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2D Phase Transitions in Langmuir Monolayers of the Aromatic 4',5'-Diphenyl-1,1':3',1''-terphenyl-4-carboxylic Acid

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Langmuir monolayers of 4',5'-diphenyl-1,1':3',1''-terphenyl-4-carboxylic acid (in short DTCA) were studied under different experimental conditions. The π -A isotherms displayed a broad plateau on a pure water subphase and two plateaus on a neutral aqueous subphase containing Cd²⁺ ions. DTCA monolayers were transferred as LB multilayer films and characterized by FTIR, X-ray diffraction, and electric surface potential measurements. From the analysis of surface potentials for LB films transferred at surface pressures corresponding to different parts of the π -A isotherm it was possible to infer that molecular orientational changes are the probable cause for the plateau in the isotherm.

Introduction

The potential applications of the Langmuir–Blodgett (LB) method in technology as well as in fundamental science have stimulated research with a wide variety of monolayer-forming materials,¹ stemming from traditional amphiphiles such as fatty acids and long-chain alcohols, physiologically active compounds such as phospholipids, polypeptides, metalloproteins, and steroids² to macromolecular substances, e.g., polymers.³ Until recent years surprisingly little work has been done on the surface properties of amphiphiles whose hydrophobic part is solely arenic, except for investigations carried out by Demchak and co-workers^{4,5} who described the behavior of *p*-terphenylamine and *p*-terphenyl methyl esters spread on the air/water interface. However, due to their solubility in water, these compounds were capable of monolayer formation only under drastic experimental conditions (on an aqueous subphase containing 4 M NaCl and at 4 °C). Since purely aromatic amphiphiles seemed to represent an unexplored group of compounds, we have instituted a project to exploit a series of aromatic compounds in which the hydrophilic headgroup is connected to an uncondensed, nonrigid ring system.^{6–10} Such molecules can be considered

as the aromatic analogues of alkanolic amphiphiles. Furthermore, owing to the presence of π -electron systems, the structure of monolayers from such compounds is likely to be quite different from that of methylene analogues. Our previous studies have shown that the presence of at least four phenyl rings in the apolar core is necessary for a molecule to have a proper hydrophilic–hydrophobic balance required for Langmuir monolayer formation.⁷ This can be expected since the hydrophobicity of a phenylene group is comparable to that of four methylene groups,¹¹ and among homologues of long chain fatty acids, only those with at least 12 methylene groups are capable of forming stable and reproducible monolayers at the air–water interface.¹ In our research into molecules possessing a symmetrical triphenylbenzene ring system (5'-phenyl-*m*-terphenyl core) and different hydrophilic groups attached to the apolar part, either at the 4 or 4' position, we found that only molecules with the carboxylic headgroup at the 4 position are capable of a stable monolayer formation at the air/water interface.⁷ Detailed investigations of 5'-phenyl-1,1':3',1''-terphenyl-4-carboxylic acid (PTCA)⁸ and its 4' derivatives^{9,10} showed that the π -A isotherms exhibit a plateau transition region, which corresponds to a ratio of ca. 2 between the areas at the start and at the end of the plateau.^{6–10}

In the present work we investigate in detail monolayer properties of a 4'-phenyl derivative of PTCA, denoted as DTCA, using surface pressure and surface potential isotherms. Preliminary Langmuir isotherms of DTCA have already been shown in refs 9 and 10. The structures of PTCA (1), MPTCA (2), and DTCA (3) are shown in Scheme 1. Our interest also lies in studying the influence of factors that were found to play a critical role in determining the stability and transferability of the monolayer, i.e., the presence of multivalent ions in the aqueous subphase (especially cadmium ions), the subphase pH, and ionic strength. Results obtained with DTCA monolayers were compared with those of PTCA.

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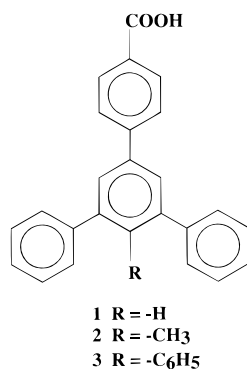
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Scheme 1. Chemical Structure of Investigated Aromatic Carboxylic Acids**II. Experimental Details**

