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## Comparative Study of Mixed Monolayers of a Calixarene with a Fatty Acid and a Non-Amphiphilic Nematic Liquid Crystal

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Many nematic liquid crystals (NLCs) lack a polar headgroup and thus are not able to form stable monolayers at the air/water (a/w) interface. A way to obtain monomolecular films of these compounds is to incorporate them into host monolayers of amphiphilic molecules. We report a comparative investigation of mixed films of Calix[4]resorcinarene O-octacarboxymethylated (CRO) with the non-amphiphilic NLC MBBA and with the amphiphilic stearic acid (SA). The comparative study is useful for a better understanding of the characteristics of the CRO-MBBA mixed films. Surface-pressure and surface-potential measurements on the monolayers at a/w interface, as well as ellipsometric and spectroscopic measurements on transferred Langmuir-Blodgett (LB) films, confirm that MBBA is additively incorporated into CRO films.

**Keywords:** Langmuir-Blodgett monolayers; amphiphilic compounds; mixed monolayers; incorporation

### INTRODUCTION

Monolayers at the air/water (a/w) interface are well-defined systems that are used to study the surface properties of amphiphilic compounds [1]. Such monolayers can be transferred onto solid substrates by the Langmuir-Blodgett (LB) technique, which ensures the deposition of mono- or multi-layered films with controlled molecular order and thickness in addition to a very high reproducibility [2]. The lack

of a hydrophilic headgroup usually disallows a molecule in forming organized monolayers at the a/w interface. However, in some cases such molecules have been incorporated into monolayers of amphiphilic compounds [3,4].

MBBA is a hydrophobic non-amphiphilic molecule and does not form ordered monolayers at the a/w interface [5]. Therefore, no LB layers of this compound can be deposited. Calix[4]resorcinarenes are cyclic oligomers made of benzene rings which form polar cavities where guest molecules can be trapped. They have been extensively studied and a number of significant industrial applications have been reported [6]. Current interest in possible applications of calixresorcinarenes includes phenomena such as binding [7] and incorporation [8] of guest compounds.

The aim of this work is to understand the interactions between CRO (host molecule) and MBBA (non-amphiphilic guest compound) in films at the a/w interface and in LB films making a comparative study of CRO-MBBA mixed monolayers with mixed monolayers of CRO and an amphiphilic compound. As amphiphile, stearic acid (SA) was chosen because of the simple structure, with a carboxylic hydrophilic head and one aliphatic chain. Monolayers at the a/w interface and LB films of this compound have been widely studied (see for instance [9]). It was necessary first to establish the conditions of formation of monolayers and LB films of CRO, and then to compare these results with those from the guest-host systems in which new interactions may occur.

## EXPERIMENT

In Figure 1 the structures of MBBA, CRO, and SA are shown.

The properties of the single and mixed monolayers at the a/w interface have been studied by recording the surface-pressure/area ( $\pi/A$ , KSV5000 trough) and the surface-potential/area ( $\Delta V/A$ , ionizing electrode method [2] using an  $^{241}\text{Am}$  electrode [10]) isotherms. The substances were spread from their chloroform solutions (0.05 mM) and the solvent was allowed to evaporate during 10 min before compression. Ultrapure Milli-Q water (resistivity  $> 18\text{ M}\Omega$ , pH = 5.5) was used as subphase solution.

LB films were prepared transferring layers onto sputtered chromium and quartz substrates (deposition pressure  $25\text{ mN m}^{-1}$ , extraction speed  $3\text{ mm min}^{-1}$ , immersion speed  $5\text{ mm min}^{-1}$ ) for ellipsometric (Rudolph Research Ellipsometer) and spectroscopic (Bio-Rad spectrophotometer) measurements, respectively. Transfer quality was followed by inspection of the transfer ratio.

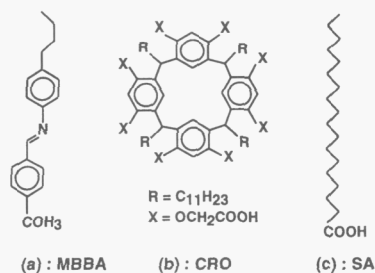


Figure 1: Compounds used in this work. (a) Nematic liquid crystal *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA). (b) Calix[4]resorcinarene *O*-octacarboxymethylated (CRO). (c) Stearic acid (SA).

