SYMMETRICALLY SUBSTITUTED VIOLOGEN SURFACTANT FILMS AT THE AIR-WATER INTERFACE AND THEIR ELECTROCHEMISTRY ON INDIUM TIN OXIDE ELECTRODES

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ABSTRACT. — The contributions of the aliphatic tail groups on the properties of three symmetrically substituted amphiphilic viologens, with saturated hydrocarbon chains of length C_{16} (I), C_{18} (II), and C_{22} (III); alone or as admixtures with arachidic acid (eicosanoic acid), were examined at the air/water interface on a film balance. Discontinuities, attributable to two dimensional aggregation (e.g., surface micellation) involving the hydrocarbon tails, were found in the pressure-area isotherms at the air/water interface. The enthalpy associated with the aggregation phase change was estimated at 300 K, via a two dimensional Clausius-Clapeyron equation, to range between -38 and -52 kJ/mol, depending on the hydrocarbon tail length. Contact angle measurements on Langmuir-Blodgett (LB) and self adsorbed films of these compounds on an indium tin oxide (ITO) electrode show that the hydrocarbon tails are not tightly packed, probably because of the size and orientation of the bipyridinium group and the presence of anions in the films. Cyclic voltammetry of the LB films showed that the potentials for the first one-electron reduction of the electroactive head group in neat symmetrical viologen films were about 250 mV more positive than the potential of viologens in the solution phase; this is attributed to dimerization of the radical cation and film reconstruction upon electron injection. The film potentials shift negative when the dimerization is suppressed by addition of arachidic acid to the spreading solution. In this case, the monocation radical is stabilized against dimerization by both ion pairing with the archidate anion and the improved hydrophobic environment due to the interaction of the aliphatic tails on the molecules in the films.

Langmuir-Blodgett film/self-assembly/viologen surfactant/cyclic voltammetry.

Introduction

There has been a sustained interest in chemically modified electrodes over the past two decades and a number of approaches have been used to immobilize electroactive species on electrode substrates [1]. Langmuir-Blodgett (LB) and self-assembled (SA) films are particularly interesting, because they afford the reproducible large scale order at the molecular level needed for the control of surface molecular architecture [2,3]. Such control is useful, for example, in studies of the rates of electron transfer at electrode substrate-film interface. The Langmuir-Blodgett (LB) technique also allows the precise, reproducible arrangement and transfer of molecules onto a solid substrate [4]. A number of workers have taken advantage of this technique to study the electrochemistry and other physico-chemical properties of thin films on solid supports [5-12].

The electrochemistry of bis-alkylated bipyridinium salts (i.e., viologens) is of considerable interest in view of their potential electrochromic applications, the reactivity of their reduced states as mediators for electron transfer reactions, and their electron acceptor properties [13]. A previous report from this laboratory described immobilized films of asymmetrically substituted viologen amphiphiles on glassy carbon and indium tin oxide (ITO) [12] and illustrated how the interaction between immobilized molecules in films affected the observed electrochemical behavior. In these studies, the first reduction wave of the immobilized amphiphilic viologens was resolved into two peaks, as predicted by Matsuda et al. [8], and this was attributed

to a high degree of order within the film and interactions between the parent and the reduced species. In unrelated work, with nonelectroactive amphiphiles self-assembled on polycrystalline gold, well-ordered monolayers were obtained only when the number of methylene groups in the hydrocarbon tail was higher than 5 in alkanethiols [14] and 10 in alkyltrichlorosilane [15], emphasizing that hydrophobic interactions between the hydrocarbon tails of immobilized molecules contribute to the stability and other properties of such films [3].

Along these lines, we have studied symmetrically substituted long chain viologens, (compounds (I) through (III)), and their mixtures with arachidic acid (eicosanoic acid) (AA) with respect to the physical properties of their films at the air-water interface, and the electrochemistry of their monolayers on ITO,
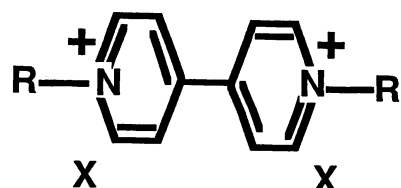
COMPOUND	STRUCTURE OF R = R'	X
I or $(C_{16})_2V$	$-(CH_2)_{15}CH_3$	Br
II or $(C_{18})_2V$	$-(CH_2)_{17}CH_3$	Br
III or $(C_{22})_2V$	$-(CH_2)_{21}CH_3$	Br

with the intention of gaining insight into the structure of the surface films formed by these molecules and how the alkyl chain length contributes to film stability. To our knowledge this represents the first systematic study of films of symmetrically substituted viologens with long hydrocarbon tails (number of carbon atoms greater than 7).

Experimental section

MATERIALS

Organic solvents were obtained from either J. T. Baker (Phillipsburg, NJ) or Fisher Scientific. House distilled water was deionized by passing through a four-cartridge Milli-Q reagent water system (Millipore, El Paso, TX). Aqueous solutions were filtered through 0.2 μm Nylon-66 filters (Rainin Instrument Co., Inc., Woburn, MA). Inorganic salts were obtained from Fisher Scientific (Certified ACS Grade) and were used without further purification. The viologens (I-III) were synthesized and purified by published procedures[16, 17].

EQUIPMENT

All monolayer preparations and transfers were performed on a Lauda preparative film balance, model P (Brinkmann Instruments Co., Westbury, NY). Pressure-area (Π-A) isotherms were recorded on a Brinkmann X-Y, Y-T multirange recorder, model BR-1101. The film balance temperature was controlled with a Lauda model RMS-6 refrigerating circulator (Brinkmann Instruments) to within 0.5° C or better. Electrochemical measurements were made on a Princeton Applied Research (PAR) system consisting of a model 175 universal programmer, a model 173 potentiostat, and a Houston Instruments model 2000 X-Y recorder. All electrode potentials were referenced to a saturated calomel electrode (SCE). Platinum gauze was used as an auxiliary electrode and measurements were made in nitrogen-deaereated solutions. Contact angles were measured on a Ramé-Hart (Mountain Lakes, NJ) model 100 goniometer, equipped with a tilting sample stage.

CLEANING OF IN-DOPED TIN OXIDE (ITO) SUBSTRATES FOR COATING

ITO pieces (Delta Technologies, White Bear Lakes, MN) were sonicated sequentially in 10% Alkonox detergent solution, water, absolute ethanol, and water for 10 min each. They were then oven dried at 120° C for 2 h and stored in a desiccator over Drierite.

MONOLAYER PREPARATION AND DEPOSITION PROCEDURES

The subphase solutions were prepared just before use. Viologen samples were dissolved in a 19:1 chloroform-methanol mixture while AA was dissolved in neat chloroform. All surfactant spreading solutions were about 3 mM in concentration. In a typical experiment, 20 to 50 μL of the spreading solution was delivered, dropwise, from a gas tight syringe (Hamilton Co., Reno, NV) held very close to the subphase surface and the spreading solvent was given 15 min to evaporate. The initial surface density of all the films was such that the pressure on the measuring barrier did not exceed 1 dyne/cm. Attempts to spread higher amounts of surfactants led to collapsed films at low surface pressures, as found by other workers[6]. Pressure-area isotherms were recorded at a constant compression rate of 9 Å²/molecule/min. Film stability was checked by determining the rate of film loss under constant pressure. An acceptable viologen film did not change by more than 1% in area in the first hour. Limiting areas were estimated by extrapolating the linear rising portions of the Π-A isotherm to zero pressure, i.e., the molecular area axis (see Fig. 1B).