4',5'-Diphenyl-1,1':3',1''-terphenyl-4-carboxylic acid (DTCA) was synthesized according to the method already described in ref 7, following the general procedure described by Zimmerman and Fischer.¹² Langmuir monolayers were prepared by spreading an aliquot of DTCA (0.4–0.45 g/L) dissolved in spectroscopic grade chloroform. Ultrapure water produced by a Nanopure (Infinity) water purification system coupled to a Milli-Q water purification system (resistivity = 18.2 MΩcm) was used as the subphase. The subphase temperature was controlled to within 0.1 °C by a circulating water system from Neslab. The ionic strength and pH of the subphase were adjusted by addition of HCl and NaCl, respectively. The molecules were spread on a subphase containing 4×10^{-4} M cadmium chloride and 5×10^{-5} M sodium bicarbonate, whose pH was ca. 6.0, for obtaining the monolayer of cadmium salt of DTCA. After spreading, the monolayers were left for 5 min for the solvent to evaporate and then compression was initiated. Routine monolayer studies were carried out with a KSV-5000 LB system (total area = 730.5 cm²), placed on an anti-vibration table in a class 10 000 clean room. The surface pressure of the floating monolayer was measured to an accuracy of 0.1 mNm⁻¹ using a Wilhelmy plate (made of chromatography paper, ashless Whatman Chr 1) connected to an electrobalance. Simultaneously, the surface potential was recorded using a vibrating plate located ca. 2 mm above the water surface. The reference electrode, made from platinum foil, was placed in the water subphase. The surface potential measurements were reproducible to ± 10 mV. Monolayers were usually compressed with a barrier speed of 25 mm/min (equivalent to a compression rate of 7.5×10^{17} Å²/min) unless otherwise specified. The monolayer stability was verified by monitoring the change in area per molecule while holding the surface pressure constant. Monolayers were transferred as LB multilayers at different target surface pressures with a dipping speed of 3 mm/min both in the up- and downstrokes. At the end of lifting the substrate from the subphase, the deposited monolayer was dried in air for 10 min. BK7 glass, thin gold evaporated glass, and calcium fluoride (CaF₂) plates were used as substrates that were cleaned thoroughly prior to use. The standard cleaning method (RCA)¹³ was applied for cleaning glass substrates while thin gold evaporated glass and calcium fluoride plates were rinsed in ultrapure water. FTIR measurements were carried out with a BOMEM-MB102 Michelson series instrument (128 scans, resolution 4 cm⁻¹) in the transmission mode. X-ray diffraction (XRD) measurements were made with a Rigaku Rotaflex (Model RU200B) X-ray diffractometer in the 2θ range of 3–20° using a Cu target. Surface potential measurements of the LB film deposited on gold/glass substrates were performed with a Trek 320B electrostatic voltmeter.

III. Results and Discussion

Langmuir Monolayers. A typical surface pressure–area (π – A) isotherm of DTCA on a pure water surface is shown in Figure 1, which also contains a π – A isotherm

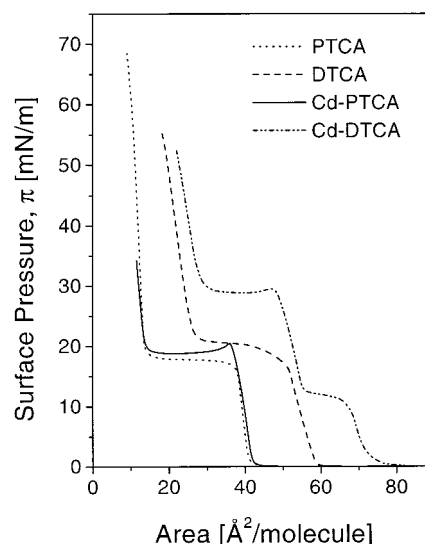


Figure 1. π – A isotherms of PTCA and DTCA spread on water and aqueous CdCl₂ + NaHCO₃ subphase (Cd-PTCA and Cd-DTCA) at 20 °C. Number of molecules spread = 1.05×10^{17} and compression speed = 25 mm/min.

of PTCA from ref 8 for comparison. As observed previously,^{9,10} the onset of surface pressure occurred at a larger molecular area for DTCA (ca. 60 Å²) than for PTCA (ca. 41 Å²). Except for this difference, the isotherms are similar, with three distinct parts: a liquid-condensed region, a clear plateau with a nearly 2-fold decrease in area/molecule, and a condensed region prior to collapse. The higher area per molecule for DTCA was expected due to the additional bulky phenyl substituent in the DTCA molecule. Earlier, we observed a similar but smaller increase in the limiting area for monolayers of PTCA with a methyl substituent (MPTCA, area ≈ 46 Å²).^{6,7} The areas of projection for vertically oriented molecules, modeled with the HyperChem computer program, for PTCA, MPTCA, and DTCA, are 44.8, 45.6, and 55.0 Å², respectively. The compressibility modulus isotherm for DTCA resembles that for PTCA,⁸ i.e., the compression modulus increases with the surface pressure upon compression in both pre- and post-plateau regions, while remaining low and constant within the plateau. The influence of various experimental parameters on the π – A isotherm of DTCA monolayers on pure water has been studied. No significant change could be observed while spreading 150–210 μ L of chloroform solution of DTCA (typical concentration is ca. 0.44 mg/mL). As for the subphase temperature, in the range between 10 and 20 °C, there is no significant change in the isotherm, but the plateau surface pressure was ca. 4 mN/m lower at the higher subphase temperature of 30 °C, in comparison to that recorded at 20 °C, analogous to that observed for PTCA.⁸ The time allowed for a monolayer spreading (5 or 30 min) before compression has no influence on the isotherms. The variation in compression speed from 5 mm/min (equivalent to 1.5×10^{17} Å²/min) to 125 mm/min (37×10^{17} Å²/min) did not alter the DTCA isotherm significantly, though a slightly higher plateau surface pressure was observed for the compression speed of 125 mm/min. Except for the case of introduction of cadmium ions, as discussed later, changing the subphase did not affect the behavior of DTCA monolayers either. This was observed for an acidic subphase (10^{-3} M HCl, pH ≈ 3.0) and a subphase with higher ionic strength (10^{-3} M NaCl, pH ≈ 6.0).

