

## LANGMUIR FILMS OF MIXTURES OF C<sub>70</sub> AND ARACHIDIC ACID

R. Castillo<sup>a</sup>, S. Ramos<sup>a</sup>, J. Ruíz-García<sup>b</sup> and C. Varea<sup>a</sup>

<sup>a</sup>Instituto de Física, Universidad Nacional Autónoma de México  
P.O. Box 20-364, D.F., 01000 (México)

<sup>b</sup>Instituto de Física. "Manuel Sandoval Vallarta", Universidad Autónoma de San Luis Potosí  
Alvaro Obregón 64, San Luis Potosí, S.L.P., 78000 (México)

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### ABSTRACT

Surface pressure-area isotherms of Langmuir films of C<sub>70</sub>/arachidic acid mixed films were measured at the water (pH=2)-air interface, at several temperatures and concentrations. Our results for the case of 25 °C and 1:1 mixtures, differ from those presented by Jehoulet, et al. (1992), and are closer to the results for C<sub>60</sub> /arachidic acid mixed films presented by those authors.

### INTRODUCTION

The recent discovery of the carbon fullerenes, first discussed by Kroto, et al. (1985) to understand the behavior of intergalactic carbon clusters, has triggered a new and exciting field of research where a great variety of new carbon structures have been discovered. These authors proposed a soccer ball structure to one of those clusters, C<sub>60</sub>, and named it as buckminsterfullerene, after the American Architect Buckminster Fuller. Now, by extension, all the related compounds to the C<sub>60</sub> are called fullerenes. The development of a synthetic method for macroscopic amounts of fullerenes given by Kratschmer, et al. (1990) enhanced the interest about the fullerenes, giving rise to a great variety of studies in their chemical, electronic, physical properties, and possible applications. In particular, thin films of fullerenes are of interest because they exhibit superconductivity upon reduction (Murphy, et al., 1991, Allemand, et al., 1991), show photo electrochemical response (Jehoulet, et al., 1991), and a very interesting electrochemical behavior (Dubois, et al., 1991).

The formation of highly incompressible and stable Langmuir films of C<sub>60</sub> at the water-air interface was first reported by Obeng and Bard (1991), at temperatures in the

range of 5–35 °C. They found that the limiting area per molecule calculated from pressure-area ( $\Pi$ -A) isotherms yielded a radius of 5.6 Å for the C<sub>60</sub> in the film, in well agreement with the data obtained from other techniques. Although these measurements are quite difficult to control and several authors have failed to obtain them, additional information about C<sub>60</sub> concentration, sample size and trough conditions presented by Bulhoes, Obeng, and Bard (1993) have given some light about the proper experimental conditions to obtain Langmuir monolayers at the water-air interface.

C<sub>70</sub> films at the water-air interface were first reported by Jehoulet, et al. (1992) at 25 °C. They deposited the films on the trough in the same manner as the C<sub>60</sub> films, and reported two transitions in their  $\Pi$ -A isotherms. The limiting areas yielded radii of  $9.0 \pm 3.0$  and  $5.8 \pm 1.6$  Å, respectively. Then, they concluded that these values were in reasonable agreement with the theoretical values expected for the prolate spheroidal C<sub>70</sub> carbon cage in two configurations, namely, the limiting areas corresponding to a film made up predominantly of C<sub>70</sub> 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 obtain thin films of fullerene derivatives. Some important examples can be mentioned, namely, films of 1-ter-butyl-1,9-dihydrofullerene-60 (Goldenberg, et al. 1993), of C<sub>60</sub>O and C<sub>61</sub>H<sub>2</sub> (Maliszewskyj, et al. 1993). The C<sub>60</sub> molecules also formed stable mixed films at the air-water interface with some organic compounds with some amphiphilic character. Some examples can be found in the recent literature as the case of arachidic acid/C<sub>60</sub> (Obeng and Bard, 1991; Jehoulet, et al., 1992; Xiao, et al., 1993) and that of octadecanol/C<sub>60</sub> (Milliken, et al., 1992). C<sub>70</sub> has also been used to form mixed films with arachidic acid. In a report due to Jehoulet, et al. (1992) they found that the  $\Pi$ -A isotherm (25 °C) showed two transitions. The limiting radius in the fully compressed film was of the order of 7.8 Å, suggesting that in contrast to the C<sub>60</sub>/arachidic acid films, the C<sub>70</sub> molecules in these films are much closer to the air/water interface and make significant contribution to the ultimate final packing. The diameters for C<sub>70</sub> obtained by electron diffraction using a simulated annealing method (McKenzie, et al. 1992) are 7.80 and 6.94 Å for the longest and equatorial diameters, respectively, which are not much different from the 7.1 Å diameter of the C<sub>60</sub> molecule obtained from X-ray measurements (Heiney, et al. 1991). Surprisingly, given the resemblance between molecules of C<sub>70</sub> and C<sub>60</sub>, the isotherms for the mixed films presented by those authors are quite different. In their work the  $\Pi$ -A isotherms for the [1:1] C<sub>60</sub>/arachidic acid mixed mixtures start to rise at c.a. 28 Å<sup>2</sup>/molec while those for [1:1] C<sub>70</sub>/arachidic acid films start to rise at c.a. 400 Å<sup>2</sup>/molec.

