Langmuir-Blodgett and Electrochemical Studies of Fullerene Films

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Surface pressure-molecular area isotherms of Langmuir films of pure C_{60} and C_{60}-eicosanoic acid (arachidic acid) mixed films were measured at the air-water interface, and the electrochemical behavior of their Langmuir-Blodgett films on a hydrophobic gold electrode in acetonitrile solutions is described. The formation of highly incompressible monolayer and multilayer films at the air-water interface was reconfirmed and was strongly dependent on the experimental conditions, such as the purity of the fullerene, spreading solvent, and the age and history of the spreading solution. The voltammetric response of Langmuir-Blodgett C_{60} films indicates a higher solubility of the reduced species than that observed for thicker films prepared by drop coating.

Introduction

We previously described the behavior of C_{60} and C_{70} films in Langmuir trough experiments and showed that under proper experimental conditions monolayer films could be prepared that showed limiting molecular areas consistent with the size of the fullerene molecules.[1] Studies of films of C_{60} mixed with eicosanoic (arachidic) acid and attempts at transferring these films to hydrophobic substrates were also described. Following the appearance of our results, several other papers describing studies of C_{60} layers at the air-water interface have appeared.[2-6] For example, Milliken et al.[2] recently reported that monolayer films of C_{60} could not be obtained at Langmuir films on water and only multilayered films formed. Similar problems in obtaining C_{60} monolayer films were reported by others,[3-5] although Maliszewskyj et al.[6] recently succeeded in forming such films. Because of the wide interest in C_{60} films, as discussed below, we describe here detailed considerations concerning the behavior of these films on a Langmuir trough, including the effect of C_{60} concentration, sample size, and trough conditions. The transfer of such films to an electrode surface and the electrochemical behavior of these, as contrasted to multilayer films formed by drop-coating,[1b,7] is also discussed.

Thin films of the fullerenes are of interest because they exhibit superconductivity upon reduction,[8] show a photoelectrochemical response,[9] and interesting electrochemical behavior[1b,7] that differs significantly from that seen for dissolved species.[10-15] For example, films of C_{60} show a large splitting between the cyclic voltammetric (CV) reduction and oxidation waves for the first and second electron-transfer reactions, which indicates considerable reorganization of the film structure.[1b,7] Moreover, the behavior strongly depends upon the electrolyte cation, and quartz crystal microbalance (EQCM)[16,17] and laser desorption mass spectrometric experiments[17] suggest trapping of ionic species in the film during the redox processes. A Raman spectroscopic study of C_{60} films and their reduction has also been reported recently.[18]

Experimental Section

Reagents. The C_{60} was separated from a commercial carbonaceous soot (Texas Fullerenes Inc., Houston, TX) as described in the literature.[12,13] Acetonitrile (H_2O = 0.001%, Burdick & Jackson, Muskegon, MI) and benzene (Spectrograde, Mallinck-

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(1) (a) Obeng, Y. S.; Bard, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 6279. (b) Jehoulet, C.; Obeng, Y. S.; Kim, Y.-T.; Zhou, F.; Bard, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4237.

(2) Milliken, J.; Dominguez, D. D.; Nelson, H. H.; Barger, W. R. *Chem. Mater.* **1992**, *4*, 252.

(3) Nakamura, T.; Tachibana, H.; Yumura, M.; Matsumoto, M.; Azumi, R.; Tanaka, M.; Kawabata, Y. *Langmuir* **1992**, *8*, 4.

(4) Guo, J.; Xu, Y.; Li, Y.; Yang, C.; Yao, Y.; Zhu, D.; Bai, C. *Chem. Phys. Lett.* **1992**, *195*, 625.

(5) Back, R.; Lennox, R. B., *J. Phys. Chem.* **1992**, *96*, 8149.

(6) Maliszewskyj, N. C.; Heiney, P. A.; Jones, D. R.; Strongin, R.; Cichy, M. A.; Smith, A. B., private communication.

(7) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456.