The results above indicate that the DTCA monolayer is compressed under equilibrium conditions and that the plateau region is not due to experimental artifacts deriving

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from nonequilibrium compression of the monolayer. Further evidence for the stability of the DTCA monolayer could be inferred through the hysteresis isotherm curves, which only appeared when the monolayer was compressed up to the plateau or post-plateau regions (the hysteresis curves are similar to those to be shown later for Cd-DTCA monolayers). No difference in the characteristics of subsequent isotherms was noticed when performing the hysteresis experiments continuously or allowing a 10 min break between successive compression–decompression cycles. The stability of DTCA monolayers on water was also studied by monitoring the decrease in area/molecule at different target surface pressures. In the pre-plateau region ($\pi = 10$ mN/m), the monolayer was very stable with a decrease in area by only about 2%. However, in the regions corresponding to the plateau (ca. 20 mN/m) and post-plateau (40 mN/m), the monolayer was less stable with a 10% decrease in area; in both cases ca. 60% of the total decrease occurred during the initial 10 min. DTCA monolayers are certainly more stable than the PTCA monolayer⁸ due to the incorporation of the phenyl substituent, which improved the hydrophilic–hydrophobic balance. In fact, PTCA containing four phenyl groups lies just on the borderline regarding the capability of monolayer formation, while DTCA, with five phenyl rings, exhibits better film-forming properties, as expected.

Interestingly, a quite different behavior was observed for DTCA monolayers spread on subphases containing cadmium ions, with two plateau transition regions, as shown in Figure 1. To the best of our knowledge, no monolayer study exists in the literature reporting such unusual behavior of the monolayer of any amphiphilic compound just with the addition of cadmium ions. Moreover, the surface pressure onset for the DTCA monolayer spread on aqueous Cd^{2+} solution appears at markedly larger molecular areas in comparison to the monolayer on the pure water subphase. This might suggest monolayer expansion, which is quite unexpected since for model amphiphilic fatty acid monolayers the addition of cadmium ions into the subphase results in a condensation effect, i.e., disappearance of the liquid condensed region, causing a shift of the surface pressure onset to smaller areas.¹⁴ Such changes have been correlated to the complexation of cadmium ions with $-\text{COOH}$ headgroups, which seems to provoke changes in the packing of fatty acid molecules¹⁴ so that there is no or only a little tilt of alkyl chains in the fatty acid salt.¹⁵ For a better understanding of this peculiar behavior of the DTCA monolayer, we performed further detailed monolayer experiments, as described below.

Figure 2a shows the effect of the concentration of cadmium ions in the subphase. The two plateau regions are visualized for the subphases containing cadmium chloride in concentration of 10^{-4} and 10^{-5} M and sodium bicarbonate (buffer added to maintain the subphase pH at approximately 6.0). But only one plateau at about 35 mN/m, which coincides with the second plateau in the other cases, was observed for the DTCA monolayer on the subphase with a micromolar concentration of cadmium ions. To distinguish between the influence of cadmium chloride and sodium bicarbonate on the appearance of the first plateau, a set of isotherms of DTCA were performed with subphases with only either cadmium chloride or sodium bicarbonate. As shown in the same graph, the isotherms obtained with only one component

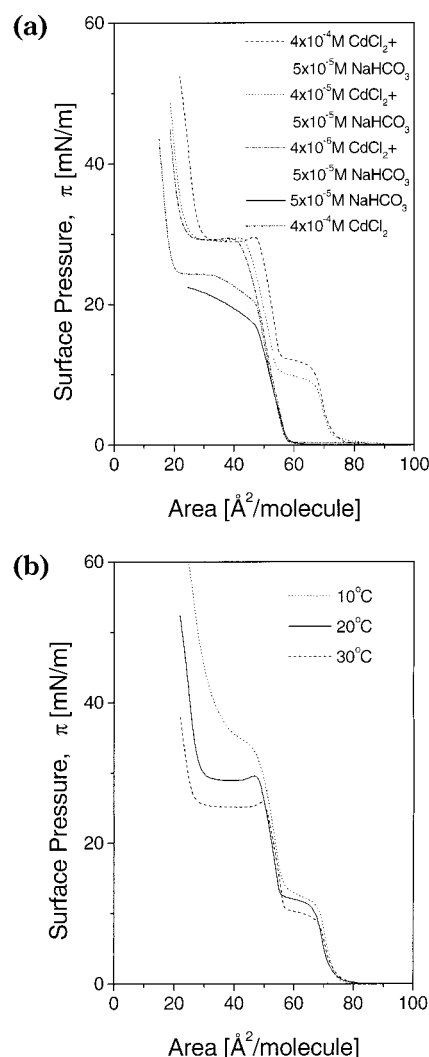


Figure 2. π - A isotherms of DTCA monolayer spread on aqueous subphases with different CdCl_2 concentrations, buffered to $\text{pH} \approx 6$ with NaHCO_3 and containing only CdCl_2 or NaHCO_3 . Compression speed = 25 mm/min, subphase temperature 20 °C.