In deposition studies, the film was compressed to a pressure of 15 to 30 dyne/cm and the automatic constant pressure mode activated. LB films were transferred at 20 to 25 dyne/cm onto the ITO piece by withdrawing the substrate from the subphase through the preformed film at the air-water interface at a speed of 0.5 cm/min. All depositions were conducted at room temperature (23 ± 2° C).

ITO electrodes were also derivatized with the viologens by simply exposing the precleaned substrates to millimolar solutions of the compounds in CH_2Cl_2 for at least 2 h at room temperature. These were then rinsed with CH_2Cl_2 and water and dried under a N_2 jet. Longer soaking in the CH_2Cl_2 did not improve the film quality or increase the amount of material adsorbed.

CONTACT ANGLE MEASUREMENTS

Contact angle measurements were made with Milli-Q water under ambient conditions. Water drops (0.01 mL) were placed at four different spots on the substrate surface and three measurements of contact angles (two at 0° and one at a 45° angle of platform inclination) were made at each spot. The mean of these measurements, over the four spots, is reported. Receding angles were measured at a 45° angle of platform inclination, and the mean difference between the angles measured at that plane inclination are reported as the contact angle hysteresis.

MOLECULAR AREA PROJECTION

Estimates for the surface-projected molecular areas at the limiting orientation of the viologen head goup were made by taking the width of the bipyridine molecule to be 6.69 Å[3a]. Assuming that each pyridinium group is symmetrical and has a length of 6.69 Å, the 1-1' C–C bond is 1.51 Å[13b] and the first methylene unit of each alkyl tail is constrained to the plane of the head group; a length of 17.6 Å is obtained for the horizontally oriented head group. These yield projected areas of 120.2 and 44.8 Å² for the immobile flat-lying and the vertically-oriented head groups, respectively.

ELECTROCHEMISTRY OF FILMS ON ITO

For electrochemical studies, films were transferred onto ITO supports (geometrical area of about 1.5 cm²) at 20 dyne/cm, with a solution of 0.3 M Na_2SO_4 and 0.1 M NaBr as the subphase. A thoroughly N_2-degassed solution of 0.2 M Na_2SO_4 (pH = 4.7) was used in the cell to preserve the integrity of the transferred films during electrochemical measurements.

Results and discussions

SURFACE PRESSURE-RESIDUAL AREA (Π-A) ISOTHERMS

The surface pressure-area isotherms of a typical symmetrically substituted long chain viologen, I, at the air-water interface on several subphases are shown in Figure 1. In general, depending on the subphase composition, the curves deviate from
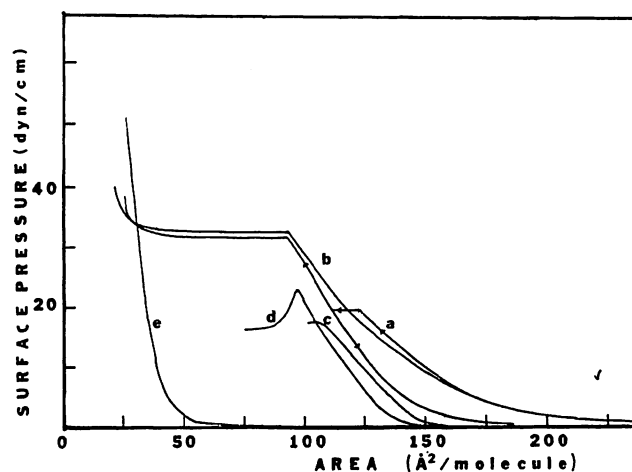

Figure 1 (a). — Surface pressure-molecular area curves for I on aqueous subphases containing: (a) 0.10 M KCl, (b) 10^{-3} M K_2SO_4, (c) 10^{-3} M $NaClO_4$, (d) 10^{-3} M KSCN, (e) 10^{-3} M KPF_6.

the baseline in the range of 100-200 Å²/molecule. This corresponds to the conditions under which the spread molecules start forming homogeneous/coherent films, i.e., the so called expanded region[4b]. Each curve, except e, is characterized by a long flat region in the range of 50-125 Å²/molecule, in which film compression did not produce changes in the surface pressure. This region corresponds to the intermediate state of the film, at which a new element enters the liquid-like phase. The new element is proposed to be the formation of two-dimensional aggregates such as micelles and liquid crystals, in which the hydrocarbon chains interact to form close-packed bundles[4b, 7, 18]. Below 50 Å²/molecule, in all cases, the surface pressure rises rather rapidly as the film is further compressed, and white crystals appeared at the air-water interface due to multilayer aggregation and film collapse. The limiting area associated with the latter discontinuity in the isotherm is of the same order as the surface-projected area of a perpendicularly oriented bipyridine group, of 45 ± 2 Å² for $C_{18}VMe^{2+}$, suggesting that the bipyridine head group is oriented almost vertically under these conditions[3, 12]. The films could be compressed and reexpanded reversibly, with no hysteresis, at all pressures up to the onset of the crystal appearance beyond which the film reexpands very slowly. Metzger et al. observed similar transitions in the pressure-area isotherms of such compounds as (4-(bis(dodecyl)amino)phenyl) carbamate-2-(hydroxymethyl)-11, 11, 12, 12-tetracyanoanthraquinodimethan at the air-water interface[7]. At the low residual areas required for the second inflection of the isotherm, surfactant loss by such processes as dissolution in subphase and solidification could potentially lead to pressure drops. However, judging from the reproducibility of the limiting pressures and areas observed, no such losses could be discerned.

The shapes of the isotherms, and consequently the details of the molecular organization in the surfactant films, depend on the composition of the subphase employed[4], i.e., the Π-A curves depend markedly on the counterions (anions) present in the subphase[6, 20]. On pure KCl and K_2SO_4 subphases, the isotherms start to deviate from the baseline at about 200 Å²/molecule, then the surface pressure rises rapidly to the onset of the surface aggregation. This is followed by an intermediate region, and further compression below 50 Å²/molecule produces another steep rise in pressure with decreasing area. On these subphases, the first transition yields a limiting area of 150 to 175 Å² per molecule, whereas the second affords about 35 Å² per molecule as the limiting area. On KSCN and $NaClO_4$ subphases the limiting area associated with the onset of aggregation decreases to about 125 Å² per molecule. The isotherm on the ClO_4^- subphase used in this work can be contrasted with those obtained for the unsymmetrically substituted viologens ($C_{16}VMe$ and $C_{18}VMe$) which exhibited only one transition under similar conditions[12]. The appearance of the intermediate stage in the isotherms appears to be related to the structure of the surfactant employed in this study, since the alkyl chain lengths were the same in both groups of viologens with the only difference being the symmetry of substitution.