(8) Rosseinsky, M. J.; Ramirez, A. P.; Glarum, S. H.; Murphy, D. W.; Haddon, R. C.; Hebard, A. F.; Palstra, T. T. M.; Kortan, A. R.; Zahurak, S. M.; Makhija, A. V. *Phys. Rev. Lett.* **1991**, *66*, 2830.

(9) Miller, B.; Rosamilia, J. M.; Dabbagh, G.; Tycko, R.; Haddon, R. C.; Muller, A. J.; Wilson, W.; Murphy, D. W.; Hebard, A. F. *J. Am. Chem. Soc.* **1991**, *113*, 6291.

(10) (a) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Liufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634. (b) Cox, D. M.; Behal, S.; Disko, M.; Gorun, S. M.; Greaney, M.; Hsu, C. S.; Kollin, E. B.; Millar, J.; Robbins, J.; Robbins, W.; Sherwood, R. D.; Tindall, P. *J. Am. Chem. Soc.* **1991**, *113*, 2940.

(11) (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

(12) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

(13) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kratschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630.

(14) (a) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. (b) Ohsawa, T.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 281.

(15) Zhou, F.; Jehoulet, C.; Bard, A. J. *J. Am. Chem. Soc.*, in press.

(16) Koh, W.; Dubois, D.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 4163.

(17) Zhou, F.; Yau, S. L.; Jehoulet, C.; Laude, D.; Guan, Z.; Bard, A. J. *J. Phys. Chem.* **1992**, *96*, 4160.

(18) Zhang, Y.; Edens, G.; Weaver, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 9395.

0897-4756/93/2805-0110$04.00/0

rodt, Paris, KY) were used as received. Tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$, Southwestern Analytical Chemicals Inc., Austin, TX) was recrystallized twice from ethyl acetate/ether (9:1) and dried under vacuum at 120 °C for 72 h. Eicosanoic acid (arachidic acid, 99%) and octadecyl mercaptan (98%, both from Aldrich Chemical Co., Milwaukee, WI) were used without further purification. The water used as subphase was purified via an ion-exchange purification train (Milli-Q System, Millipore Inc., El Paso, TX) and filtered through a 0.5-μm nylon filter (Rainin Instrument, Woburn, MA).

Electrodes and Cells. In the electrochemical experiments of LB films, a gold film (ca. 0.2 μm thick) was vacuum evaporated onto a chromium layer (ca. 100 Å) supported on a glass plate through an aluminum template to produce a working electrode (geometric area, ca. 0.10 cm^2). Prior to the experiments the electrode surface was made hydrophobic by immersion for 3 h in a 1% octadecyl mercaptan ethanolic solution and then rinsed copiously with absolute ethanol and dried with a stream of pure argon. All electrochemical experiments were performed in one-compartment cells with a platinum flag as the counter electrode and a silver wire as the quasi-reference electrode in a drybox or under an argon blanket outside the drybox.

Apparatus. Cyclic voltammograms were performed with a PAR 173 potentiostat/galvanostat and a PAR 175 universal programmer (Princeton Applied Research Corp., Princeton, NJ). A Houston Model 2000 *x–y* recorder was used to record the cyclic voltammograms. In the Langmuir trough experiments, a modified Lauda Model P film balance system (Brinkmann Instruments Inc., Westbury, NY) with a home-built Teflon trough was used to obtain the surface pressure–area isotherms and to transfer the L–B films to the electrodes. The trough is 10 mm in depth and the separation between the measuring and moving barriers defined an initial working area of ~400 cm^2. The trough was routinely calibrated over about the same range of compression as the C_{60} experiments with 25–50 μL amounts of 1 mM arachidic acid solution.