(either cadmium chloride or sodium bicarbonate) resemble each other and exhibited only one plateau transition region, in contrast to the isotherm for the subphase containing both components. This clearly demonstrates that complexation of cadmium ions to the $-\text{COOH}$ headgroup and accompanying changes in the molecular packing at the air–water interface occur only at a subphase of $\text{pH} \approx 6.0$. With the addition of cadmium chloride into the subphase, the pH decreases due to the hydrolysis of salt into HCl and $\text{Cd}(\text{OH})_2$. At this lower subphase pH the DTCA molecules are nonionized and seem not to be complexed with cadmium ions from the subphase. On the other hand, with the addition of only sodium bicarbonate, the subphase pH is about 6.0 and the DTCA molecules are ionized; however, there were no cadmium ions in the subphase to complex with. The finding is in accordance with reports on metal ion complexation with the fatty acid, where complexation of metal ions did not occur at low pH but was complete at a neutral subphase pH.^{16,17}

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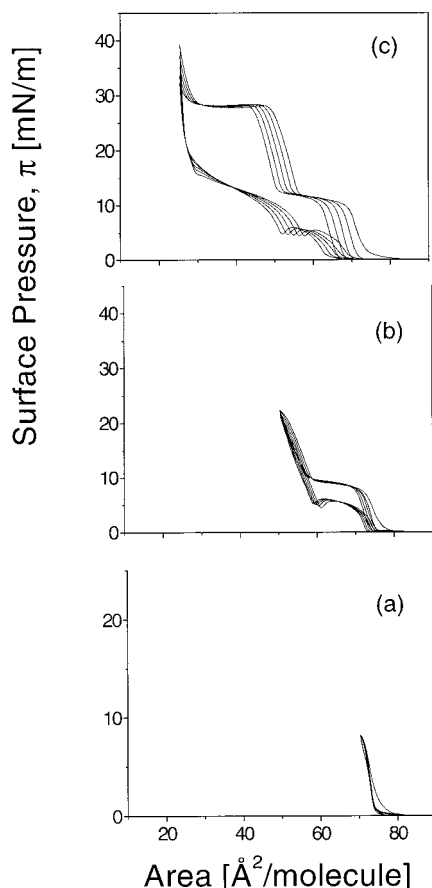


Figure 3. Hysteresis isotherms of DTCA monolayer on the $\text{CdCl}_2 + \text{NaHCO}_3$ subphase at 20 °C. The monolayer was compressed with 25 mm/min to (a) first condensed region ($\pi = 8$ mN/m), (b) second condensed region ($\pi = 22$ mN/m), (c) third condensed region ($\pi = 40$ mN/m).

The π - A isotherms of Cd-DTCA monolayers obtained under different subphase temperatures are shown in Figure 2b, with two plateaus for all temperatures employed. Similar to the case of DTCA monolayers on pure water, the transition surface pressures decreased with subphase temperature for Cd-DTCA monolayers. When the compression speed was varied from 5 to 125 mm/min, the isotherm was slightly shifted toward higher areas at higher speeds and the surface pressure of the first plateau decreased with the compression speed (data not shown). Again, these results indicate that the Cd-DTCA monolayer is reasonably stable. Further evidence for such stability has been obtained with the hysteresis isotherm results shown in Figure 3. During experiments carried out at the first condensed region ($\pi = 8$ mN/m, curve a), noticeable hysteresis could be observed only during the first compression-decompression cycle. No hysteresis was noticed during subsequent cycles. The hysteresis was progressively pronounced for isotherms obtained by compressing the monolayer to the second (22 mN/m) and third (40 mN/m) condensed regions (curves b and c). In the latter cases, an unusual "minimum" in the fall of surface pressure could be noticed during decompression. The area at which this local minimum occurs decreased in subsequent cycles.