Similar but much sharper transitions were observed in the isotherms measured on subphases containing both Br⁻ and SO_4^{2-} anions as shown in Figure 1B. Even small amounts of strongly associating anions, such as Br⁻ introduced into the film with the surfactant as counterions, can lead to detectable changes in the observed isotherms[6, 19]. Thus, because the viologens were in the form of Br⁻ salts, the experiments with pure viologen were conducted on a subphase containing 0.3 M $Na_2SO_4$and 0.1 M NaBr. The limiting areas of the various viologens studied in this work, on this subphase, are collected in Table I. The limiting areas obtained at the first transition in the isotherms are consistent with the 4, 4'-bypiridine head groups
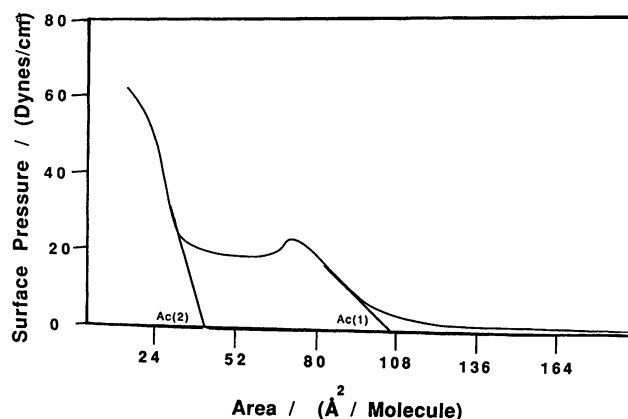

Figure 1 (b). — Surface pressure-molecular area curve for I on 0.3 M Na_2SO_4 and 0.1 M NaBr.

lying flat on the liquid surface (Fig. 2A), whereas those corresponding to the second inflection appear to indicate an edge-on orientation of the head group (Fig. 2B). The overshoot at the first transition point, as shown in Figure 2B, was characteristic of all of the symmetrical amphiphilic viologen films studied on this subphase. They were reproducible at all compression rates and over the temperature range studied (5-33° C).
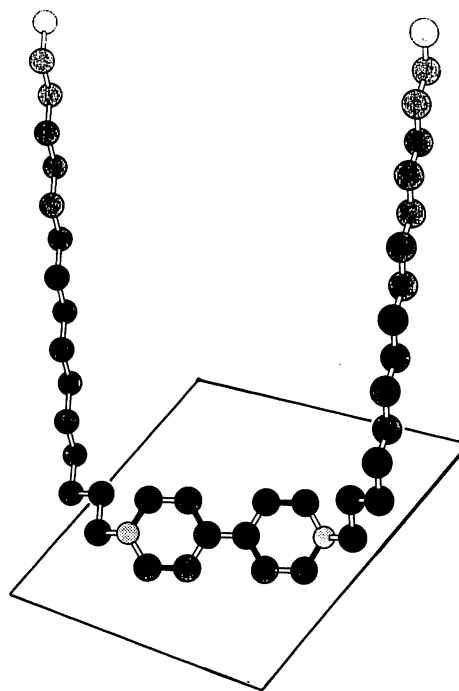

Figure 2 (a). — Possible molecular orientation of viologen units at large limiting areas (~ 150 Å²/molecule). Anions and solvent not shown.

On a KPF_6 subphase, only one transition was observed, with a limiting area of about 42 Å²/molecule for I; i.e., the film is essentially condensed at low surface pressures at room temperature. This unusual behavior can be attributed to the hydrophobic character of the anion, which encourages tight ion pairing in the film[20]. This reflects some subphase penetration into the surfactant film and illustrates how the subphase composition can influence the observed properties of the films. Such ion pair-induced film condensation is common with ionized films on salt subphases[6].

Expanded isotherms arise when the immersion requirements of the head group result in a tilting of the tail groups away from
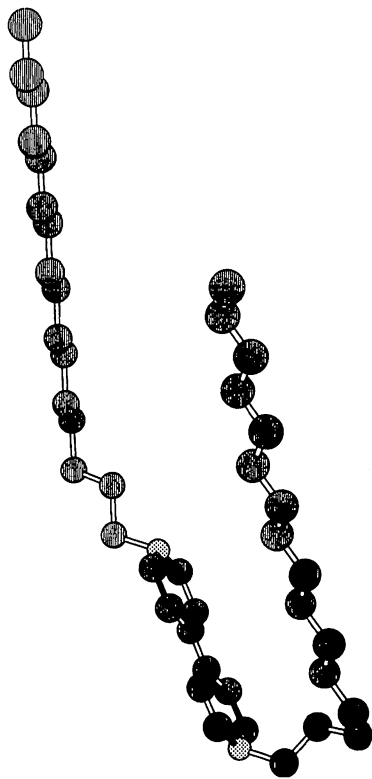
Figure 2 (b). — Possible molecular orientation of viologen units at small limiting areas ($\sim$ 50 Å^2/molecule). Anions and solvent not shown.

the vertical position, while the nature of the aggregates formed depends on the structure of the amphiphiles [18]. At large molecular areas it can be inferred that the hydrocarbon tails probably point away from the vertical, since the limiting area depends on the length of the hydrocarbon tail group of the compound. Such an orientation of the surfactant molecules, with head groups lying flat on the surface and tails pointing away from vertical, will exclude some area around each head group into which other molecules cannot intrude without the tails interacting. When the film compression forces the tails to within the interaction separation, they aggregate to minimize the surface free energy. Thus, the aggregation can be viewed as an activated process and the work required to bring the molecules to within micellation separation will depend on the length of the hydrocarbon chain.

The enthalpy of the aggregation was calculated from the temperature dependence of the pressures (Π_c) and the limiting areas (A_c) at the transition points, with the two-dimensional analogue of the Clausius-Clapeyron equation:

$$\frac{d\Pi_c}{dT} = \frac{\Delta H}{T\Delta A} \tag{1}$$

where ($d\Pi_c/dT$) is the slope of the Π_c as a function of temperature, ΔA is the change in molecular area accompanying the phase transition ($A_{c1} - A_{c2}$), and T is the temperature (K) [21-24].

The calculated enthalpy changes range from $-$ 38 kJ/mol for I, to $-$ 52 kJ/mol for III (Table I). These enthalpy values compare favorably with the literature value of $-$ 40 kJ/mol obtained for the phase changes in bolaform amphiphiles with rigid hydrophobic bixin cores, which was attributed to a rearrangement of the two dimensional monolayer [7b].

In these viologen films, the transition from the intermediate state to the fully condensed film apparently involves both the erection of the head group to a position perpendicular to the in-

Table I. – Molecular limiting areas and enthalpy changes associated with discontinuities in the pressure-area isotherms for compounds I-III at the air-water interface on (0.3 M Na$_2$SO$_4$ + 0.1 M NaBr).