Procedure. In the Langmuir trough experiments, fresh C_{60} or C_{60}/arachidic acid solutions in benzene were used as spreading solutions. Small amounts (<5 μL) of these solutions were applied to at least 10 sites on the water surface with a 50-μL Hamilton syringe. After 15–20 min (the time needed for benzene evaporation), the isotherms were obtained by compressing the film continuously at 2 cm/min. The C_{60} film at the air–water interface was very sensitive to any surface impurities on the water phase and to vibrations or other disturbances, and pains were taken to avoid these. The trough was placed on a marble slab supported by concrete blocks cemented together and to a concrete floor on the ground floor of our building. (It is located near our scanning tunneling microscopes in a particularly vibration-free location.) After each experimental run, the trough was carefully washed with ethanol and water. Before spreading the C_{60} film the water surface was swept several times to remove any trace surface impurities. The purity of the water in the subphase was verified before the experiment by sweeping the barrier and measuring the surface pressure in the absence of C_{60}. No detectable rise of surface pressure was observed with pure water. Electrochemical measurements were carried out with LB films of C_{60} and C_{60}/arachidic acid transferred to hydrophobic gold electrodes. The Au electrodes were vertically immersed into a subphase before C_{60} solution spreading. L–B transfer of compressed films onto Au-coated electrodes was done at different constant pressures (15–50 mN/m) by mechanically withdrawing the electrode very slowly (~60 μm/s) through the C_{60} layer at the air–water interface.

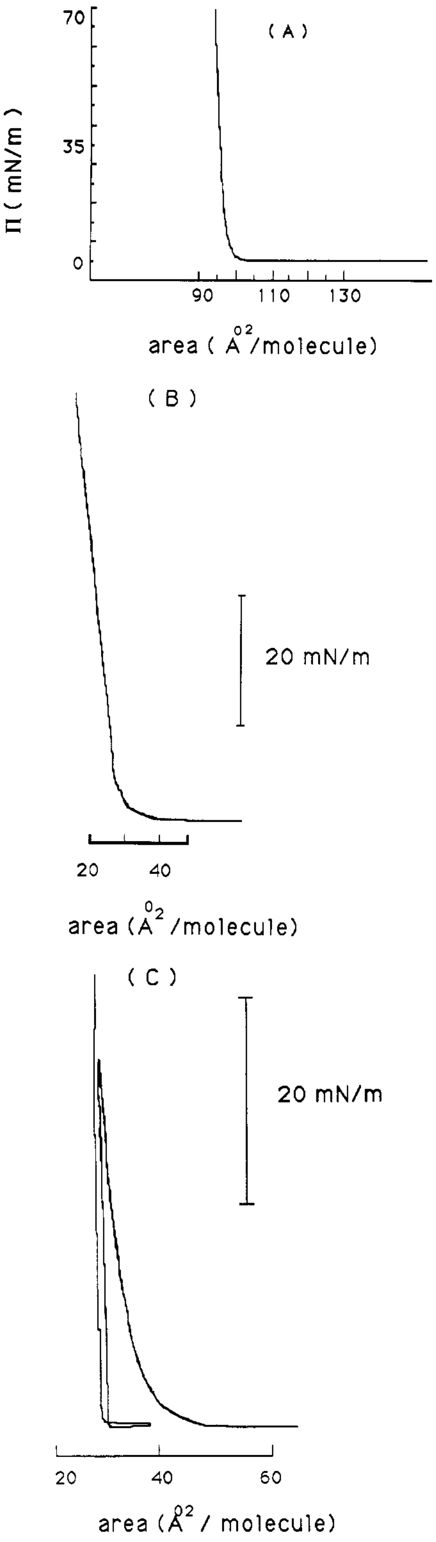

Figure 1. Surface pressure–area isotherms of C_{60} on a pure aqueous subphase at 21 °C: (A) 50 μL of 10^{-4} M C_{60} solution; (B) 200 μL of 10^{-4} M C_{60} solution; (C) 100 μL of 5 × 10^{-4} M C_{60} in one compression–expansion cycle.