Such a minimum in the decompression curve has recently been reported for poly(styrene)-poly(ethylene oxide) diblock copolymer monolayers^{18,19} and lignin monolayers.²⁰ In the former case, the minimum was interpreted

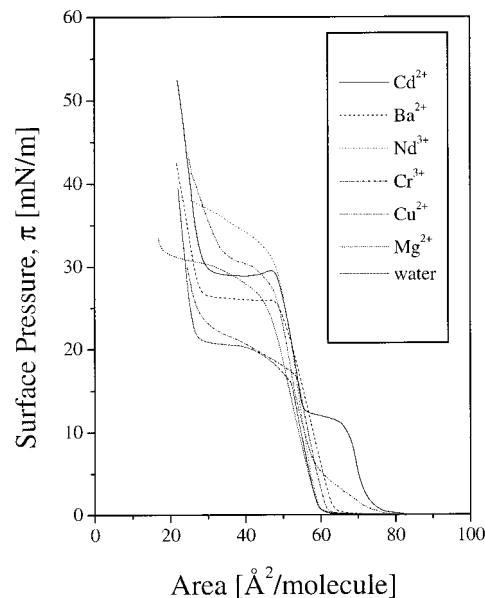


Figure 4. π - A isotherms of DTCA monolayer on aqueous subphases containing different ions, buffered to pH ≈ 6 with NaHCO_3 , compressed with 25 mm/min at 20 °C.

as the monolayer being overexpanded, a situation similar to that observed with 3D fluids in solid-liquid and liquid-gas transitions.¹⁸ However, for the DTCA and Cd-DTCA monolayers the minimum depends on various experimental conditions such as target surface pressure, compression speed, and position of the Wilhelmy plate with respect to the compression direction (either parallel or perpendicular). Therefore, analogous to the case of lignin monolayers,²⁰ the minimum is rather due to the different kinds of mechanical forces experienced by the plate during monolayer compression, and could therefore be classified as an experimental artifact.

As we observed an unusual behavior of the DTCA monolayer spread on the subphase containing Cd^{2+} , our studies have been extended to other metal ions. In all cases, NaHCO_3 was added to the subphase containing a particular metal salt in order to maintain the pH at ca. 6. The pressure-area isotherms are shown in Figure 4. A significant change in the monolayer characteristics can be observed for subphases containing Cd^{2+} ions. In all other cases the course of the isotherm is similar to that obtained on water with one plateau region; the isotherms are only slightly more expanded and the main difference occurs for surface pressure values at which the plateau is reached. As suggested in ref 10, orientational changes leading to inclination of molecules upon compression may be responsible for this plateau region. The two plateau regions which appear in the π - A isotherms of DTCA on a Cd^{2+} subphase suggest that a final molecular rearrangement is probably attained through two intermediate orientational steps that differ in energy requirements.

To get further insight into the phenomena occurring at the plateau region/s, the electric surface potential was measured for the DTCA floating monolayers on various subphases (Figure 5). For aqueous subphases containing 10^{-3} M NaCl or HCl, the surface potential starts to increase at molecular areas between 70 and 80 \AA^2 and rises steeply reaching the maximum of 0.46 and 0.56 V, respectively. For monolayers spread on pure water as well as on a

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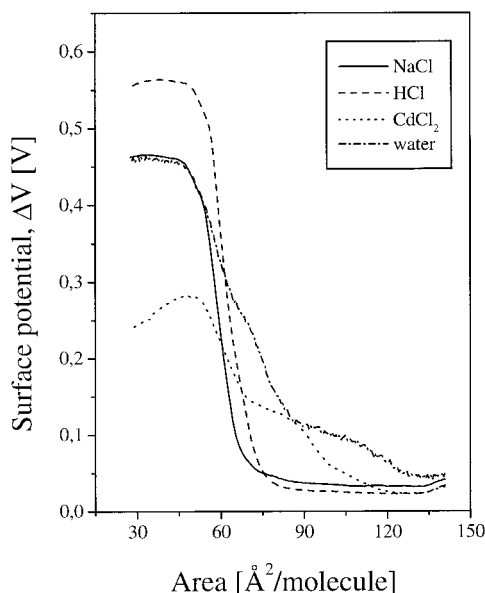


Figure 5. Surface potential–area isotherms of DTCA monolayer on different subphases at 20 °C.

subphase with Cd^{2+} ions, the surface potential starts to increase at larger molecular areas (130 \AA^2 for water and 120 \AA^2 for aqueous Cd^{2+}). The surface potential rises gradually until ca. 68 \AA^2 , which corresponds exactly to the beginning of the first plateau in the π - A isotherm on the aqueous Cd^{2+} subphase (see Figure 1), after which a change of slope occurs. While on the subphase containing cadmium ions this change is attained via a clear pseudo-plateau transition, on pure water only, a sharp “kink” appears. Such changes in the ΔV - A isotherms also appear in the effective dipole moment (μ_n)-area dependencies (see below). It is believed that while the slope in the μ_n - A isotherm remains the same, no orientational changes of film-forming molecules occur upon compression.²³ It is thus evident that at an area of ca. 68 $\text{\AA}^2/\text{molecule}$, on both water and Cd^{2+} subphases, there exists a phase transition due to orientational changes in the DTCA monolayer. While this transition is clear in the π - A isotherms recorded on aqueous cadmium subphases, on pure water it occurs at a surface pressure too low to be detected. Therefore, the sequence of phase transitions for DTCA on water and Cd^{2+} subphases may be regarded as being the same, but the first transition occurs on water at a surface pressure that is not detectable.