Compound	R	Ac $(1)^a$	$Ac(2)^b$	ΔH^c/kJ mol^{-1}
I	C$_{16}$H$_{33}$	110 ± 10	30 ± 10	38.0
II	C$_{18}$H$_{37}$	140 ± 10	40 ± 10	47.5
III	C$_{22}$H$_{45}$	160 ± 10	50 ± 10	52.5

[a] Limiting area associated with the discontinuity at large areas, in units of Å^2/molecule; [b] Limiting area associated with the discontinuity at low areas, in units of Å^2/molecule; [c] Enthalpy of aggregation.

terface and rearrangement of the hydrocarbon tails, as indicated by the limiting areas obtained for the fully compressed films and their dependence on the length of the hydrocarbon tails. Both of these processes probably contribute to the observed enthalpy changes. The energetics of phase changes in charged films, as described above, also depend on the amount and nature of the counterions in the subphase [19, 25]. Thus, provision must also be made for the rearrangement of the surfactant-subphase ion pair in any model of the observed energetics of the phase changes.

When films are transferred by lifting an ITO electrode through an interface, the pressure at the film should relax to near that at the foot of the first transition. Thus these LB films should be essentially in the form of the head group lying flat on the ITO surface, presumably with incorporated anions for charge neutrality, with a limiting area of about A_{c1}.

MIXED FILMS OF VIOLOGEN SURFACTANTS AND ARACHIDIC ACID

Figure 3 shows surface pressure-area isotherms of mixed films of viologen I and AA on 0.1 M KCl. The isotherms were recorded as a function of the molar concentrations of I and AA in the spreading solution (τ = [I]/[AA]) and the abscissa is calculated in terms of the area per AA molecule. The limiting area per molecule of I in the mixed film with AA was calculated by the formula:

$$A_{s'} = (A_I - A_{AA})/\tau \tag{2}$$

where A_I is the final limiting area of I in its pure film and A_{AA} is the corresponding quantity for pure AA, both on 0.1 M KCl.
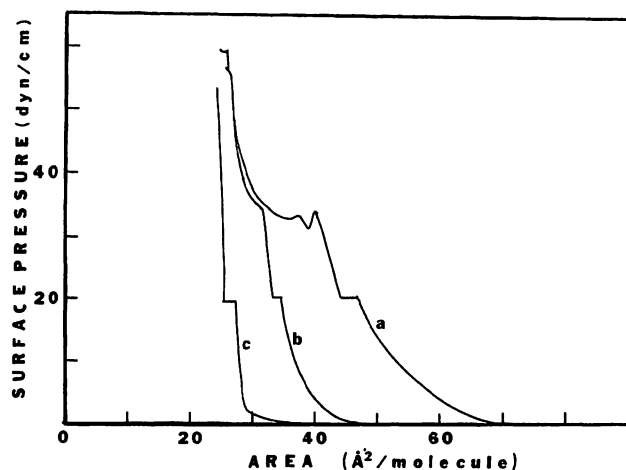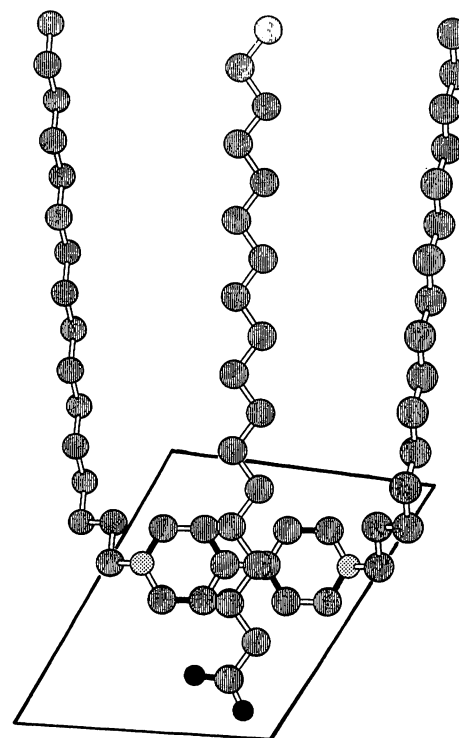

Figure 3. — Surface pressure as a function of residual area per arachidic acid for mixed films with I at various mixing ratios (τ = [I]/[AA]) in spreading solution, on 0.1 M KCl (pH = 5.5); (a) τ = 0.4; (b) τ = 0.3, (c)τ = 0.2.

Table II. – Dependence of the apparent limiting area of I on the mixing ratio (τ) with arachidic acid, in 0.10 M KCl.

τ	Limiting area/Å^2 unit[a]
∞	175
0.4	96
0.3	60
0.2	45

[a] Calculated according to equation 2; assuming A_{AA} = 20 Å^2/molecule.

The film properties were strongly dependent on the mixing ratios. The smaller the τ value (i.e., the higher the relative amount of AA in the film), the more condensed the film. This strongly suggests that specific interactions, such as van der Waals forces, operate between the viologen and the AA molecules and is consistent with the observations of other workers[6]. Table II lists the values of the calculated limiting areas per viologen molecule at different values of τ. An area of about 45 Å^2 per molecule at τ of 0.2 corresponds roughly to the cross section of two hydrocarbon chains or just the projected area of the vertically oriented bipyridine head group. This suggests that either the bipyridine head groups or the AA molecules do not make any contribution to the limiting area. This, however, is due to the non-additivity of the limiting molecular areas in intimately mixed films[4c], as illustrated in Figure 4.

MOLECULAR ORIENTATION FROM CONTACT ANGLE DATA

Contact angles are sensitive to surface polarity, while the contact angle hysteresis is an index of the surface uniformity; both are good probes of the local order in the surface films[15]. Table III compares the contact angles and the contact angle hysteresis of water on films of the amphiphilic viologens and arachidic acid on ITO. In general, the contact angles on the LB films are higher than on the adsorbed films, which reflects a greater hydrophobicity of the surfaces of the LB films. In the LB films, the applied surface pressure forces the surfactant molecules to adopt a more organized conformation which exposes more of the hydrocarbon tails and less of the ITO surface. In contrast, the lower angles on the absorbed films may be attributed to a more random orientation of the hydrocarbon tails which makes it possible for the water to interact to some extent with the ITO surface and the polar head groups, as well as lower coverage by the surfactant. The magnitudes of the contact angles observed on both LB and adsorbed films were too low to represent a predominantly hydrocarbon-covered surface; they did not change significantly with transfer pressure. The relatively low contact angles of the viologen films can be attributed, in part, to the poor packing of the hydrocarbon tails in the presence of the counterions to the charged head groups. Further-

Figure 4. — Possible molecular orientations in a compact mixed monolayer of viologen and arachidic acid.

more, in the flat head group configuration the two dimensional motion of the hydrocarbon tails may exclude some area around the molecules, which can prevent the tails from packing tightly enough to yield high contact angles. Since contact angles below 10° were not observed, there were probably no macroscopic patches of bare ITO on the surface. Clean ITO surfaces routinely yielded contact angles of less than 10° with water. The observed contact angle hysteresis also did not vary significantly with packing conditions, but appeared to increase slightly with increasing alkyl chain length. This is further support for the absence of isolated macroscopic domains of surfactants in the films studied.

