Langmuir Films of Calix[8]arene/Fullerene Complexes

R. Castillo* and S. Ramos

Instituto de Fisica, UNAM. P.O. Box 20-364, D. F. 01000, Mexico

R. Cruz, M. Martinez, and F. Lara

Instituto de Quimica, UNAM. P.O. Box 70-213, D. F. 04510, Mexico

J. Ruiz-Garcia

Instituto de Fisica, UASLP, Alvaro Obregon 64, San Luis Potosi, S. L. P. 78000, Mexico

We present the pressure area isotherms for Langmuir films made of calix[8]arene, the calix[8]arene/C_{60} complex, and the calix[8]arene/C_{70} complex, all of them measured at 306.1 K. A Brewster angle microscope was used to observe the phases shown by the π−A isotherms. In these three cases, we found a solid phase and its solid−gas coexistence but no expanded liquid phases. The Langmuir films made of calix[8]arene and the calix[8]arene/C_{60} complex are very similar. The experimental information is consistent with the assumption that C_{60} is situated inside the cavity of calix[8]arene. The Langmuir films of calix[8]arene and the calix[8]-arene/C_{70} complex are not very similar; we present a discussion to explain the origin of this difference.

Introduction

The recent discovery of carbon fullerenes[1] has triggered a new and exciting field of research where a great variety of new carbon structures have been discovered. The development of a synthetic method to obtain macroscopic amounts of fullerenes[2] enhanced the interest about the fullerenes, giving rise to a great variety of studies. In particular, some works have been devoted to obtaining Langmuir films of fullerene derivatives. The purpose of this paper is to present our experimental results carried out in Langmuir films made of calix[8]arene (5,11,17, 23,29,35,31,47-octa-*tert*-butylcalix[8]aren-49,50,51,52,53,54, 55,56-octol) and of calix[8]arene/fullerene (C_{60} or C_{70}) complexes, see Figure 1. We present here the pressure area isotherms (π−A) for Langmuir films made of calix[8]arene, of the calix[8]arene/C_{60} complex, and of the calix[8]arene/C_{70} complex, all of them measured at 306.1 K. Also, observations using a Brewster angle microscope were made in those Langmuir films to characterize the phases appearing in the π−A isotherms.

The formation of highly incompressible and stable Langmuir films of C_{60} at the water−air interface was first reported by Obeng and Bard,[3] at temperatures in the range 278−308 K. They found that the limiting area per molecule calculated from π−A isotherms yielded a radius of 5.6 Å for the C_{60} in the film, in good agreement with the data obtained from other techniques, although these experiments are quite difficult to control and several authors have failed to obtain the same results. Additional information about C_{60} concentration, sample size, and trough conditions presented by Bulhoes, Obeng, and Bard[4] has given some light on the proper experimental conditions to obtain Langmuir monolayers at the water−air interface. C_{70} films at the water−air interface were first reported by Jehoulet et al.[5] at 298.1 K. They produced C_{70} films on a trough in the same manner as C_{60} films and reported two transitions in their π−A isotherms. The limiting areas yielded radii of 9.0 and 5.8 Å, respectively. They concluded that these values were in reasonable agreement with the theoretical values expected for the
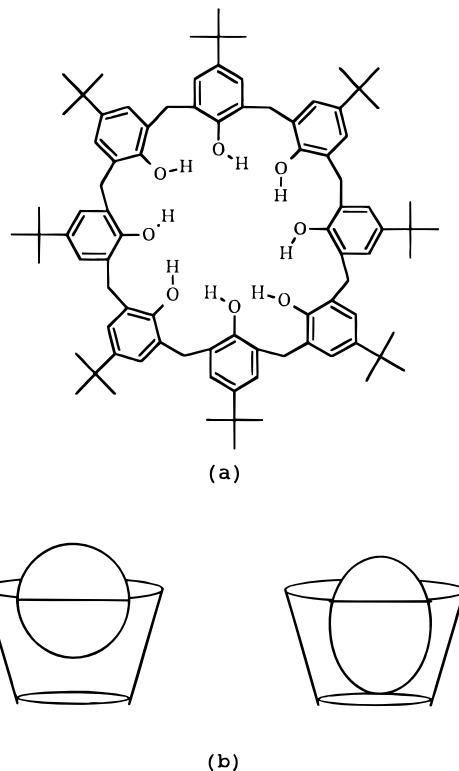