Results and Discussion

Langmuir Trough Experiments at the Air–Water Interface. Figure 1 displays the effect of the spreading solution concentration and sample size of pure C_{60} solutions on the pressure–area isotherm at the air–water interface. On a pure aqueous subphase, at low concentration (lower than 5 × 10^{-5} M) and small sample size (≤50 μL), it was possible to obtain monolayer films that could be compressed and remained stable at surface pressures up to 70 mN/m (Figure 1A). The limiting area per molecule, obtained by extrapolation of the rising portion of the isotherm to $\pi = 0$, was 98.2 ± 2.3 Å²/molecule (where the uncertainty represents the standard deviation of eight experiments at concentrations below 5 × 10^{-5} M), which is consistent with the C_{60} cross-sectional area determined by X-ray powder diffraction.[19] Monolayers compressed up to 40 mN/m could be reexpanded with no hysteresis

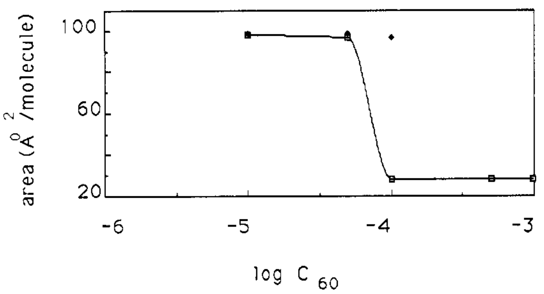

Figure 2. Dependence of the molecular area on C_{60} concentration for different sample sizes (◆) 50 μL; (□) 100 μL.

in the pressure–area isotherm. These results are similar to those published previously.[1a]

With more concentrated solutions ($\geq 10^{-4}$ M) and larger sample sizes (≥100 μL; Figure 1B) the apparent cross-sectional area at high pressure was about 28 $Å^2$/molecule, indicating that the film became multilayered. Such multilayers were more rigid than the monolayers and it was surprising that these films could withstand pressures of about 100 mN/m for 6 h without collapsing. The high pressures attained with these films indicate that they are not in thermodynamic equilibrium (i.e., where $\pi = \gamma_w - \gamma_f$, $\gamma_w = 72$ mN/m and γ_f = surface tension of water covered by film). Rather, at high compression, the films behave like rigid "rafts" that can mechanically push against the trough barrier. Reexpansion of the C_{60} multilayers at pressures of about 20 mN/m (Figure 1C) resulted in a rapid decrease in the surface pressure to values close to zero. Upon subsequent recompression, the surface pressure remained close to zero until the area per molecule was decreased to well below that of the initial compression, at which point the pressure increased rapidly to afford a different pressure–area isotherm. This hysteresis can be rationalized by a model in which the multilayer C_{60} film fragments into rafts of aggregates which do not relax to fill the increasing surface area when the surface pressure is released. These rafts would stack up upon subsequent recompression. The extent of hysteresis, as measured by the differences in the limiting areas between compressions, exhibited a strong dependence on the spreading conditions of the solution onto the air-water interface. To avoid the formation of multilayers at the air–water interface prior to compression, it was important that the amount of C_{60} did not exceed a monolayer coverage within the area defined by the expanding benzene droplet before its evaporation.

The dependence of the area per molecule on the concentration of C_{60} solution for different sample sizes is depicted in Figure 2. Using larger sample sizes (≥200 μL) and benzene as the spreading solvent, we obtain limiting radii of 3.0 Å. The decrease in the area observed for the larger sample size (Figure 2B) is attributed to the formation of C_{60} multilayers, and this suggests that the C_{60} does not bind strongly to water as the traditional amphiphilic surfactants do.

During the compression of these multilayer films we observed, at pressures of about 10 mN/m, anisotropic solid domains that coexisted with a fluid isotropic phase on the surface. These solid domains appeared close to the moving barrier in the form of elongated, bright, individual needles. These needles remained on the surface of the subphase when the pressure was relieved and were stable when transferred to a hydrophobic glass slide. Figure 3 is an optical micrograph of a needle on a hydrophobic glass substrate. Some needles showed branches, although these were only observed for a few specimens.