The contact angle of LB films of AA transferred under the same conditions as the viologens is about 56°, whereas that on an adsorbed AA film on the same substrate is 107 ± 7°. The former values are indicative of exposed or accessible carboxylate head groups[15b], while the latter values are indicative of a compact hydrocarbon interface.

The contact angles of water on fatty acid films have been demonstrated to decrease on prolonged contact with water (on the order of hours) and with interfacial aging. These observations have been attributed to the reorientation of the fatty acid molecules in the LB films[15c]. With LB films of stearic, myristic, and

**Table III.** – Contact angle data for Milli-Q water on films on ITO compounds[a].

Compound	LB films		Self adsorbed films	
	Contact Angle	Hysteresis	Contact Angle	Hysteresis
I	50 ± 3	9 ± 5	49 ± 3	7 ± 5
II	63 ± 5	18 ± 3	48 ± 8	14 ± 6
III	61 ± 4	21 ± 3	46 ± 2	13 ± 3
AA	56 ± 8	20 ± 3	107 ± 5	28 ± 5

[a] LB films of I to III formed from a subphase of 0.3 M NaSO₄ and 0.1 M NaBr; LB films of AA from 0.1 M KCl (pH = 6). Self adsorbed films produced by immersing the ITO electrodes in CH₂Cl₂ solutions of the Br⁻ salts of I to III, followed by rinsing with CH₂Cl₂ and water. AA films made by exposing ITO to a 1 mM AA solution in CH₂Cl₂: MeOH (19:1). The contact angle of clean ITO was < 10°.

lauric acids, equilibrium contact angle measurements indicate that about 50% of the immobilized molecules reorient at 25° C. The activation energy of the molecular reorientation (~ 28 kcal/mol) is reasonably close to the calculated cohesive energy of stearic acid (~ 25 kcal/mol) [15c]. This would imply that in a compact adsorbed film there is little or no rotation, while reorientation can occur more readily in the LB film.

CYCLIC VOLTAMMETRY OF THE SURFACE IMMOBILIZED FILMS

Table IV summarizes the electrochemical characteristics of the immobilized viologen films on ITO, and Figure 5 shows a series of cyclic voltammograms for the one electron reduction of a typical LB film of a viologen, I, at a scan rate (v) of 50 to 500 mV/s. The onset of ITO reduction at about − 0.7 V and the onset of the second reduction of the viologen prevent the complete resolution of the first reduction peak.
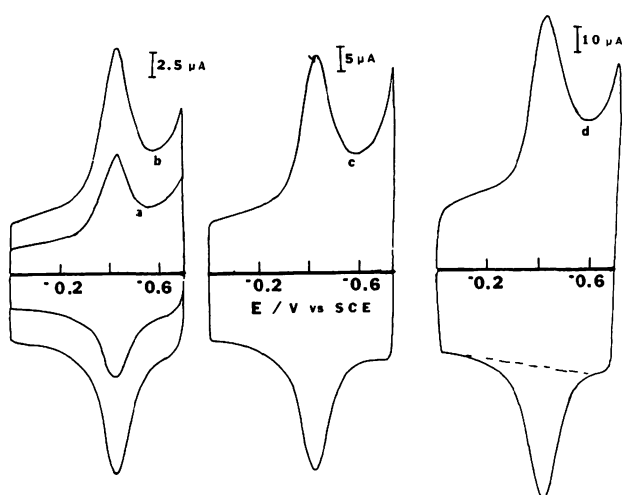
Figure 5. — Cyclic voltammograms of monolayers of $(C_{16})_2V^{2+}$ transferred onto ITO (electrode area: 1.46 cm^2) at 20 dyne/cm from 0.3 M Na$_2$SO$_4$ - air interface, in 0.20 M Na$_2$SO$_4$ electrolyte at scan rates of (a) 50, (b) 100, (c) 200, and (d) 500 mV/s.

The difference between the cathodic and anodic peak potentials, ΔE_p, for the LB films of I and II generally ranged from about 10 to 40 mV; for III, however, the peak splitting was about 110 mV. ΔE_p increased with increasing v, implying that a kinetic limitation, e.g., slow electron transfer, or slow structural changes [1,3b] accompany the charge transfer or that there is film resistance. In the adsorbed films, the ΔE_p of I and II were slightly larger than in the LB films, with III again showing a much larger value, suggesting that a slow process also occurred in the adsorbed film of this compound.

The orientation of viologen cation radicals in monolayer assemblies depend on the nature of the substituents on the head group, as well as on the anions [27]. For example, by examining the absorbance of p-polarized UV-visible radiation the head groups of I in mixed monolayers were shown to be inclined at 46° to the substrate surface [27a]. Viologen films can also reorient fairly rapidly (in a matter of minutes) from lying flat to an oblique position, and then assume random orientations with time [27b]. Slow rearrangements during electron transfer result in peak splittings larger than those for nernstian waves.

A reversible one-electron surface wave should have a peak width at half height ($\Delta E_{1/2}$) of 90.6 mV. However, values of 130 mV were obtained for the LB films of I and II, while a value of 100 mV was obtained for III. The peak broadening may be indicative of repulsive interactions between the immobilized electroactive surfactant molecules, e.g., coulombic repulsions between the dicationic head groups [28]. The narrower peak obtained for III suggests that the attractive interactions of the longer tails may compensate for the repulsive interaction between the head groups. The redox peaks of the adsorbed films were generally broader than those of the corresponding LB film peaks, with the broadness increasing strongly with the length of the alkyl chains on the head group. This broadening might be caused by the overlay of a number of closely spaced peaks with slightly different E_p values, resulting from different conformations in the freely formed film [1]. Thus we attribute the peak broadening in the LB films to intrafilm interactions, and that in the adsorbed films to an overlay of a number of peaks. Alternatively, the peak broadening could also result from the aggregation of the radical cations as the reduced film ages. The fact that the peaks are narrower for LB films of III suggests a relatively small film reconstruction in relation to films of I and II. In contrast, there is a significant film restructuring in I and II. Rearrangements in amphiphilic viologen films are said to lead eventually to the formation of micelles on the substrate [27b]. Thus, it could be that films of III contain preformed aggregates while those of I and II are transformed into micelles upon charge injection. If the immobilized amphiphiles form micelles, then the interaction between the head groups would decrease with increasing alkyl tail chain length. The radii of the micelles would increase with the increasing chain length; thus increasing the separation between the head groups.

The cathodic peak current, $i_{p,c}$, corrected for background, varied linearly with v up to 200 mV/s, with a less rapid increase at faster scan rates. Stirring the electrolyte solution did not affect either the shapes or the currents of the voltammograms, as would be expected for a surface immobilized redox couple. The amount of reduction charge passed was evaluated by graphical integration of the background-corrected voltammograms, as shown in Figure 5; the surface coverages (Γ_c) obtained for films transferred at 20 dyne/cm are given in Table IV. The co-

Table IV. – Electrochemical data for LB films and self adsorbed films on ITO [a].