For areas below the first transition, the surface potential rises steeply, reaching a maximum of 0.46 V on pure water and 0.28 V on an aqueous Cd^{2+} subphase. Interestingly, the surface potential attains its maximum value at the same molecular areas in both cases (i.e., at 50 \AA^2) which matches exactly with the area for the beginning of the plateau region (second transition for the case of the aqueous Cd^{2+} subphase). After that, the surface potential slightly decreases. The lower surface potentials for the monolayer spread on the aqueous Cd^{2+} are due to the large negative contribution from the double-layer potential since the monolayer is fully ionized under these experimental conditions, as demonstrated in the FTIR spectra of the transferred films (see next section).

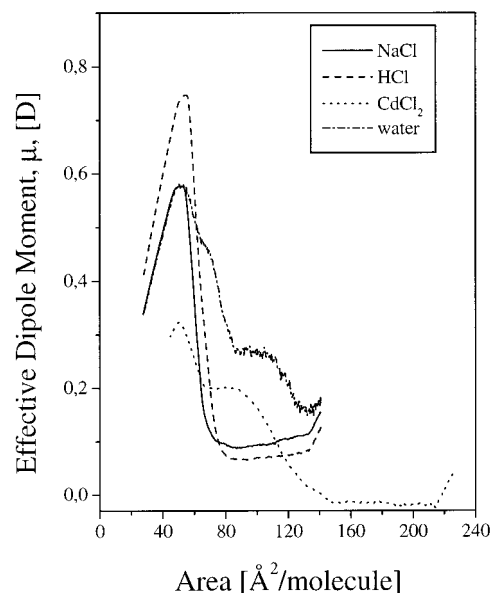


Figure 6. Effective dipole moment–area isotherms of PTCA monolayer on the surface of different subphases at 20 °C.

A semiquantitative analysis of the surface potential isotherm was made. Using the Helmholtz equation²⁴ in the form:

$$\Delta V = \mu_n / (A\epsilon_0)$$

where μ_n is the normal (to the interface) component of the apparent dipole moment (so-called effective dipole moment), A is the area per molecule, and ϵ_0 is the vacuum permittivity, it is possible to calculate μ_n at different stages of compression, as shown in Figure 6. The effective dipole moment increases simultaneously with the electric surface potential, showing a similar change of slope on water and cadmium subphases, characteristic of the first phase transition. After reaching the maximum value at molecular areas of ca. 50 \AA^2 , corresponding to the second plateau transition, the effective dipole moment decreases drastically. As it has been analyzed for monolayers of PTCA and some of its 4'-derivatives,¹⁰ such a decrease in effective dipole moment may be due either to multilayer formation or gradual inclination of film molecules; the former hypothesis was suggested to be unlikely based on the analysis of Brewster angle microscopy images (indicating monolayer homogeneity up to the middle of the plateau region) as well as taking into consideration the high reproducibility of the isotherms.¹⁰ The effective dipole moment–area isotherm clearly indicates that the DTCA monolayer undergoes structural changes upon compression. Namely, the first change of slope in the μ_n - A , which corresponds to the first plateau region in the π - A isotherms detectable only on the Cd^{2+} subphase, leads to a steeper dependence, which may be associated with molecular reorientation from a horizontal to a vertical position. When μ_n is maximum, the molecules assume a perpendicular orientation with respect to the water surface. Upon further compression, coinciding with the second plateau in the π - A isotherm on the Cd^{2+} subphase, the molecules incline and consequently the effective dipole moment decreases. The effective dipole moment–area isotherm for DTCA on the Cd^{2+} subphase is shifted toward lower molecular areas, and thus the monolayer is more

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condensed in the presence of cadmium ions. This agrees with findings for model aliphatic amphiphiles. In the next section we shall show that the analysis of surface potential data for transferred LB films allows one to support the hypothesis that molecule tilting is responsible for the second transition.

LB Film Transfer and Characterization. Monolayer transfer has been performed at various target surface pressures in different regions of the surface pressure isotherm on both aqueous HCl and aqueous Cd^{2+} subphases. In the pre-plateau region, the monolayer was stable and transferred at a constant surface pressure of 5 mN/m for DTCA as well as Cd-DTCA. In both cases, the monolayer was transferred in this region as mixed Y-Z type LB films, i.e., transfer during lifting was close to unity while on dipping it was 0.2–0.5. Attempts to transfer Cd-DTCA in the first plateau region ($\pi = 11$ mN/m), second condensed region ($\pi = 20$ mN/m), second plateau ($\pi = 30$ mN/m) and third condensed region ($\pi = 35$ mN/m) were also successful and led in all cases to Y-deposited LB films with no significant difference for different substrates. It has to be mentioned, however, that monolayers compressed up to the second plateau and third condensed regions were unstable and it was not possible to deposit more than 7 layers. On the other hand, for the DTCA monolayer on the aqueous HCl solution, the deposition was mixed Y-Z-type in both pre-plateau and plateau regions. A similar type of deposition was obtained from the pure water subphase. These monolayers were found to be unstable in comparison to that on the aqueous HCl subphase. Optimization of experimental conditions for monolayer transfer may nevertheless lead to better results if in future one carries out a systematic study with this specific purpose. The transferred LB films from monolayers in different regions were visually uniform and characterized by FTIR, XRD, and surface potential measurements.