The main purpose of this paper is to present our results for mixed Langmuir films made of C<sub>70</sub> and arachidic acid at several temperatures and concentrations. Our results are different from those presented by Jehoulet, et al. (1992) and closer to those of the C<sub>60</sub>/arachidic acid mixed films.

## EXPERIMENTAL SECTION

**REAGENTS.** The  $C_{70}$  (> 98 % purity) was supplied by Mer Corporation (Tucson, AZ, USA). The arachidic acid (99 % eicosanoic acid) was supplied by Merck (Merck, Darmstadt, Germany). Dry Benzene (Chromatographic grade, > 99.7) was used as solvent for the preparation of the fullerene spreading solution. This was supplied by Merck (Merck-Mexico S.A., Mexico). For cleaning the trough, we used chloroform (HPLC grade, 99.9 %) from Sigma-Aldrich (Sigma Chemical Co. and Aldrich Chemical Co., Inc., USA). As subphase for all the Langmuir films, we used Millipore water (18.2 M $\Omega$ , Super Q system, Millipore Corporation, USA) filtered through a 0.2  $\mu$ m Barnsted final filter (model D3750, Barnsted/Thermolyne, IA, USA). pH was modified to pH=2, with addition of HCl before the spreading of the  $C_{70}$  /arachidic acid/benzene solution.

**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 with a pneumatic tube incorporated into a steel base, and the whole equipment was placed on a concrete table cemented to a concrete floor on the ground floor of our building. The barriers are made of PTFE fitted with stiffening bars defining a working circular area, starting at 1000 cm<sup>2</sup>. All experiments were carried out in a dust-free environment.

**PROCEDURE.** Fresh  $C_{70}$  /arachidic acid solutions [1:1] in benzene (ca.  $5.68 \times 10^{-5}$  M, for each component) were deposited at the water/air interface. Small amounts (5  $\mu$ L) of these solutions were applied to at least 15 sites on the water surface with a 100  $\mu$ L Hamilton syringe. After 5 minutes this procedure was repeated until we had the desired quantity of the mixture in the film. Then, after 20 to 30 minutes, the time allowed for benzene evaporation, the isotherms were obtained by compressing the film continuously at a rate of 40 cm<sup>2</sup> /min. Time series with this and equivalent systems have shown that after 15min there is no effect of the solvent used for spreading.

As many other groups, we measured the  $\Pi$ -A isotherms for the  $C_{60}$  and  $C_{70}$  films. We obtained isotherms in which the pressure starts to increase at an area of around 100  $\text{\AA}^2$ /molec. These isotherms were not as steep as those obtained by Jehoulet, et al. (1992), and the pressure before the collapse was only about 20mN/m. In these measurements we followed the suggestions given by Bulhoes, et al. (1993) and used benzene as solvent. We could not, however, follow their advice related to the amount of dispersing solution due to the size and geometry of our trough. In the circular geometry of the trough used, the barriers form an "isosceles triangle" with the Wilhelmy plate close to the vertex between the two barriers, thus molecules of  $C_{60}$  and  $C_{70}$  tend to form multilayers rather than rearrange in the form of a monolayer. We believe that this is a kinetic effect where, in the triangular geometry, molecules in the vertex are compressed more rapidly and can not rearrange throughout the whole surface as the barriers are closing. This effect is more important in molecules like fullerenes so labile to form multilayers.