(a)

(b)

Figure 1. (a) Structural formula for calix[8]arene. (b) Diagrammatic representation as "ball and basket" nanostructure for the calix[8]arene/C_{60} complex and for the calix[8]arene/C_{70} complex.

prolate spheroidal C_{70} carbon cage in two configurations. Namely, the limiting areas correspond to a film made up predominantly of C_{70} molecules with their long axis parallel to the interface at low pressures and one in which the molecules predominantly stand vertically at high pressures.

Quite recently, several works have been devoted to obtaining thin films of fullerene derivatives. Some examples can be mentioned, namely, films of 1-*tert*-butyl-1,9-dihydrofullerene-60,[6] of $C_{60}O$,[7] and of $C_{61}H_2$.[7] The C_{60} molecules also formed

stable mixed films at the air−water interface with organic compounds with some amphiphilic character. Some examples can be found in the recent literature. Such is the case for the system arachidic acid/C_{60}[3,5,8] and that of the octadecanol/C_{60}.[9] C_{70} has also been used to produce mixed films with arachidic acid. In a report by Jehoulet et al.,[5] they found that a $\pi-A$ isotherm (298.1 K) for C_{70} showed two transitions. Surprisingly, given the resemblance between molecules of C_{70} and C_{60}, the isotherms for the mixed films presented by those authors are quite different. Recently, our group presented results for mixed Langmuir films made of C_{70} and arachidic acid at several temperatures and concentrations.[10] Those results are different from those presented by Jehoulet et al.[5] and, as expected, closer to those of the C_{60}/arachidic acid mixed films.

Langmuir films made of systems with strong host−guest interactions are very interesting if, in addition, the guest is a fullerene molecule. Several host−guest interactions with fullerenes have been reported, namely, complexes with 1,4-hydroxyquinone,[11,12] with azacrown compounds,[13] and with calix[8]arenes.[14] The study of the interactions between fullerenes and calix[8]arenes in those complexes had led not only to develop a new purification method[15] to obtain C_{60} and C_{70} but also to water soluble fullerenes complexes with a potential biomedical application,[16,17] solar energy conversion materials, and new electronic devices.[18] Mono- and multilayer studies of mixtures of fullerenes (C_{60} and C_{70}) and amphiphilic molecules containing a lipophilic cavity formed by azacrown compounds have been carried out by Diederich et al.[13] They proposed, on the basis of their experiments, that the C_{60} molecule was located inside the cavity of the azacrown molecule.

Experimental Section

Reagents. C_{60} (>99.99% purity) and C_{70} (>98% purity) were supplied by Mer Corporation (Tucson, AZ). Chloroform (HPLC grade, 99.9%) from Sigma-Aldrich (Sigma Chemical Co. and Aldrich Chemical Co., Inc.) was used as solvent for the preparation of the fullerene spreading solution and for cleaning the trough. As subphase for all the Langmuir films, we used Millipore water (18.2 M, Super Q system, Millipore Corporation) filtered through a 0.2 μm Barnsted final filter (model D3750, Barnsted/Thermolyne, IA).

Chemistry. Calix[8]arene and C_{60} or C_{70} were dissolved in dry benzene in a 1:1 stoichiometry and heated under reflux for 4 h.[19] After this time, a green-yellow solid was formed for the case of the calix[8]arene/C_{60} complex. For the case of the calix-[8]arene/C_{70} complex a brown solid was obtained. In both cases, the mother solution became colorless, which leads us to conclude the absence of the fullerene in solution. After filtration, the calix[8]arene/C_{60} complex was identified by spectroscopic methods.[20] Elemental analysis. Found: C, 87.70; H, 5.78. Calcd. for $C_{148}H_{112}O_8$: C, 88.07; H, 5.59.