These needles were not observed when the same sample size was spread on the trough using dichlorobenzene as the solvent with the C_{60} first dried under vacuum at 240 °C in order to eliminate most of the benzene. This observation suggests that these aggregates are formed by the interaction between the residual adsorbed benzene and C_{60} molecules. The formation of these needles was very fast at low surface pressures, and it was impossible to observe in the isotherm a broad plateau characteristic of a first-order transition.[20] The solvent used for spreading, and perhaps even residual solvent from C_{60} preparation, may be important in film formation. It is known, for example, that even small amounts of solvent affect the form of crystalline polymorphs of C_{60} produced and that traces of solvent are difficult to remove from C_{60} even upon heating at elevated temperature in vacuum.[21]

Following our earlier demonstration that the C_{60} molecules from stable mixed films with arachidic acid (AA) at the air–water interface,[1a] we investigated the surface properties of mixed C_{60}–AA layers. Figure 4 shows surface pressure–area per molecule isotherms for surface films of pure AA and for mixtures of C_{60}:AA at molar ratios of 1, 2, and 3. In contrast to our earlier report,[1a] we found that an increase in the C_{60} content in the mixed spreading solution resulted in an increase of the film resistance to compression. The isotherm of the mixture C_{60}:AA (1:1) showed a large hysteresis; the extent of hysteresis in the isotherms increased with increasing C_{60} concentration in the mixture.

The average area per molecule for the various mixtures plotted against mole fraction of C_{60} is shown in Figure 5, where the solid line represents the calculated values based on the ideal mixture equation.[22] The negative deviation of observed limiting area from that predicted for an ideal mixed film indicates a stronger interaction between C_{60} and AA in the film than between C_{60} and water. This is attributed to the C_{60} affinity to the more hydrophobic medium created by the packed hydrocarbon tails of the AA molecule. This is consistent with the known solubility of C_{60} in solvents such as benzene and its insolubility in polar solvents such as water and acetonitrile.

Formation of LB Films. To compare the electrochemical behavior of thin LB films of C_{60} with thick films of C_{60} (drop-coated), we attempted to transfer LB films from the air-water interface to a solid substrate. The main advantage of the films produced by the LB transfer technique, compared to drop-coated films, is the better

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[19] (a) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R.; *Nature* **1990**, *347*, 354. (b) Fleming, R. M.; Siegrist, T.; March, P. M.; Hessen, B.; Kortan, A. R.; Murphy, D. W.; Haddon, R. C.; Tycko, R.; Dabbagh, G.; Mujsce, A. M.; Kaplan, M. L.; Zahurak, S. M. In *Clusters and Cluster-Assembled Materials*; Averback, R. S.; Nelson, D. L.; Bernhole, J., Eds.; MRS Symposia Proceedings 206; Materials Research Society: Pittsburgh, 1991. (c) Fischer, J. E.; Heiney, P. A.; McGhie, A. R.; Romanow, W. J.; Denenstein, A. M.; McCauley Jr., J. P.; Smith III, A. B. *Science* 1991, *252*, 1288.

[20] (a) Bell, G. M.; Combs, L. L.; Dunne, L. J. *Chem. Rev.* **1981**, *81*, 15. (b) Middleton, S. R.; Iwahashi, M.; Pallas, N. R.; Pethica, B. A. *Proc. R. Soc. London, A* 1984, *396*, 143. (c) Hifeda, Y. F.; Rayfied, G. W. *Langmuir* **1992**, *8*, 197.

[21] Atake, T.; Tanaka, T.; Kawaji, H.; Kikuchi, K.; Saito, K.; Suzuki, S.; Achiba, Y.; Ikemoto, I. *Chem. Phys. Lett.* **1992**, *196*, 321.

[22] Gaines, G. L. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience Publishers: New York, 1966; p 282.