## RESULTS AND DISCUSSION

### Monolayers at the air/water interface

In general, the incorporation or the binding of guest-molecules into the monolayer of a host molecule is ruled by the physico-chemical properties of the host monolayer. Parameters such as surface-concentration, surface-potential, and orientation of the CRO molecules at the a/w interface are expected to play an important role in the host-guest interaction. In Figure 2 the  $\pi/A$  and  $\Delta V/A$  isotherms of pure CRO from chloroform solution are shown together with some monolayer parameters extracted from the isotherms. In general  $\pi/A$  isotherms of calixresorcinarenes are influenced by the nature of the spreading solvent [11] because of the inclusion of solvent molecules into the CRO cavity. In other words, the solvent has an effect on the molecular packing of CRO at the a/w interface. In this context it was important to ensure the reproducibility of the isotherms. CRO monolayers, with chloroform as spreading solvent, were found to be reproducible and stable, since no surface aggregation at the interface and no solubilization in the water subphase occurred during compression: isotherms made from spreading solutions of different molarities were identical.

The rising area-per-molecule,  $A_0$ , is consistent with the presence of eight COOH groups, each of which occupies approximately  $0.18 \text{ nm}^2$ . No change in the limiting area with temperature was observed. The

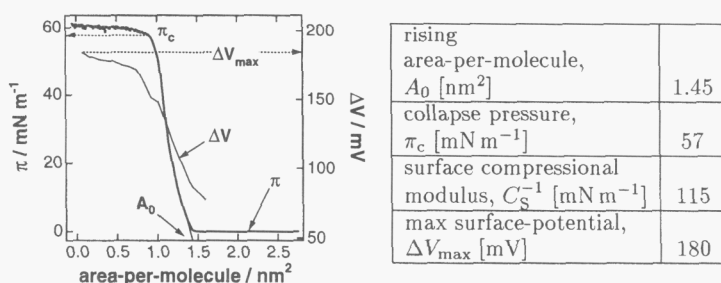


Figure 2:  $\pi/A$  and  $\Delta V/A$  isotherms of pure CRO from chloroform solution at  $T=20^\circ$ . Some important monolayer parameters are listed in the table.

compressional modulus  $C_S^{-1}$  is defined as (see for instance [1, 2]):

$$C_S^{-1} = A \left( \frac{\partial \pi}{\partial A} \right)_T, \quad (1)$$

where  $A$  is the area-per-molecule. The value of  $115 \text{ mN m}^{-1}$  indicates that the film is in a liquid-no-strictly-condensed phase in the entire field of existence of the monolayer.

From the surface-potential measurements it was possible to estimate the tilt angle of the CRO chains.  $\Delta V_{\max}$  is proportional to the vertical component of the molecular dipole moment  $\mu$ :

$$\Delta V_{\max} = \frac{\mu \cos \theta}{A \epsilon_0}. \quad (2)$$

We obtained  $\mu_{\text{exp}} = 0.4 \text{ D}$  from the CRO  $\Delta V/A$  isotherm at  $25 \text{ mN m}^{-1}$  (LB deposition pressure) which, compared to the estimated value of  $0.6 \text{ D}$  obtained from semi-empirical calculations using the PM3 method [12], gave a tilt angle of 48 degrees.

We prepared mixed solutions of CRO-MBBA and CRO-SA with different molar ratios and studied the behavior of the mixed monolayers at the a/w interface. Since MBBA does not form monolayers [5], in the study of the CRO-MBBA isotherms it is more useful to consider the *area-per-host-molecule*,  $A_h$ , defined as:

$$A_h = \frac{\text{area of the trough}}{\text{number of host molecules}} = A \frac{\text{total number of molecules}}{\text{number of host molecules}}. \quad (3)$$

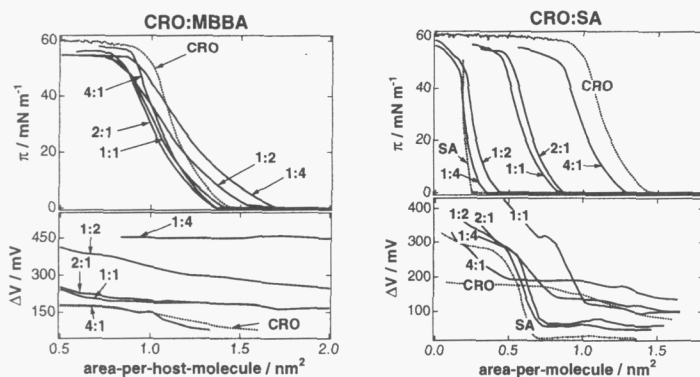


Figure 3:  $\pi/A_h$  (cfr. Equation 3) and  $\Delta V/A_h$  isotherms of CRO-MBBA mixed monolayers and  $\pi/A$  and  $\Delta V/A$  isotherms of CRO-SA mixed monolayers. The proportions of CRO to the guest compounds are indicated.