## RESULTS AND DISCUSSION

The results of our measurements for the pressure area isotherms of the Langmuir mixed films of  $C_{70}$ /arachidic acid at the water (pH=2)-air interface are presented in figures 1-3.

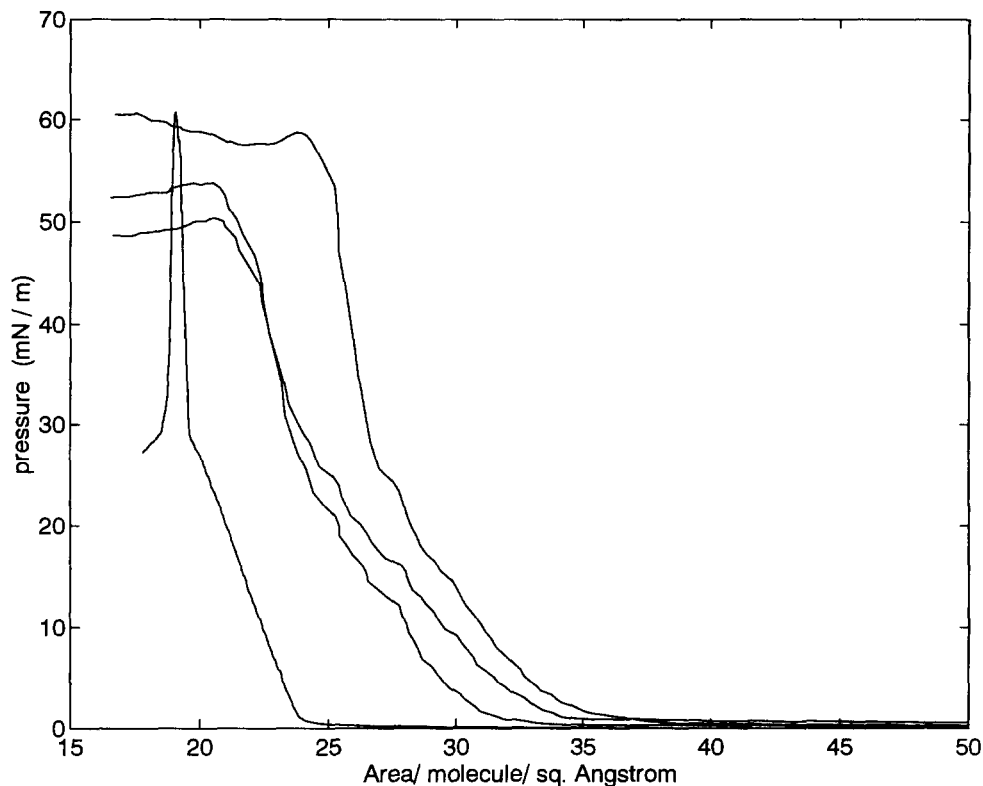


Figure 1.- This figure presents the  $\Pi$ -A isotherms for the  $C_{70}$ / arachidic acid films [1:1] (from right to left) for 8, 50 and 25 °C. The last isotherm to the left corresponds to pure arachidic acid at 25 °C, that was included for comparison.

In figure 1, we present the  $\Pi$ -A isotherms for a [1:1] concentration and at three different temperatures, 50, 25 and 8 °C. We have included, also, the  $\Pi$ -A isotherm for pure arachidic acid at 25 °C, as determined by us using the described technique. From these isotherms we identify two phase transitions. The first one is a phase transition between two fluid phases which we could classify as the transition between the gas and liquid-condensed phases. The isotherms start in the coexisting region which ends at 32  $\text{\AA}^2/\text{molec}$  for the isotherm of 25 °C and at 35  $\text{\AA}^2/\text{molec}$  for the other two isotherms. At higher pressures we observe the pure liquid-condensed phase. The other transition, of the liquid-condensed to a more solid-type phase, occurs at 25-27  $\text{\AA}^2/\text{molec}$  for the three isotherms. In the compression of the liquid condensed phase

we observe several changes in slope in the  $\Pi$ -A isotherms suggesting the formation of several layers of  $C_{70}$  over the monolayer of arachidic acid. These, however are not very well reproducible.