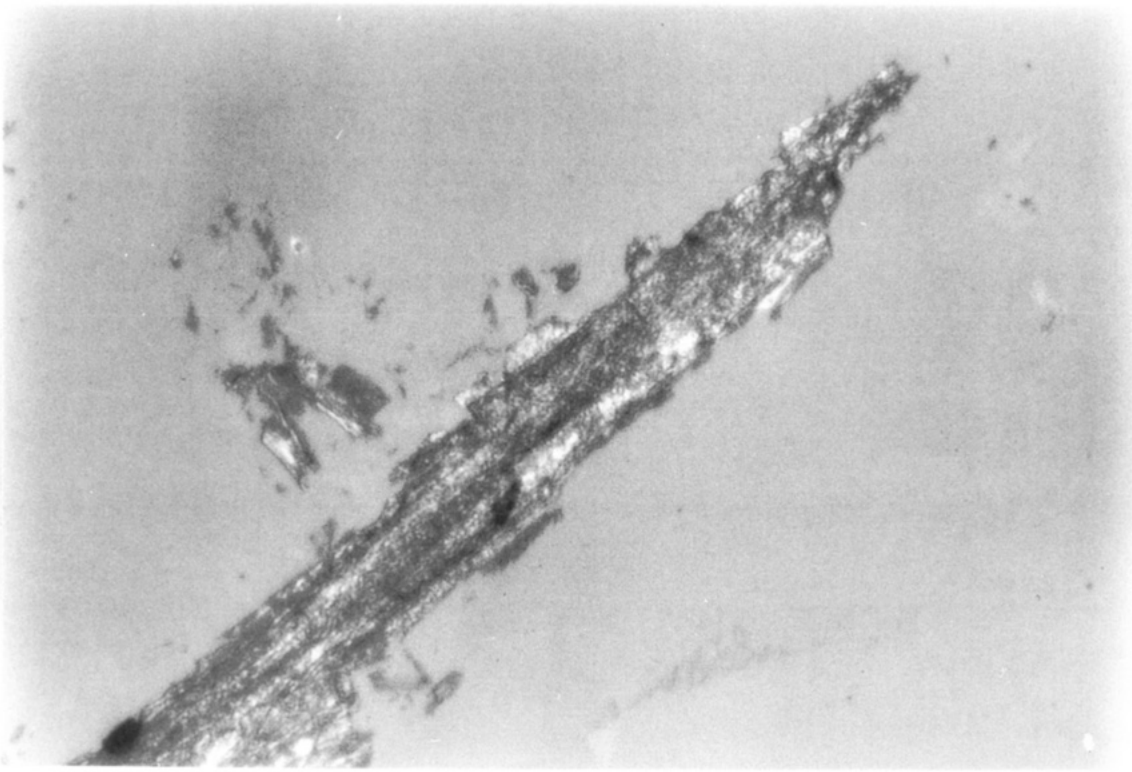

Figure 3. Optical microscope image of a needle transferred to a hydrophobic glass slide at π = 20 mN/m by lifting the glass at a constant rate of 10 μm/s, magnification 335×.

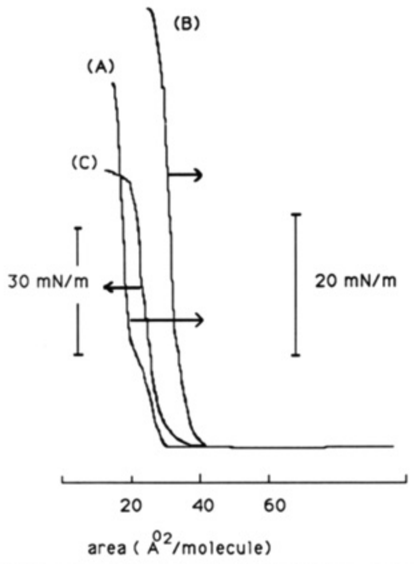

Figure 4. Surface pressure–area isotherms of C_{60}:AA mixed films on pure water at 21 °C. Mole fraction of C_{60}: (A) 0; (B) 1; (C) 2.

control of the amount of electroactive C_{60} in the surface film. In all cases, the films were transferred onto a hydrophobic gold surface (as described above). The optimal transfer pressure for coherent LB films varied from 15 to 30 mN/m, depending on film composition. Films transferred at $\pi > 30$ mN/m were invariably nonuniform and showed yellow domains of disperse aggregates interspersed with clear regions of bare substrate. In other words, the successful transfer of LB films by vertical dipping required stability of the surface layer, which is generally obtained with pressures in the range of $15 < \pi < 30$ mN/m. As discussed in previous reports,[1,3,4] formation of LB films of C_{60} is possible, although it is difficult to prepare high-quality films.