The FTIR spectra of DTCA LB films produced from monolayers spread on an acidic subphase and on water containing cadmium ions are shown in Figure 7. The film transferred from the acidic subphase (curve a) exhibited a strong absorption peak at 1686 cm^{-1} corresponding to the C=O stretching vibration, an absorption peak at ca. 1600 cm^{-1} due to ring C=C stretching vibrations, at 1415 cm^{-1} corresponding to C–O–H bending, and a strong band at 1280 cm^{-1} for C–O stretching. The appearance of intense vibrational absorption peaks for both C–O–H bending and C–O stretching may indicate dimer formation. These FTIR features are similar to those of a DTCA cast film, indicating no significant ionization of COOH groups for an acidic subphase. In contrast, the FTIR spectrum of the LB film transferred from a subphase containing cadmium ions (curve b) exhibited a strong absorption peak at ca. 1600 cm^{-1} for ring C=C stretching vibration and strong peaks at 1527 and 1398 cm^{-1} for the asymmetric and symmetric C=O stretching vibrations of the carboxylate anion, respectively. The absence of a vibration absorption peak at 1688 cm^{-1} for the free acid group indicates complete ionization of the acid headgroups in the presence of cadmium ions in the pH = 6.0 subphase.

The Cd-DTCA monolayers were also transferred onto glass substrates from an aqueous Cd^{2+} subphase in all parts of the isotherm, i.e., in the first condensed, first plateau, second condensed, second plateau, and third condensed regions. Only the LB films transferred from the first plateau region (at 11 mN/m) exhibit two weak peaks in the X-ray diffractograms, which are assigned as 001 and 002 peaks and lead to a bilayer distance of $27 \pm 0.3\text{ \AA}$. This value is close to that expected from the

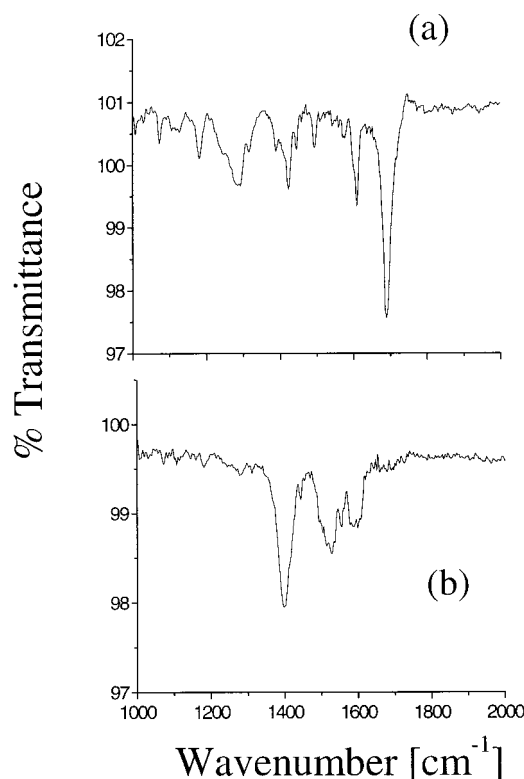


Figure 7. Transmission FTIR spectra of LB films with 31 layers of (a) DTCA and (b) Cd-DTCA.

estimated length of a DTCA molecule, i.e., ca. 12.3 \AA (the length of the molecular long axis varies by 0.5 \AA for the different conformations of the DTCA molecule), as determined by the HyperChem computer modeling program. In all other cases no peaks can be seen. In contrast to DTCA, LB films from cadmium salts of long chain fatty acids usually exhibit a set of intense diffraction peaks.

Surface potential measurements have been carried out with the DTCA LB films on gold/glass substrates, transferred from water and HCl, as well as Cd-DTCA LB films with different numbers of layers deposited at different regions of the isotherms. The surface potentials for the DTCA LB films with different numbers of layers are listed in Table 1, which also includes the type of deposition, film uniformity, and maximum monolayer potential for comparison. Films were considered as very uniform when the variation in surface potential was within the accuracy limit of the setup, i.e., $\pm 10\text{ mV}$, while scanning the film with the probe. The surface potential for transferred LB films, V_{LB} , may be taken as the sum of two contributions, namely, from the dipoles within the film and from the film–substrate interface. It usually increases with the number of layers before reaching saturation, which depends on the type of compound and demonstrates that substrate effects no longer affect the potential. This was observed in all films investigated here. According to the XRD data, order was only observed for the Cd-DTCA films that were transferred at 11 mN/m, so these are the most reliable data for a semiquantitative analysis. For a nonionized monolayer transferred onto a solid substrate, usually the surface potential of the LB film is lower than for the monolayer counterpart owing to the negative contribution from the film/substrate interface. For ionized monolayers, however, the analysis is more complicated, for it depends on whether the contribution from the double layer will have an effect on the surface potential of the LB film. For cadmium stearate, for instance, V_{LB} is usually close to the maximum monolayer potential, which means