In figure 2, as above, we present the  $\Pi$ -A isotherms for 2, 4, 6, and 10 °C. For comparison, we included  $\Pi$ -A isotherm for pure arachidic acid at 10°C determined by us. As before, we observe two phase transitions, from gas to liquid-condensed ending at c.a. 33-34 Å<sup>2</sup>/molec, and from liquid -condensed to solid (c.a. 26 Å<sup>2</sup>/molec). We found that the pressure at which the second transition occurs is insensitive to temperature, in this temperature range. As before, during compression of the liquid condensed phase, we observed some structure which becomes more reproducible and apparent as we lower the temperature. We believe that those slope changes are related to multilayering of the  $C_{70}$  over the arachidic acid film.

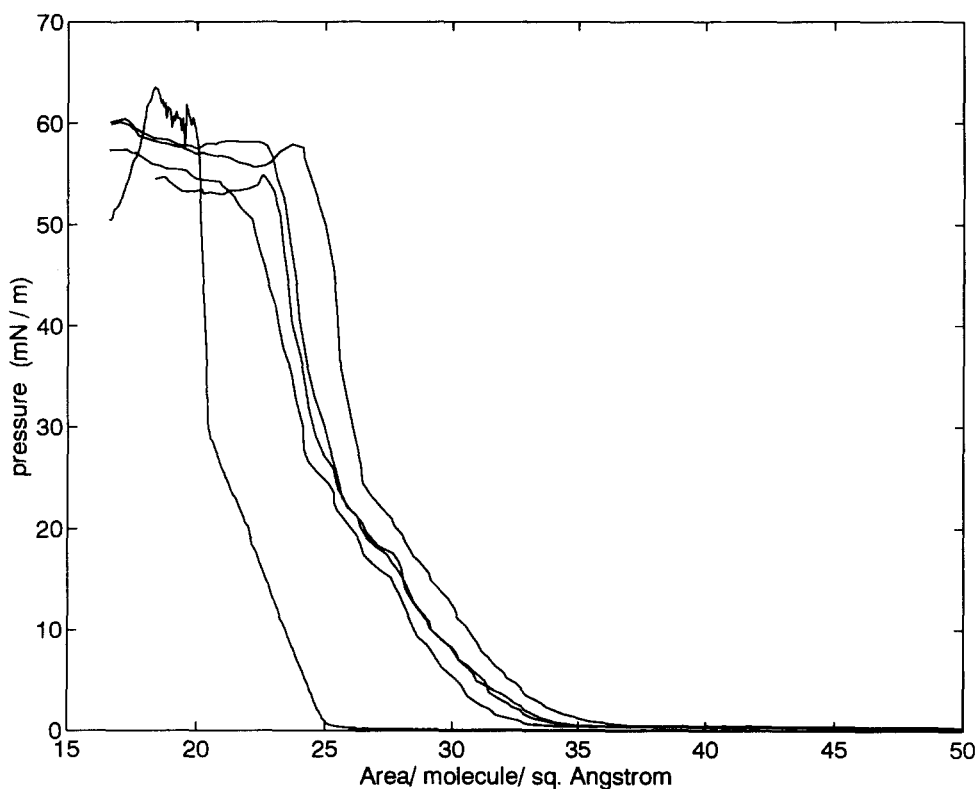


Figure 2.- This figure presents the  $\Pi$ -A isotherms for the  $C_{70}$ / arachidic acid films [1:1] (from right to left) for 6, 4, 2 and 10 °C. The last isotherm to the left corresponds to pure arachidic acid at 10 °C, for comparison.

In all cases we found that the initial rise in pressure of the  $\Pi$ -A isotherms occurs at areas lower than 40 Å<sup>2</sup>/molec and found no indication of an initial rise at

400 Å<sup>2</sup>/molec as Jehoulet, et al. (1992) report. Such large areas would imply that C<sub>70</sub> molecules are in contact with the water at the water-air interface in the liquid condensed phase. Contrary to this we found that C<sub>70</sub> molecules avoid as much as possible contact with water. Since the solid phase of arachidic acid/C<sub>70</sub> mixed films occurs at 27-35 Å<sup>2</sup>/molec and the solid phase of C<sub>70</sub> pure films occurs at 116 Å<sup>2</sup>/molec. We estimate that there are between 3 and 4 layers of C<sub>70</sub> molecules on top of the arachidic acid film.