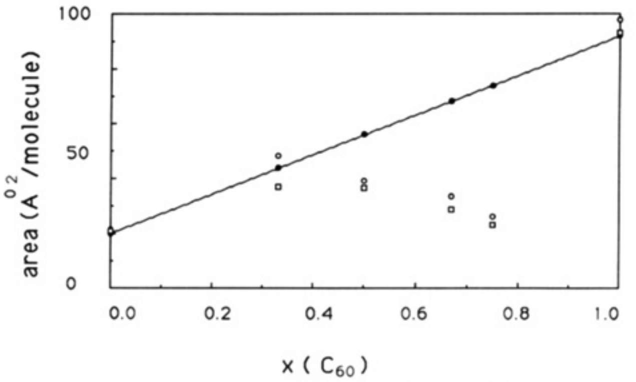

Figure 5. Average molecular area of the mixed films versus mole fraction of C_{60} (solid line with black dots was calculated from the ideal mixing equation), for different sample sizes (○) 50 μL and (□) 100 μL.

Electrochemical Behavior of LB Films. The electrochemical response of pure C_{60} films on gold electrodes was investigated by cyclic voltammetry in a 0.1 M $TBABF_4$–acetonitrile solution.[1b,7,16,17] A set of cyclic voltammograms of LB films of C_{60} produced under different conditions is shown in Figure 6. The negative potential sweeps were limited to the second cathodic wave, to avoid the formation of C_{60}^{3-}, which is more soluble in acetonitrile than the −2 and −1 species.[16,17]

There appears to be a strong relationship between the electrochemical properties and the film-transfer conditions; an increase in the peak current and a decrease in the peak widths were observed with increase of the transfer pressure. The peak splitting, ΔE_p, was about 210 mV for the film transferred at low pressures (<30 mN/m). Because rather large amounts of C_{60} must be used in these experiments and the films are very susceptible to vibration, transfers under these conditions did not produce uniform monolayers on the electrode. Although ΔE_p increased with