In contrast with the results of Atwood[15] but in agreement with those of Suzuki et al.,[21] we found that, under the conditions described above, calix[8]arene has the same affinity for C_{60} as for C_{70}, and forms a complex easily with it. Under the conditions described above, we found from elemental analysis that the stoichiometry for the calix[8]arene/C_{70} complex was 1:1. Elemental analysis. Found: C, 88.43; H, 4.95. Calcd. for $C_{158}H_{112}O_8$: C, 88.73; H, 5.28. However, a comment must be made here. Under prolonged reaction time, 12 h, a 1:2 calix-[8]arene/C_{70} complex was obtained, as previously described by Suzuki et al.[21] The stoichiometry was also determined from elemental analysis. Found: C, 91.52; H, 3.83. Calcd. for $C_{228}H_{112}O_8$: C, 91.91; H, 3.79. In our experiments, we used only the complex with a 1:1 stoichiometry.
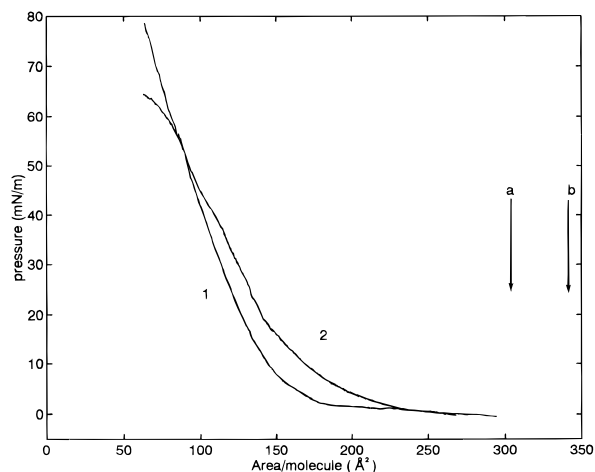

Figure 2. $\pi-A$ isotherm (306.1 K) for calix[8]arene (1) and for the calix[8]arene/C_{60} complex (2). Letters correspond to the BAM images of Figure 4.
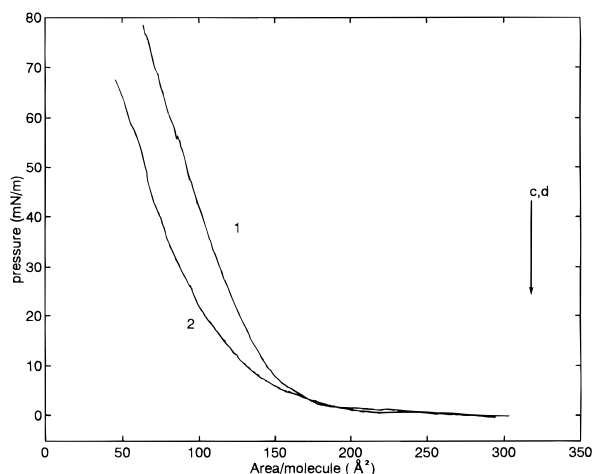

Figure 3. $\pi-A$ isotherm (306.1 K) for calix[8]arene (1) and for the calix[8]arene/C_{70} complex (2). Letters correspond to the BAM images of Figure 4.

Apparatus. All films were prepared on a computerized Nima LB trough (model TKB 2410A, Nima Technology LTD, England) using a Wilhelmy plate to measure the surface pressure. The trough was isolated from vibrations using a pneumatic tube incorporated into a steel base. The barriers are made of PTFE fitted with stiffening bars defining a working circular area, starting at 1000 cm^2. All experiments were carried out in a dust-free environment.

The Brewster angle microscope (BAM) observations were performed in a BAM1 plus (Nanofilm Technologie GmbH, Germany) using a 222 cm^2 Teflon rectangular Langmuir trough (R & K Ultrathin Organic Film Technology, Germany). The BAM analyzer gave the best contrast while kept at 0° or 180°.

The Nima LB trough and the BAM with its associated trough were placed on concrete tables cemented to a concrete floor on the ground floor of our building. The temperature in both troughs was kept constant with the aid of two water circulator baths (Cole-Parmer 1268-24 and Haake F3-K). The subphase was at constant temperature within a precision of 0.1 K.

