = 0.5$. On the other hand, the isotherms for $0.2 < x < 0.5$ (Figure 2) have a "smooth" appearance similar to that of the pure soap. At $x > 0.5$ the isotherms show a "break" which is characteristic of the pure alcohol isotherm.

We have made the following assumptions from these observations: There are associations between one molecule of soap and one molecule of alcohol at $x > 0.2$ (1-1 associations).

—At $x = 0.5$ the entire film consists of 1-1 associations.

—At $0.2 < x < 0.5$ there are free soap molecules together with 1-1 associations on the water surface which explains the "smooth" aspect of the isotherms.

—At $x > 0.5$ there is coexistence between free alcohol molecules responsible for the "break" in the isotherm and 1-1 associations.

We have plotted the theoretical curve for the mean molecular area as a function of x (Figure 4 curve c) in order to check our hypothesis. This curve is composed of two straight lines having the equations:

$$A_C = (A_A - 2A_1)x + A_1 \qquad \text{for } 0.2 < x < 0.5 \text{ and} \tag{1}$$

$$A_C = (2A_2 - A_A)x + A_A - A_2 \qquad \text{for } x > 0.5 \tag{2}$$

where the molecular areas are the following: $A_1 = 18.15$ Å^2 for the pure soap,

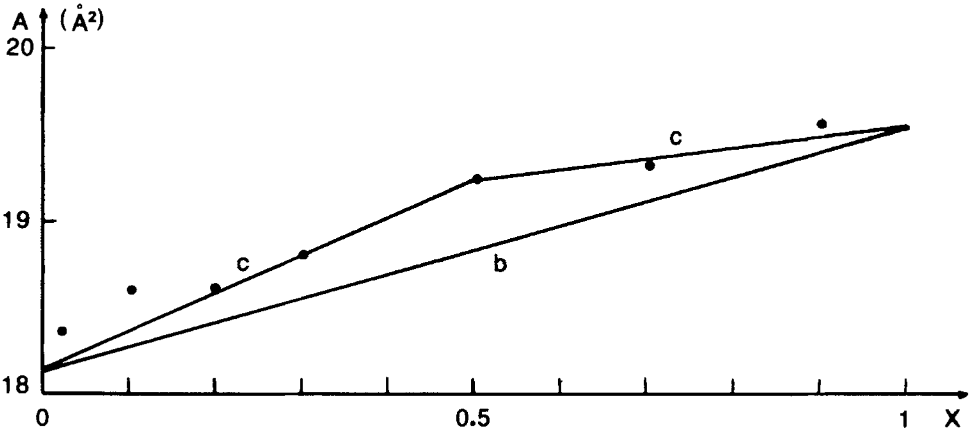

FIGURE 4 Mean molecular area A as a function of octadecanol molfraction x for the mixed films of potassium docosanoate and octadecanol. Curve b: ideal mixture. Curve c: calculated from (1) and (2). Inserted: the experimental points. $\Pi = 30$ $mN \cdot m^{-1}$.

A_2 = 19.55 Å^2 for the pure alcohol and A_A = 38.50 Å^2 for the 1-1 association. S_A is twice the molecular area measured at $x = 0.5$.

The experimental points are correctly situated on the theoretical curve with the exception of those for low x-values ($x < 0.2$). This is consistent with our hypothesis as shown in Figure 4. The curve for an ideal mixture is given for comparison purposes (Figure 4 curve b).

The measured molecular areas are considerably above the calculated curve for low x-values. The interactions in this region must thus be of a different kind, but we have not investigated this point further.

DISCUSSION

The present study has indicated that the mixed film of potassium docosanoate-octadecanol consists partly of 1-1 associations between the two amphiphile molecules and partly of pure soap molecules at alcohol molfractions $0.2 < x < 0.5$. The observed area increase indicates repulsive associations. If the effect of decanol on potassium dodecanoate in the nematic aggregates is similar to the alcohol effect in the mixed film, one can assume that the micellar aggregates also contain 1-1 associations together with pure soap at the alcohol ratio $x = 0.26$.

The distribution of 1-1 associations within the amphiphile layer is unlikely to be uniform. Hendrikx[11] has shown that the alcohol is concentrated in certain areas of the anisotropic nematic aggregates obtained from soap and decanol. A non uniform distribution of two different amphiphiles was also reported by Doane[12] in other anisotropic micellar aggregates.

Our results show that the alcohol character of the isotherm appears at $x > 0.5$. This indicates areas of pure alcohol in the film.

Hendrikx also reported that the alcohol was located in the less curved parts of the nematic micelles both in the potassium dodecanoate-decanol-water system and in the sodium decylsulfate-decanol-water system.

The mixed film studies of amphiphile molecules similar to those in the nematic systems mentioned above have led to opposite results: in our study, the addition of octadecanol to the potassium docosanoate film has resulted in film expansion; mixing hexadecanol or octadecanol into sodium docosylsulfate film led to film contraction[9,10]. Charvolin[13] has related this last result to a decrease of the interface curvature in micellar lyophases.

The fact that we have carried out our experiments at pH 12 and that different counterions were present in our film study and in the studies from the literature might explain the different behavior of the two kinds of mixed films, but requires further investigation.

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