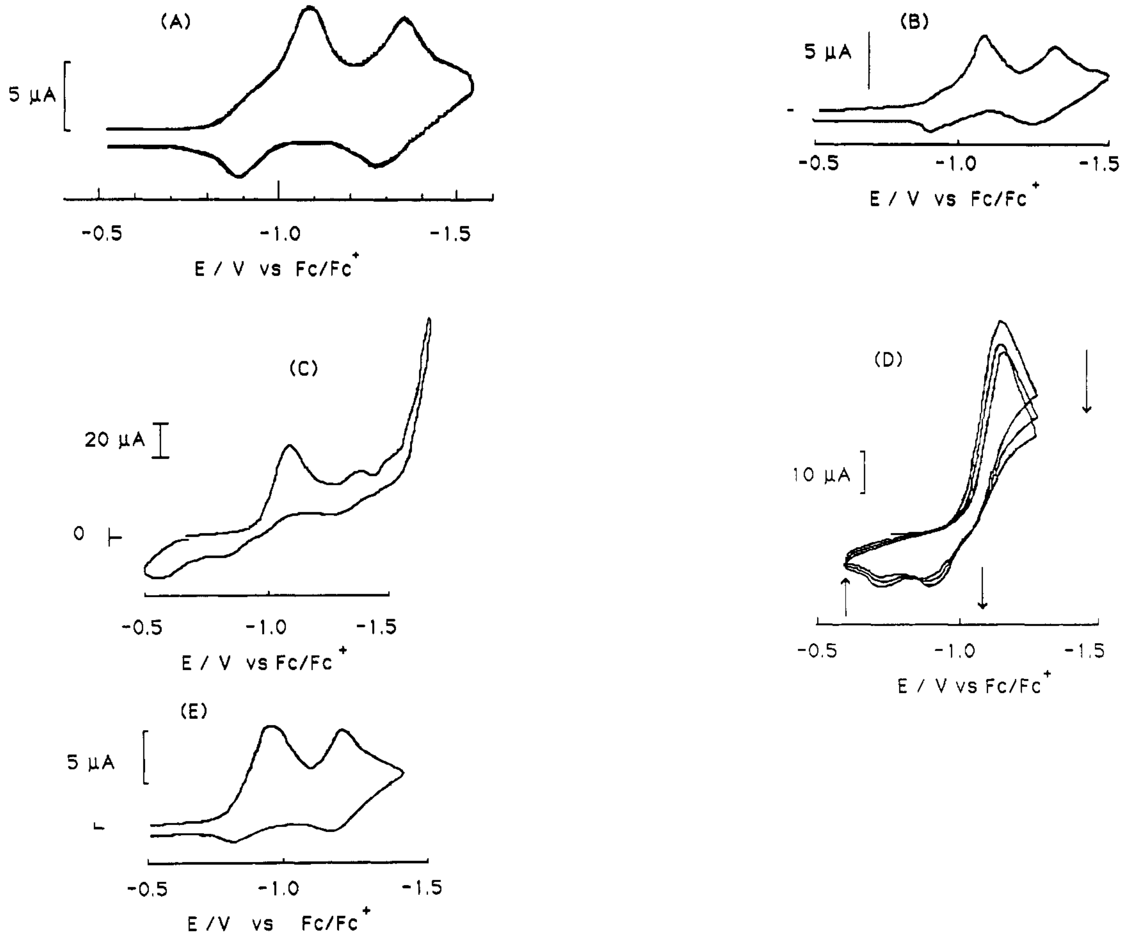

Figure 6. Cyclic voltammograms of L–B films of C_{60} on a hydrophobic gold electrode in a 0.1 M $TBABF_4$/acetonitrile solution. Pure C_{60} solution film transferred vertically. (A) 50 μL of 10^{-4} M C_{60} at $\pi = 5$ mN/m (B) similar to (A) but at $\pi = 20$ mN/m; (C) 100 μL of 5×10^{-4} M C_{60} at $\pi = 50$ mN/m; (D) repetitive voltammograms under the same conditions as in (C); (E) mixture C_{60}:AA 1:1, $\pi = 5$ mN/m; $v = 0.2$ V/s.

increasing transfer pressure, it remained smaller than the value observed for thicker films (Figure 6A,B). Using more concentrated spreading solutions and a large sample size, the conditions that produce multilayer films, the electrochemical response of films transferred at 20 mN/m was closer to that observed for drop-coated films. In Figure 6C, the cyclic voltammogram was characterized by a sharper cathodic peak and a larger peak splitting (ca. 400 mV) that approached the value found for thick films.

During repetitive potential cycling on an electrode coated with a thicker film, the cathodic current decreased, as did the corresponding anodic current (Figure 6D). Increasing the number of cycles resulted in the appearance of an anodic peak at more negative potentials. This anodic process, whose current increased with the number of cycles, could be attributed to the oxidation of solution phase C_{60}^-, in agreement with the EQCM experiments,[1b,17] which suggested that the drop-coated films tend to dissolve slightly after the first cathodic peak.

The cyclic voltammograms for the C_{60}–AA films transferred to the gold electrode (Figure 6E) exhibited a voltammetric curve similar to that of a pure C_{60} film transferred at $\pi < 30$ mN/m from small samples sizes. A sharp cathodic peak and a broad anodic peak were observed in most of the voltammograms with mixed films.

The peak splitting decreased with the AA content, and the ratio between the anodic and cathodic charge was higher than that determined for pure C_{60} films, probably due to the higher stability of the mixed film. The shift of the cathodic peak potential to more positive values is probably associated with the interaction between the C_{60}^- and the AA tail.

Conclusion

Langmuir trough studies of C_{60} films show, in agreement with earlier[1] and more recent[6] studies, that monolayer films of C_{60} can be prepared at the air–water interface, but the formation of such films requires careful control of the conditions. For example, the concentration and size of the spreading droplets are important in the production of desired films. Monolayer or multilayer films of C_{60} can be made by the LB technique, and cyclic voltammograms of these films demonstrate that they are more stable toward rearrangement than the thicker films formed by drop-coating. Langmuir trough studies of the mixed films of C_{60} with arachidic acid suggest that C_{60} molecules reside in the hydrocarbon environment of the arachidic acid tails.

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