Procedure. Fresh solutions of calix[8]arene, calix[8]arene/C_{60}, and calix[8]arene/C_{70} in chloroform (3.67 × 10^{-4}, 4.31 × 10^{-5}, 3.87 × 10^{-5} M, respectively) were deposited onto the unbuffered water subphase at the working temperature. Small amounts (5 μL) of these solutions were applied to at least 15 sites on the water surface with a 100 μL Hamilton syringe. After 5 min, this procedure was repeated until we had the desired
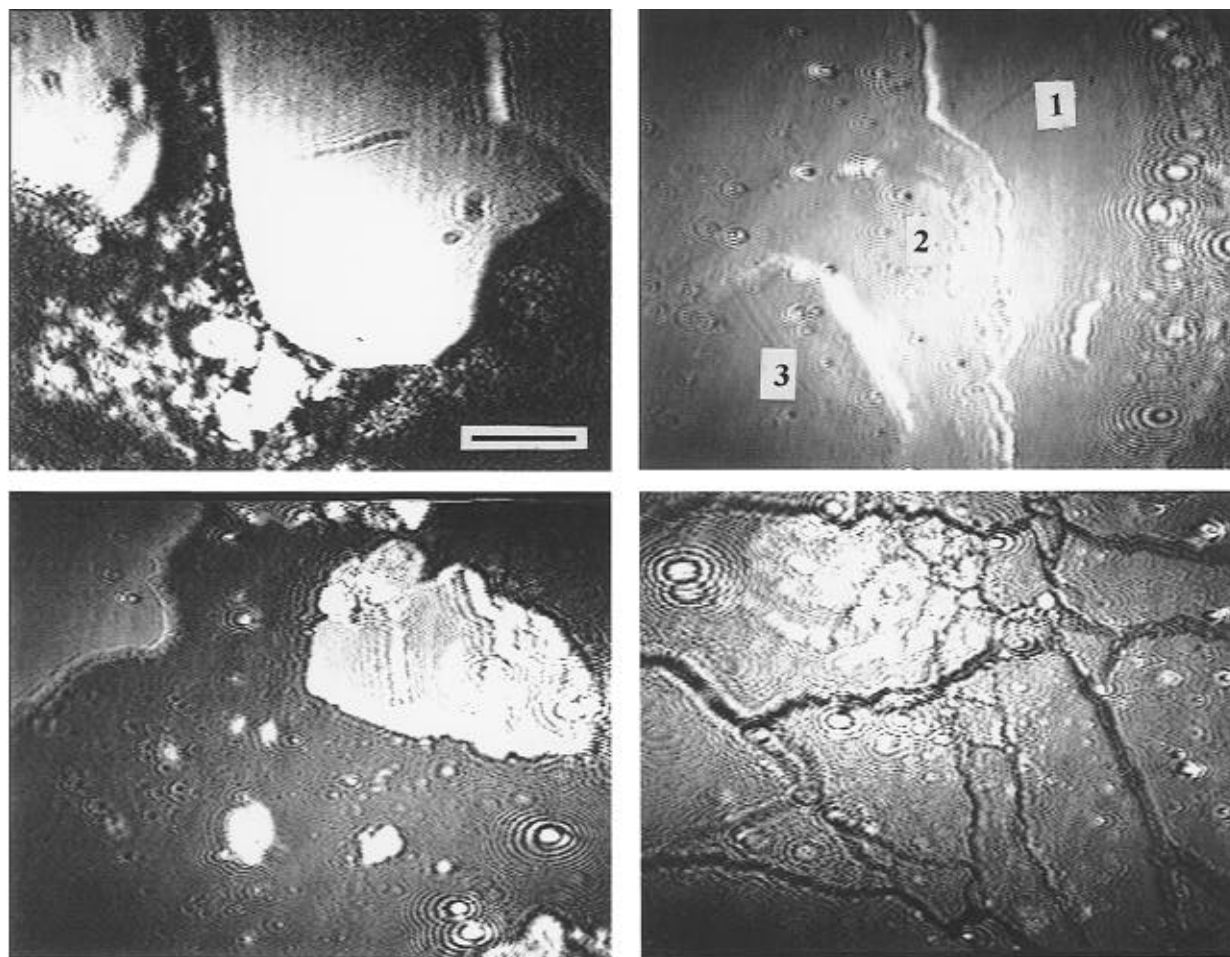
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Figure 4. Brewster angle microscope images: (a, top left) calix[8]arene ($A = 301.6$ Å^2/molecule, $\pi = 0.1$ dyn/cm). Black line represents 100 μm. (b, bottom left) calix[8]arene/C$_{60}$ complex ($A = 341.9$ Å^2/molecule, $\pi = 0.0$ dyn/cm). (c, top right) calix[8]arene/C$_{70}$ complex ($A = 317.5$ Å^2/molecule, $\pi = 0.0$ dyn/cm). (d, bottom right) calix[8]arene/C$_{70}$ complex ($A = 317.5$ Å^2/molecule, $\pi = 0.0$ dyn/cm). See the text.