Compound	E_p/V vs SCE	ΔE_p/mV	$\Delta E_{1/2}$/mV	$10^{-10}\ \Gamma_c$/mol cm^{-2}
LB films				
I	− 0.420	20	130	1.4
II	− 0.450	20	130	1.6
III	− 0.435	110	100	2.0
Self adsorbed films				
I	− 0.445	30	140	0.5
II	− 0.420	30	190	1.4
III	− 0.450	100	250	1.1

[a] Data pertain to $v = 200$ mV; solution = 0.2 M Na$_2$SO$_4$.

Table V. – Dependence of the charge under the cathodic wave (Q_c) of an LB film of I on ITO ^{a}.

v/mV s^{-1}	10^{10} Γ_v/mol cm^{-2}
50	1.4
100	1.4
200	1.4
500	1.3

^{a} Films was transferred at 20 dyne/cm. Measurements were made in N$_2$-degassed 0.2 M Na$_2$SO$_4$ solution, under N$_2$ blanket.

verages in both types of films were about the same, within the precision of the measurements, and was 1×10^{-10} mol/cm^2 ($\sim$ 180 Å^2/molecule). Such coverages are in accord with head groups lying flat on the electrode. Γ_c was independent of scan rate from 50 to 500 mV/s, within 10% for the LB film of I (Table V). This suggests that all of the electroactive centers in these films are in contact with the electrode, in contrast with the observations of other workers[9, 27b].

The double layer capacitance of the electrode (C_d) is a function of the structure of the electrode-solution interface, and is a measure of the charge distribution at the electrode surface[29]. It is thus an index to the compactness of immobilized films on modified electrodes. Whereas for the bare ITO electrode, C_d is 35 µF/cm^2, the LB and adsorbed film-coated electrodes exhibited capacitances of 28 and 17 µF/cm^2, respectively, as determined from the charging currents in voltammograms at v = 200 mV/s in 0.2 M Na$_2$SO$_4$. These measured capacitances were independent of scan rate. The observed capacitance values suggest that the counterions in the film are almost as close to the electrode surface as those in the absence of the film.

Film porosity was evaluated by comparing the area normalized current and the peak to peak separation (ΔE_p) of a redox probe on bare and film-coated electrodes. On the film-coated electrodes, only a 10% diminution was observed in the reduction current, of 2 mM Ru (bpy)$_3^{3+}$, relative to the bare electrode. The ΔE_p value was unaltered in the presence of the im-

mobilized film. The electrochemical behavior of the viologen films did not change in the presence of the Ru (bpy)$_3^{2+/3+}$ probe. The small current decrease and the insensitivity of ΔE_p of the probe to the presence of the film strongly suggests that either the electrode is only partly covered[29b] or the film is highly porous. Since transfer ratios of close to unity were observed on all of the LB film transfers, we attribute the high penetration to the film being rather loosely packed.

The compounds under study were insoluble in aqueous media and were very slightly soluble in acetonitrile, hence we were unable to study their solution phase electrochemistry. However, as long as the substituent groups on the electroactive center do not interact with its π-electron system and the reduced (radical cation) species dimerize to same extent, the reduction potentials of these compounds are expected to be almost identical. Thus, for comparison, we have adopted the reduction potential of methyl viologen (MV^{2+}) in aqueous media, – 0.69 V/SCE, as their reference formal potential[30]. The mean value of $E_{p, c}$ and $E_{p, a}$ ranged from – 0.42 to – 0.45 V vs SCE at a sweep rate of 200 mV/s, at least 250 mV more positive than the MV$^{2+/+}$ potential. A possible explanation for the large observed potential shift lies in the differences in the stabilities of the parent viologen and the monocationic product of the reduction process. The latter is probably stabilized by improved hydrophobic interactions within the film[3a]. Thus, the observed shifts in redox potentials may be attributed to the difference between the free energy of aggregation and the simple one electron reduction process.

Table VI is a comparison of the redox potentials ($E_{1/2}$) for the first one-electron reduction of a number of viologens. The $E_{1/2}$-values of the immobilized materials are all shifted positive with respect to that of dissolved MV^{2+} in aqueous media. A comparison of the E_p values of [C$_{10}$VC$_{10}$SH]$^{2+}$ immobilized on a gold electrode in different media illustrates the effect of supporting electrolyte on these values. In ClO$_4^-$ media, the E_p values are shifted to more negative potentials compared to Cl$^-$, although not as negative as that of dissolved MV^{2+}. This, together with the observed decrease in electrode capacitance in ClO$_4^-$ media, has been interpreted to mean that the self assembled films of
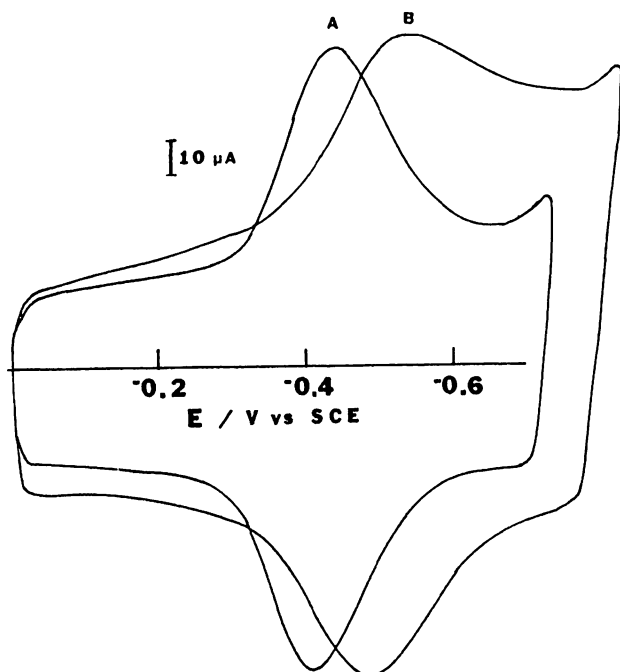
Table VI. – Redox potentials for the first one-electron reduction of selected viologens.

Viologen	$E_{1/2}$/V vs SCE	Conditions	Ref.
[(C$_{16}$)$_2$V]Br$_2$ (I)	– 0.42	LB films on ITO, in 0.2 M Na$_2$SO$_4$.	This work
[(C$_{18}$)$_2$V]Br$_2$ (II)	– 0.45	LB films on ITO, in 0.2 M Na$_2$SO$_4$.	This work
[(C$_{22}$)$_2$V]Br$_2$ (III)	– 0.44	LB films on ITO, in 0.2 M Na$_2$SO$_4$.	This work
[(C$_{16}$VMe]Br$_2$	– 0.49	LB films on ITO, in 0.2 M NaClO$_4$.	12
[C$_{22}$VMe]Br$_2$	– 0.54	LB films on ITO, in 0.1 M NaClO$_4$.	12
[C$_{10}$VC$_{10}$SH]$^{2+}$	– 0.35	Selft assembled film on gold, in 0.1 M NaCl.	3c
	– 0.5	Selft assembled film on gold, in 0.1 M NaClO$_4$.	3c
[C$_{18}$VC$_2$] $^{2+}$	– 0.47	Self assembled film on Pt or Au, in 0.2 M NaSO$_4$.	30g
[C$_{16}$VC$_2$]$^{2+}$	– 0.66	Intercalated in α-cyclodextrin, in 50 mM NaCl.	31b
[C$_{18}$VC$_2$]	$\sim$ – 0.66	Intercalated in α-cyclodextrin, in 50 mM NaCl.	31b
MV^{2+}	– 0.69	On glassy carbon, in 50 mM NaCl.	30a
	– 0.65	On glassy carbon, in 70 mM SDS, 50 mM NaCl.	30a
	– 0.68	On glassy carbon, in 5% w/v Triton-X100, 50 mM NaCl.	30a
	– 0.69	On glassy carbon, in 70 mM CTAB, 50 mM NaCl	30a
[(C$_8$)$_2$V]$^{2+}$	– 0.71	Not specified.	30b
[C$_{18}$VPy]$^{2+}$	– 0.90	Mixed self assembled film with C$_{16}$H$_{33}$SH on gold in 0.1 M KCl.	26
	– 0.78	Spin cast film of neat viologen on gold, in 0.1 M KCl.	26
[C$_{18}$VM]$^{2+}$	– 0.51	Adsorbed on gold, in 0.5 M KCl.	3a