Instead, for the mixtures CRO-SA we will consider the area-per-molecule because both compounds are amphiphilic. In Figure 3 the  $\pi/A$  and  $\Delta V/A$  isotherms of CRO-MBBA and CRO-SA are shown respectively. In Figure 4 the extrapolated  $A_h$  (CRO-MBBA) and  $A$  (CRO-SA) at different surface pressures, as well as the collapse pressures, of the mixed monolayers are shown as a function of the molar ratio of CRO in the mixtures.

Let us examine the CRO-SA mixed monolayers first, which are both amphiphilic monolayer-forming compounds. The properties of a monolayer in which the two components are immiscible will reflect those of the two separate single component films [1]: the area occupied by the mixed film,  $A_{\text{mix}}$ , will be the sum of the areas of the two separate films,  $A_{\text{CRO}}$  and  $A_{\text{SA}}$ , weighted with the molar fraction of the two components,  $N_{\text{CRO}}$  and  $N_{\text{SA}}$ :

$$A_{\text{mix}} = N_{\text{CRO}} A_{\text{CRO}} + N_{\text{SA}} A_{\text{SA}}. \quad (4)$$

Thus, in non interacting mixed monolayers  $A_{\text{mix}}$  should follow a linear relation with  $N_{\text{CRO}}$  or  $N_{\text{SA}}$ . Any deviation from this linear behavior (also called *line of no interaction*) is evidence of interactions in the mixed monolayer, that could be attractive or repulsive, and make the mixed films more or less stable than the single compounds ones.

The analogs of miscibility or immiscibility of mixed monolayers in which one of the two components is not amphiphilic, are *cooperative* or

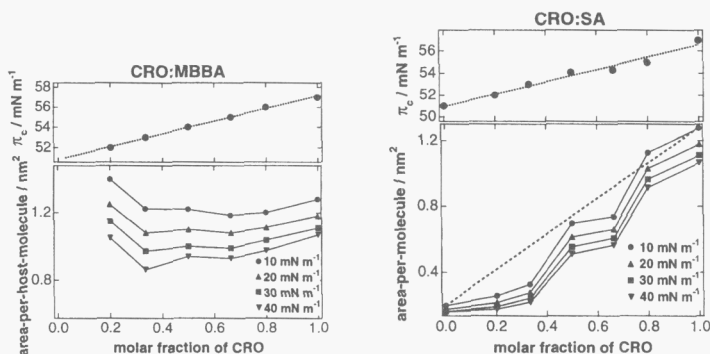


Figure 4: Extrapolated  $A_h$  (CRO-MBBA) and  $A$  (CRO-SA) at different surface pressures, and collapse pressures, as a function of the molar ratio of CRO for the different mixed monolayers.

*additive incorporation.* In the first case, the guest molecules interact with the host ones and there are deviations from the linear relation of Equation 4. Since the guest compound does not form monolayers, Equation 4 takes in this case the following form:

$$A_{\text{mix}} = N_h A_h, \quad (5)$$

where  $N_h$  is the molar fraction of the host compound and  $A_h$  is the area-per-host-molecule defined in Equation 3.

On increasing SA surface concentration CRO-SA isotherms (Figure 3) shift towards smaller area-per-molecule and their shape, as well as the behavior of the surface-potential, resemble more and more that of stearic acid. From Figure 4 is evident that mixed monolayers CRO-SA with a low molar fraction of SA are immiscible as  $A_{\text{mix}}$  lies on the line of no interaction or above it (repulsive interactions). Increasing the molar ratio of SA the interactions become attractive and the monolayers become more compressed and stable.

Instead, CRO-MBBA  $\pi/A_h$  isotherms are not very much influenced by the addition of MBBA (Figure 3). Only for high concentrations of MBBA (1:2 and 1:4) the films become more compressed. On the contrary, the surface-potential  $\Delta V$  is considerably influenced and increases as the molar fraction of MBBA increases, due to MBBA's  $\text{CH}_3$  groups that contribute positively to the surface potential ( $\mu_{\text{CH}_3} = 0.351 \text{ D}$ ). From Figure 4 is evident that MBBA is additively incorporated into CRO's monolayers:  $A_h$  shows almost no change on



Table 1: Monolayer thickness,  $t$ , as estimated from ellipsometric measurements.

CRO		CRO-MBBA		CRO-SA	
$t$ [nm]		$t$ [nm]		$t$ [nm]	
1.3		4:1	1.5	4:1	1.0
		2:1	1.7	2:1	0.8
		1:1	1.8	1:1	1.0
		1:2	2.0	1:2	0.7
		1:4	2.0	1:4	0.7

increasing the molar fraction of the liquid crystal: MBBA molecules penetrate into the CRO's cavity with their  $\text{OCH}_3$  groups oriented towards the polar headgroup ( $\text{COOH}$ ) of the host molecules [5]. Only for very high molar fractions of MBBA (1:4) the films seem to be unstable as  $A_h$  increases: MBBA molecules in excess are squeezed out the monolayer and the isotherm is destabilized.