quantity of the compound in the film. Then, after 20−30 min, the time allowed for chloroform evaporation, the isotherms were obtained by compressing the film in the Nima LB trough continuously at a rate of 20 cm^2/min ($\sim$9 Å^2/(molecule min)). Using the same technique, we prepared the Langmuir films to be observed with the BAM.

It is important at this point to make a comment. Calix[8]-arene/fullerene complexes at high concentrations are unstable in most solvents. This is probably due to the calix[8]arene/fullerene complex equilibrium constant and the slight solubility of the fullerene molecules. On the other hand, preparation of Langmuir films needs a solvent with good spreading properties over the water surface, not forming clusters of the complex in solution, and with high volatility. Fulfilling all these conditions at the same time is difficult. Benzene, toluene, and chloroform were tested as spreading solutions. The first two gave turbid solutions at very low concentrations, while chloroform did not. Therefore, we decided to use chloroform as the spreading solvent. To maintain the complex stable and in solution, this was dissolved at a very low concentration (those quoted above), i.e. at such a concentration where, if the complex is broken, the fullerene, as well as the calix[8]arene, will still be in solution. In particular, at the concentrations worked here, there was no evidence of decomposition of the complexes.

Results and Discussion

The results of our measurements are presented in Figures 2 and 3, that is the π−A isotherms for the Langmuir films of calix[8]arene, of the calix[8]arene/C$_{60}$ complex, and of the calix-[8]arene/C$_{70}$ complex deposited onto the water−air interface, at 306.1 K.

In Figure 2, we present representative π−A isotherms for calix[8]arene and for the calix[8]arene/C$_{60}$ complex. At relatively high area per molecule (280 Å^2/molecule), the surface pressure is quite low for both systems. The isotherms start with a long plateau which ends at ca. 180 Å^2/molecule for the case of calix[8]arene and ca. 230 Å^2/molecule for the case of the calix[8]arene/C$_{60}$ complex. In both cases, further compression shows a continuous rise of the isotherms, resembling those presented by condensed phases, although there is no sharply definable start of the one-phase region. The long plateau, followed by a continuous rise, suggests a phase transition between the gas phase and a condensed phase. This was confirmed by the BAM observations (see below). During the compression process of the apparently condensed phase of the calix[8]arene/C$_{60}$ complex, we observed some changes not completely reproducible (little kinks) in the slope of the π−A isotherm.

In Figure 3, we present the π−A isotherms for calix[8]arene and for the calix[8]arene/C$_{70}$ complex. Qualitatively, they are similar to those presented in Figure 2. Here also a phase transition between the gas phase and a condensed phase is suggested. During the compression of the apparently condensed phase of the calix[8]arene/C$_{70}$ complex, we observed several changes in the slope of the π−A isotherm and kinks. In comparison with the previous case, here those kinks were less reproducible.

We obtained several isotherms for other temperatures, going down to 283.1 K, but these isotherms suffered from kinetic effects. They showed a dip in the pressure after which the pressure increased steeply. Therefore, an increase in the temperature and a reduction in the speed of compression would reduce the kinetic effects. Here, we report our experiments only at 306.1 K, since here they were quite reproducible. These experiments were carried out at a very low speed of compression. We believe that those kinetic effects are related to nucleation of the condensed phases and to the difficulty of the condensed phase domains to coalesce. Our results carried out in the Nima LB trough and in the R & K trough agree qualitatively. Differences are within the experimental error of the isotherm measurements. We made several cyclic isotherms. They showed hysteresis, as usually seen in this kind of measurements when multilayering or collapsing of the film occurs. During the recompression of calix[8]arene, its isotherms showed a plateau ending at ca. 100 $Å^2$/molecule. On further recompression, the isotherm becomes steeper than the isotherm obtained during the first compression. When we reach ca. 65 $Å^2$/molecule, there is a clear kink revealing multilayering. The same pattern is followed by the calix[8]arene/C_{60} complex, although the plateau ends at ca. 140 $Å^2$/molecule and the kink is observed at areas of ca. 100 $Å^2$/molecule. For the calix[8]-arene/C_{70} complex, the plateau ends at ca. 90 $Å^2$/molecule and the kink is at ca. 60 $Å^2$/molecule.