$[C_{10}VC_{10}SH]^{2+}$ form much more compact films in ClO_4^- than in Cl^- media, due to the differences of specific anion-viologen interactions[3b].

Comparison of the E_p values of I, II, and III, as well as II and $[C_{18}VC_2]^{2+}$ films in 0.2 M Na_2SO_4 indicate that viologen symmetry of substitution makes little or no difference in determining the reduction potentials. Water and anions have been shown to be reversibly ejected from these films upon reduction and reincorporated upon reoxidation[3c]. This observation suggests that the film becomes more hydrophobic upon reduction. Any factor that enhances film hydrophobicity, such as increasing the number and length of alkyl chains on the viologen head group, would increase the stability of the reduced species. The conclusion from the results here, and previous studies of long chain viologens, is that the + 1 species is stabilized relative to the + 2 form by the less polar environment of the hydrocarbon chains. This relative stabilization is of the order of 0.2 eV or 19.3 kJ/mol.

Figure 6 is a comparison of the cyclic voltammograms of LB films of pure I and a I-AA mixture (at $\tau = 0.3$) on ITO. The voltammogram peaks of the mixed film are broadened (Table VII) and the peak potentials are shifted to more negative values compared to pure I. The peak potentials depend upon the AA content of the film; the larger was the AA content of the spreading solution, the more negative were the peak potentials, as il-
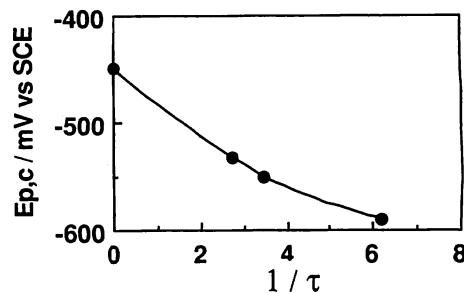
lustrated in Figure 7. The pressure-area isotherms of the mixed films of I and AA indicate an intimate mixing of the two surfactants over a wide range of mixing ratios in such a mixture. The dilution of I with AA diminishes the extent of coulombic repulsions between the I molecules, as well as increases the van der Waals interactions in the film[31]. There is also the possibility of ion pair formation between the carboxylate anions of AA and the viologen moiety[32] enhances the hydrophobic environment. Furthermore, the dilution and less polar environment presumably decrease the tendency of the monocations to dimerize. As in the adsorbed films of neat viologens, the peak broadening in these mixed films may be attributed to the overlap of a number of closely related peaks.

Figure 7 is quite informative in terms of the stabilization of the monocation viologen radical against dimerization. If ion pair formation were the most important mechanism for stabilizing MV^+, the redox potentials would shift negative with increasing amounts of AA in the film, up to the point where there are about two molecules AA to each I molecule. However, the change in redox potential with increasing AA concentration continues well beyond that point, with a fall off occurring when the film contains about a six-fold excess of the diluent. This suggests that the added AA contributes to the stabilization of the film as a result of the improved hydrophobic interactions between the hydrocarbon tails, as well as by coulombic effects.

Figure 6. — A comparison of the cyclic voltammograms of a pure viologen monolayer (A, electrode area: 1.51 cm^2) with that of a mixed film of the viologen with arachidic acid in ratio of 1:3.45 (B, electrode area: 1.62 cm^2). Subphase and supporting electrolyte were both 0.10 M KCl.

Figure 7. — Variation of the peak potential for the first reduction of I on ITO, in 0.2 M Na$_2$SO$_4$, in mixed films of I and AA with relative AA content of the film. (1/τ = [AA]/[I] in spreading solution).

Table VII. — Comparison of full width at half height ($\Delta E_{1/2}$) of the reduction peaks of neat (I) film with mixed, (I) + AA, film.

v/mV s^{-1}	$\Delta E_{1/2}$/mV	
	I	I + AA
50	110	170
100	120	170
200	130	170
500	130	170

The surface redox waves were very sensitive to the presence of dissolved oxygen in the electrolyte, and in well degassed solutions the voltammograms show essentially equal areas under cathodic and anodic peaks. As observed by Finklea et al., traces of oxygen in the electrochemical cell cause the cathodic peak to increase dramatically and the anodic peak to disappear[26]. In this study the integrated charge under the cathodic peak in an undegassed solution corresponded to about two and one half times that of the monolayer. This observation supports that of Finklea et al., that O$_2$ is reduced by the radical cation form in films.

Conclusions

The discontinuities in the pressure-area isotherms of the films of the symmetrically substituted viologens and their mixtures with arachidic acid at the air-water interface are attributed to a phase change which appears to involve a change in the head group position from lying flat on the surface to a more perpendicular position, and a reorganization of the hydrocarbon tails. The enthalpy change that accompanies the phase change depends on the length of the hydrocarbon tails; the longer are the tails, the higher are the energy requirements for the phase

change. Films of these compounds can be transferred or adsorbed onto solid indium tin oxide electrodes, and couloumetric assay shows monolayer coverage by the viologens to be in approximate agreement with areas deduced from isotherm measurements. Contact angle measurements and electrochemical permeation experiments indicate that the hydrocarbon chains are not tightly packed in either LB or self assembled films. This is attributed to the presence of anions in the films, and the inability of the molecules to pack well because of the size of the head groups.

The redox potentials for the first one-electron reduction of immobilized viologens are about 250 mV more positive than those for viologens in solution. This is attributed to stabilization of the + 1 form relative to the + 2 form because of the more hydrophobic environment. This is supported by the large peak to peak separations observed in the cyclic voltammograms and the fact that the redox potentials shift towards more negative potentials in mixed films with arachidic acid.

REFERENCES

[1] See e.g., Murray R. W., In "Electroanalytical Chemistry", Bard A. J., Ed., Marcel Dekker: New York, 1984, vol. 13, 191.

[2] (a) Kuhn H., Mobius D., Angew. Chem. Int. Ed. Engl., 1971, 10, 620; (b) Thin Solid Films, 1983, 99, 1; (c) ibid., 1985, 132-134, 1 (First and Second International Conference on Langmuir-Blodgett Films).