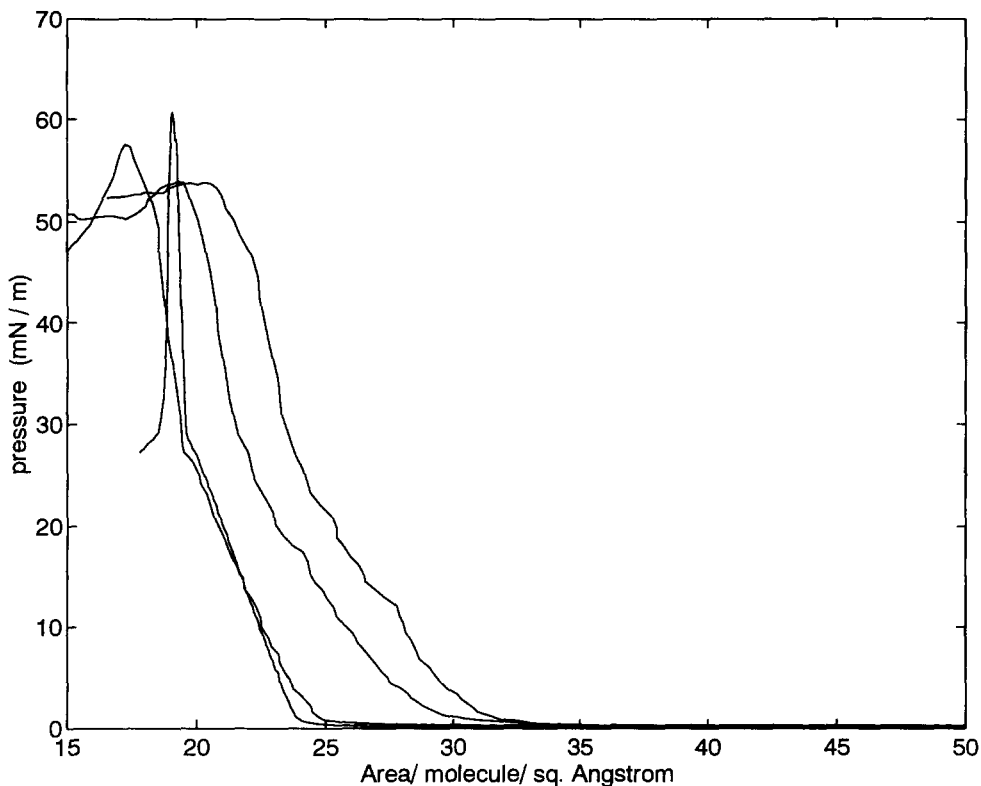


Figure 3.-  $\Pi$ -A isotherms for the C<sub>70</sub>/ arachidic films at 25 °C, for different concentrations of arachidic acid. From left to right: C<sub>70</sub>/ acid = [1:1], [1:1.15], and [1:3]. In addition, we include the pure arachidic acid isotherm at the same temperature (the steeper isotherm in this figure).

In figure 3, we present our results for several mixed films where the proportion of C<sub>70</sub> was changed. The results are for the following proportions of C<sub>70</sub> /Acid: [1:1], [1:1.15] and [1:3]. Here, we can observe how the C<sub>70</sub> molecules modify the  $\Pi$ -A isotherms as the concentration in the film is increased. For a [1:1] concentration the solid phase is expanded with respect to the pure arachidic acid. As expected, this expansion is reduced as the concentration of the C<sub>70</sub> molecules is reduced. This expansion is similar to that for the case of [1:1] mixtures of C<sub>60</sub>/arachidic acid and much smaller than reported before (Jehoulet, et al., 1992), in agreement with the

"rugby" ball structure of  $C_{70}$  with a slight pinching of the waist, with a size close to  $C_{60}$ .

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