In Figure 4, we show BAM images for some thermodynamic states defined in the $\pi-A$ isotherms, just presented above, for pure calix[8]arene, for the calix[8]arene/C_{60} complex, and for the calix[8]arene/C_{70} complex. At very low pressures, the films are in a two-phase-coexistence region. In those figures, a solid phase (white regions) and a gas phase (dark regions) can easily be recognized. We observed that the continuous rise of the surface pressure in the $\pi-A$ isotherms was associated with a disappearance of the gas phase. The bright spots in the images on the solid phase are small mountain-shaped clusters of molecules that are hard to keep in focus with the rest of monolayer. They are magnified in the way of Newton-rings-like by the BAM apparatus. No expanded-liquid phases were observed in any case. This could be due to the range of the attractive part of the intermolecular potential, which determines whether or not a given substance can have a stable liquid phase. In particular, there is numerical evidence that for C_{60}, a molecule with an anomalously narrow attractive well, the liquid—vapor transition should be absent.[22,23]

BAM images of pure calix[8]arene and the calix[8]arene/C_{60} complex (Figure 4a and b) show very similar features; i.e., at low pressure (below 300 $Å^2$/molecule), they show big irregular solid domains in coexistence with a considerable amount of the gas phase, and except for small clusters in the solid phase, no multilayer areas were observed. During the observations at lower areas, solid domains covered in many occasions the whole field of view. This characteristic could be relevant to obtain Langmuir—Blodgett films of those compounds.

On the other hand, the calix[8]arene/C_{70} complex showed very different features from those of the pure calix[8]arene: it shows coexistence between the solid multilayer and the gas phase at low surface pressure. Figure 4c shows a region where one can see a three-layer solid phase of the calix[8]arene/C_{70} complex. Each layer is denoted number 1, 2, or 3 in this figure. Here, there was no discernible change in the intensity of regions 1, 2, and 3 using the BAM analyzer that could indicate regions with different molecular orientation. Therefore, we believe that the difference in intensity in Figure 4c is due to the different heights
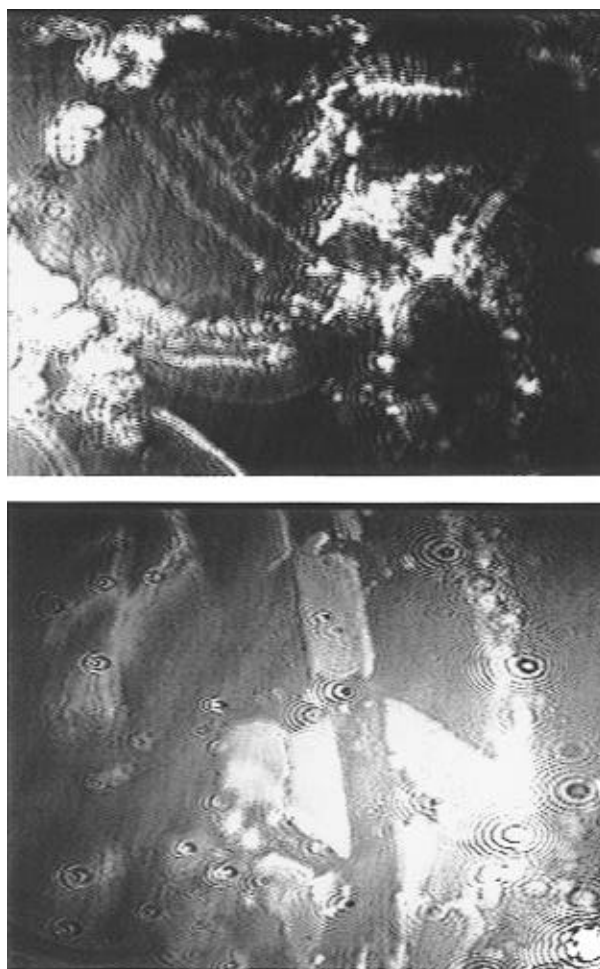