Table 1. Surface Potentials for DTCA-LB Films

subphase	no. of layers	$\pi = 5$ mN/m 1st cond reg	$\pi = 11$ mN/m 1st plateau	$\pi = 20$ mN/m 2nd cond reg	$\pi = 30$ mN/m 2nd plateau	$\pi = 35$ mN/m 3rd cond reg
aq. Cd^{2+}	1	0.27 V	0.18 V	0.23 V	0.23 V	0.30 V
	3	0.27 V	0.23 V	0.31 V	0.31 V	0.43 V
	7	0.35 V	0.34 V	0.40 V	0.39 V	0.43 V
	15	0.43 V	0.48 V	0.41 V		
deposition		Y-Z-type	Y-type	Y-type	Y-type	Y-type
film quality		uniform (± 0.01 V)	very uniform	uniform (± 0.01 V)	uniform (± 0.01 V)	uniform (± 0.01 V)
ΔV (Langmuir monolayer)		0.145 V ($A = 70 \text{ \AA}^2$)	0.18–0.22 V ($A = 65\text{--}60 \text{ \AA}^2$)	0.28 V (ΔV_{max}) ($A = 50 \text{ \AA}^2$)		
aq. HCl	15	0.33 V	0.40 V			
deposition		Y-Z-type	Y-Z-type			
film quality		very uniform	very uniform			
ΔV (Langmuir monolayer)		0.50 V ($A = 55 \text{ \AA}^2$)	0.56 V (ΔV_{max}) ($A = 40 \text{ \AA}^2$)			
water	15	0.35 V				
deposition		Y-Z-type				
film quality		good (± 0.03 V)				
ΔV (Langmuir monolayer)		0.38 V ($A = 55 \text{ \AA}^2$)	$\Delta V_{\text{max}} = 0.46$ V			

that the large negative contribution from the double layer is lost, being replaced by the negative contribution from the interface. This seems to be the case for the Cd-DTCA monolayers transferred onto a gold/glass substrate. In comparison to the other LB films, it could be rather intriguing that a 15-layer film from Cd-DTCA displayed a higher surface potential than the other 15-layer DTCA films transferred from pure water and acidic subphase, since the latter had higher monolayer potentials. However, it must be stressed that the highest potential was observed for the Cd-DTCA film transferred at 11 mN/m, which was the only one to show order in the XRD studies. Therefore, the Y-character and the order predominating in the Cd-DTCA films must have led to higher potentials, since in the other films the dipolar contribution from the film-forming molecules may have been decreased by disorder. Such an effect is probably related to the ability of cadmium ions to complex with COOH headgroups, which for alkanolic acids allows the aliphatic chains to be perpendicular to the substrate upon transfer.

That the surface potential does not depend strongly on the pressure at which transfer occurs means that bilayer formation is unlikely to take place during the phase transition in the surface pressure isotherms. If a monolayer before the plateau is transformed into a bilayer after the plateau, one should expect substantial change in surface potential of transferred monolayers at the different regimes, since cancellation of dipolar contributions would be inevitable. One may argue, nevertheless, that molecular reorientation that would then be the only cause for the plateau could also affect the monolayer surface potential, which was demonstrated to be the case, and consequently the measured surface potential in the LB film. However, effects from such molecular reorientations were probably overcome by further orientation upon transfer, which is

a more likely hypothesis than a reversible monolayer–bilayer transformation during transfer.

IV. Conclusions

It has been shown that DTCA easily spreads and forms monolayers at the air/water interface, with the lift-off area in surface pressure isotherms being comparable to the area of projection of a vertically oriented molecule. Langmuir monolayers recorded on water exhibit a characteristic broad plateau, which spans a region corresponding to a decrease in molecular area by a factor of ca. 2. In the presence of Cd^{2+} ions, however, two plateau regions appear in the course of the isotherm, and the surface pressure onset occurs at markedly larger molecular areas than on water. If surface pressure isotherms are analyzed in isolation, one may be misled to conclude that the incorporation of Cd^{2+} ions in the subphase leads to an unexpected monolayer expansion. However, detailed analysis of electric surface potential and effective dipole moment isotherms indicates that DTCA monolayers on water also display two phase transitions, though the first one is not detectable in the surface pressure measurement. This first transition is connected with molecular reorientation from the horizontal to vertical position, while the other is due to the inclination of closely packed molecules upon compression. Indeed, by transferring DTCA monolayers from various subphases and at different stages of monolayer compression, we could infer from surface potential measurements that a molecular arrangement of inclined molecules is the cause for the second transition in the π/A isotherms.

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