#### LB monolayers: ellipsometric and spectroscopic characterization

LB films were prepared depositing 3 or 5 monolayers onto chromium-sputtered plates for ellipsometric measurements and 1 single monolayer onto quartz plates for spectroscopic measurements. The deposition surface-pressure was  $25 \text{ mN m}^{-1}$ . For the first monolayers on both substrates we always obtained a transfer ratio, TR, larger than unity:  $\text{TR} \approx 1.2$ , which seems to be typical of calixarenes (see for instance [11]). The other 2 or 4 monolayers were transferred with a TR very close to unity.

The results of the ellipsometric measurements are listed in in Table 1. In the case of pure CRO, from a comparison between the measured monolayer thickness and the length of the hydrocarbon chains (1.65 nm) it was possible to estimate that the chains were tilted of an angle  $\theta = 51(\pm 5)$  degrees, which is in agreement with the previous tilt angle estimation by surface-potential measurements. In the case of CRO-MBBA LB films, the monolayer thickness are larger than that of single CRO monolayers and increase with increasing MBBA concentration, which indicates that MBBA is present in the LB films and that deposition does not cause molecular rearrangement or collapse in the monolayers. On the contrary, the small thickness measured in the case of CRO-SA LB films, confirm the monolayer instability already observed at the a/w interface.

The results of the spectroscopic measurements are shown in Figure 5. Both CRO and MBBA absorb at 284 nm. The height of the peaks

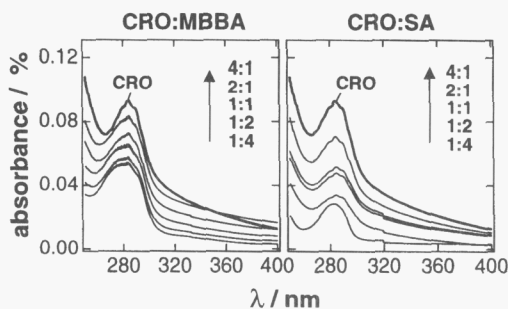


Figure 5: UV-spectra of the mixed monolayers deposited onto quartz plates.

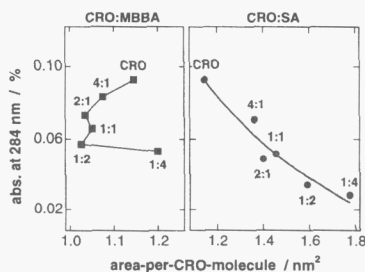


Figure 6: Intensity of the UV spectra at 284 nm as a function of the area per molecule. The markers are the experimental values. The dotted line in the CRO:SA graph is a fit of the experimental data to a function inversionally proportional to the area-per-CRO-molecule.

in the CRO-MBBA spectra is not only due to a change in surface density of the CRO molecules. If so, the intensity of the peak at 284 nm should be proportional to the surface density of CRO molecules, i.e. inversionally proportional to area-per-CRO-molecule. Figure 6 shows the absorption at 284 nm as a function of the area-per-CRO-molecule in the various CRO-MBBA and CRO-SA mixed LB films. The figure reveals that MBBA is present in the deposited monolayers and contributes to the UV-spectrum. On the other hands, since SA does not contribute to the spectrum at those wavelengths, we expected the intensity of the peak to depend only on the surface density of CRO molecules, i.e. to be inversionally proportional to the area occupied by the CRO molecules.

## CONCLUSIONS

A comparative study of mixed CRO-MBBA and CRO-SA films has been carried out in order to achieve a better understanding of the interactions in guest-host monolayers.

In CRO-SA mixed layers interactions occur that cause the films not to be always stable. Repulsive interactions occur for low molar fractions of SA that destabilize the monolayers at the a/w interface and cause collapse and/or molecular rearrangement during transfer of the films onto solid substrates. Attractive interactions occur for high molar fractions of SA and the monolayers at the a/w interface are stable. However, the transfer seems to cause destabilization of the films.

On the other hand, mixed CRO-MBBA films are stable and easily transferable as long as the molar fraction of MBBA is not too large (in which case the MBBA molecules in excess are squeezed out of the monolayer during compression). MBBA results to be additively incorporated into CRO monolayers.

The mechanism of additive incorporation of MBBA in CRO films resembles that of alignment of LCs on surfactants. As MBBA penetrates into the cavity of CRO apparently without any specific interaction, so LC molecules penetrate into the chain region of the surfactant and align the LC bulk: the alignment can be very stable even without strong interactions between the LC and the aligning layer.

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