Figure 5. Brewster angle microscope images: (a, top) collapsed calix-[8]arene ($A = 153.8$ $Å^2$/molecule, $\pi \approx 10$ dyn/cm); (b, bottom) calix-[8]arene/C_{60} complex ($A \approx 80$ $Å^2$/molecule, $\pi \approx 8-9$ dyn/cm).

of the multilayers. In addition, the amount of gas phase for this complex was very small when compared with those for the other two systems under study, at about the same area per molecule and surface pressure. The solid phase basically covered the whole area of the trough. The solid phase of the calix[8]arene/C_{70} complex was also quite fragile, as is shown in Figure 4d. Here, an instant before this picture was taken, the film was basically made of one piece and, suddenly, it broke apart, producing channels of gas phase. This was due to a nondetectable tiny vibration produced on the surface, as a result of moving the objective of the microscope when focusing the area under study. Formation of gas channels was often observed throughout the sample.

For the three systems under discussion, as the samples were compressed, the solid domains did not coalesce easily. They tend to "crash" with each other and heal as the compression is carried out. Furthermore, as they crash, they showed more and bigger clusters on the top of the monolayers, giving the appearance of a collapsed film, see Figure 5a. At a relatively high surface pressure both calix[8]arene and the calix[8]arene/C_{60} complex started to form double layers, as is shown in Figure 5b. All those events that occur during the compression process explain the changes in slope and the kinks observed on the $\pi-A$ isotherms, as well as why they are not very reproducible. The formation of multilayers and the fragility of the films of the calix[8]arene/C_{70} complexes also explain the features of the isotherms of this system.

From the isotherm measurements, we made a rough estimate of the effective diameter for calix[8]arene and for the calix[8]-

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arene/C_{60} complex. The values were on the order of 15.6 $\pm$ 1.4 and 17.3 $\pm$ 1.9 Å, respectively. They were obtained from an average of 10 and 8 isotherms for calix[8]arene and the calix-[8]arene/C_{60} complex, respectively, at the point at which the surface pressure of the isotherm started to rise. This point also corresponds to the disappearance of most of the gas phase, as was observed by the BAM. Those values and the similar appearance of the Langmuir films for those systems suggest that the C_{60} molecule is indeed inside the calix[8]arene molecule. The difference in the effective diameters could be due to the swelling of the calix[8]arene net due to carbon−carbon interactions between the carbons of the net and those of the C_{60} molecule. Nevertheless, isotherm data alone are not enough to deduce detailed molecular arrangements. Therefore, the C_{60} lying on the top of the calix[8]arene monolayer is a possibility that must be evaluated in future work.

For the case of the calix[8]arene/C_{70} complex, the results are more difficult to understand. One line of reasoning could be that, thanks to its elongated geometry, the C_{70} can go to the bottom of the calix[8]arene basket. Therefore, the C_{70} would be closer to the water surface. The C_{70} films are prone to form clusters and multilayers to avoid the water−C_{70} interaction. In a similar way, from a very early stage, i.e. at the gas−solid coexistence, the calix[8]arene/C_{70} complex would prefer to form multilayers rather than monolayers. One argument against this point of view can be given. The greater area coverage of the solid phase at very low surface pressures, when compared with those of the other two systems studied here, suggests that we have more molecules than those formed by the calix[8]arene/C_{70} complex. The easiest way to understand this effect is to assume that the calix[8]arene/C_{70} complex is broken. This picture leads us to conclude that the C_{70} molecule is not inside the basket formed by the calix[8]arene molecule in the film. Another point in favor of this suggestion is that the calix[8]-arene/C_{70} bond is very weak. One piece of evidence for this is the capability of this complex to be in different stoichiometries, as described in the Experimental Section.

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