[3] (a) Widrig C. A., Majda M., Langmuir, 1989, 5, 689 and references therein; (b) De-Long H. C., Buttry D. A., Langmuir, 1990, 6, 1319.

[4] (a) Gaines G. L., Insoluble Monolayers at Liquid - Gas Interfaces, Wiley-Intersciences: New York, 1966, Chap. 8; (b) ibid, Chap. 4; (c) ibid, Chap. 6.

[5] Zhang X., Bard A. J., J. Phys. Chem., 1988, 92, 5566.

[6] Gaines G. L., Behnken P. E., Valenty S. J., J. Am. Chem. Soc., 1979, 100, 6549.

[7] (a) Metzger R. M., Schumaker R. R., Cava M. P., Laidlaw R. K., Penetta C. A., Torres E., Langmuir, 1988, 4, 298; (b) Metzger R. M., Wiser D. C., Laidlaw R. K., Takassi M. A., Mattern D. L., Panetta C. A., Langmuir, 1990, 6, 350.

[8] Mutsuda H., Aoki J., Tokuda K., J. Electroanal. Chem., 1987, 217 15.

[9] Daifuku H., Aoki K., Tokuda K., Matsuda H., J. Electroanal. Chem., 1985, 183, 1.

[10] Kuhn H., Mobius D., Bucher H., In Physical Methods of Chemistry; Weissberger A., Rossiter W. B., Eds.; Wiley: New York, 1972, Vol. 1, Part (III) B.

[11] (a) Facci J. S., Falcigno P. A., Gold J. M., Langmuir, 1986, 2, 723; (b) Facci J. S., Langmuir, 1987, 3, 525.

[12] (a) Lee C. W., Bard A. J., J. Electroanal. Chem., 1988, 239, 441; (b) Lee C. W., Bard A. J., Chem. Phys. Lett. 1990, 170, 57.

[13] (a) Willman K. W., Murray R. W., J. Electroanal Chem., 1982, 133, 211; (b) Chen P., Curry M., Meyer T. J., Inorg. Chem., 1989,

[28], 2271; (c) Russel J. H., Wallwork S. C., Acta. Cryst., 1972, B28, 1527; (d) Szentrimay R., Yeh P., Kuwana T., In "Electrochemical Studies of Biological Systems", Sawyer D. T., Ed.; American Chemical Society; Washington, D. C., 1977, 173.

[14] Netzer L., Iscovivi R., Sagiv J., Thin Solid Films, 1983, 100, 67.

[15] (a) Troughton E. B., Bain C. D., Whitesides G. M., Nuzzo R. G., Allara D. L., Porter M. D., Langmuir, 1988, 4, 365; (b) Holmes-Farley S. R., Reamly R. H., McCarthy T. J., Deutch J., Whitesides G. M., Langmuir, 1985, 1, 725; (c) Yianons P. N., J. Colloid Sci., 1962, 17, 334.

[16] Tundo P., Kippenberger D. J., Politi M. J., Klahn P., Fendler J. H., J. Am. Chem. Soc., 1982, 104, 5352.

[17] Bruinink J., Kregting C. G. A., Ponjee J. J., J. Electrochem. Soc., 1977, 124, 1854.

[18] (a) Kunitake T., Ohahata Y., Shimomura M., Yasunani S., Takarade K., J. Am. Chem. Soc., 1981, 103, 5401; (b) Cadenhead D. A., Demchak R. J., J. Chem. Phys., 1968, 49(3), 1372; (c) Knobler C. M., Science, 1990, 249, 870.

[19] (a) Goddard E. D., Kao O., Kung H. C., J. Colloid and Interface Sci., 1967, 24, 297; (b) Goddard E. D., Kao O., Kung H. C., J. Colloid and Interface Sci., 1968, 27, 616; (c) Goddard E. D., Croat. Chim. Acta, 1970, 42, 143; (d) Gaines G. L., J. Chem. Phys., 1978, 69(6), 2627.

[20] (a) Lewis N. A., Obeng Y. S., J. Am. Chem. Soc., 1988, 110, 2306; (b) Blackbourn R. L., Hupp J. T., Chem. Phys. Lett., 1988, 150, 399.

[21] Eriksson J. C., J. Colloid and Interface Sci., 1971, 37, 659.

[22] Stewart M. V., in Topics in Stereochemistry; Allingner N. L., Eliel E. L., Wilen S. H., Eds., Wiley, New York, 1982, 13, 195.

[23] Johansen O., Kowala C., Mau A. W. H., Aust. J. Chem., 1979, 32, 1453.

[24] Glazer J., Alexander A. E., Trans. Faraday Soc., 1951, 47, 401.

[25] Nakahara H., Fukuda K., Sato M., Thin Solid Films, 1985, 133, 1.

[26] (a) Bunding Lee K. A., Mowry R., McLennan G., Finklea H. O., J. Electroanal. Chem., 1988, 246, 217; (b) Finklea H. O., Fedyk J., Schwab J., In "Electroanalytical Surface Science", Soriage M. P., Ed.; ACS Symposium Series n° 378, ACS: Washington, D. C., 1988, 431.

[27] (a) Nagamura T., Isoda Y., Sakai K., Ogawa T., J. Chem. Soc. Chem. Commun., 1990, 703; (b) Bewick A., Cunningham D. W., Lowe A. C., Makromol. Chem. Macromol. Symp., 1987, 8, 355.

[28] (a) Laviron E., J. Electroanal. Chem., 1974, 52, 395; (b) Laviron E., Roullier L., J. Electroanal. Chem., 1980, 115, 65; (c) Daifuku H., Aoki K., Tokuda K., Matsuda H., J. Electroanal. Chem., 1985, 183, 1.

[29] (a) Bard A. J., Faulkner L. R., "Electrochemical Methods", Wiley New York, 1980, 7; (b) Sabatani E., Rubinstein I., J. Phys. Chem., 1987, 91, 6663.

[30] (a) Kaifer A. E., Bard A. J., J. Phys. Chem., 1985, 89, 4876; (b) Kawata T., Yamamoto M., Jpn. J. Appl. Phys., 1975, 14, 725; (c) Bird C. L., Kuhn A. T., Chem. Soc. Rev., 1981, 10, 4; (d) Willner I., Goren Z., Mandler D., Maidan R., Degani Y., J. Photochem., 1985, 28, 215; (e) Maidan R., Goren Z., Becker J. Y., Willner I., J. Am. Chem. Soc., 1984, 106, 6217; (f) Korower E. M., Cotter J. L., J. Am. Chem. Soc., 1964, 86, 5524; (g) Diaz A., Kaifer A., J. Electroanal. Chem., 1988, 249, 333.

[31] (a) Hayano S., Fujihira M., Bull. Chem. Soc. Jpn., 1971, 44, 2051; (b) Diaz A., Quintela P. A., Schuette J. M., Kaifer A. E., J. Phys. Chem., 1988, 92, 3537.

[32] Fujihira M., Araki T., Bull. Chem. Soc. Jpn., 1986, 59, 2375.