

Adsorption of large inorganic polyanions under a charged Langmuir monolayer: an ellipsometric study

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In previous studies of Langmuir films made of the dimethyldioctadecylammonium bromide the exchange of small counter-ions against large inorganic anions type polyoxometalates induced a densification of the monolayer. However, when the polyanions concentration in the subphase exceeded a critical value the monolayer re-expanded. In this work, we demonstrate, by means of ellipsometric measurements, that those effects can be explained by the adsorption of a first layer of inorganic anion under the organic layer then by the formation of a second diffuse layer when the polyanion concentration continues to increase. This process can be detected and analyzed in our system because of the large size and relatively high refractive index of the inorganic anions.

1. Introduction

The organization of a Langmuir film depends on well-known parameters such as temperature and surface pressure but can be also strongly modified by compounds dissolved in the subphase on which the monolayer is spread.¹ This is particularly true in the case of charged Langmuir films interacting with ions of the subphase. Since the first experiments performed by Langmuir with fatty acids in the presence of mono- or divalent ions, various studies have shown the structural changes in negatively charged or ionizable monolayers.² More recently, positively charged layers (generally quaternary ammonium) have been also studied and present interesting behaviors. In particular, Langmuir films made of dimethyldioctadecylammonium bromide (DODA) are highly sensitive to the nature and concentration of ions dissolved in the subphase. Indeed, the surface pressure measurements of the DODA monolayers spread on pure water at room temperature shows a monotonic increase upon compression, without the characteristic coexistence plateau corresponding to a liquid expanded–liquid condensed transition (LE/LC).³ However, Brewster angle microscopy (BAM) experiments revealed that such a transition takes place even though it cannot be clearly identified on the isotherms.^{4,5} At low surface pressure the BAM images of the monolayer are homogeneous with an overall slight reflectivity corresponding to LE phase. When the surface pressure is increased, small brighter spots of the LC domains appear and increase in size and number during compression. This biphasic state persists till the collapse pressure. It seems that for DODA lipid, the strong repulsion between polar heads in the monolayer prevents from reaching a high-packing state and induces the important kinetic effects, which in turn smooth the isotherm. Screening the electrostatic interactions by addition of NaCl salt to the subphase modifies the isotherm in the way that the kink relative to LE/LC transition appears.³

In a previous paper,⁶ it has been pointed out that exchange of Br^- counter-ions against specific polyvalent inorganic anions induces large changes in the monolayer organization which goes from a mainly LE state to a LC state even at low surface pressure. Those particular anions belong to the family of closed packed metal oxides of formula $\text{X}_a\text{M}_b\text{O}_c^{n-}$ ($\text{M} = \text{Mo}, \text{V}, \text{W}, \text{etc.}$ and $\text{X} = \text{P}, \text{Si}, \text{B}, \text{Co}, \text{Fe}, \text{etc.}$). More precisely, they have the so-called Keggin structure^{7,8} which consists of a central heteroatom X in a tetrahedral cavity surrounded by four M_3O_{13} groups formed by three octaedra sharing edges (see insertion in Fig. 1).

In ref. 6 the effect of Keggin heteropolyoxotungstates ($\text{XW}_{12}\text{O}_{40}^{n-}$ with $\text{X} = \text{H}_2, \text{P}, \text{Si}, \text{B}$ or Co) on Langmuir films of DODA was studied. It has been shown that when spread on the subphase containing even small quantities of polyanions, the isotherms of DODA are shifted toward small areas per molecule and they become steeper. This evolution of the isotherms reflects the condensing effect of the polyanions on the

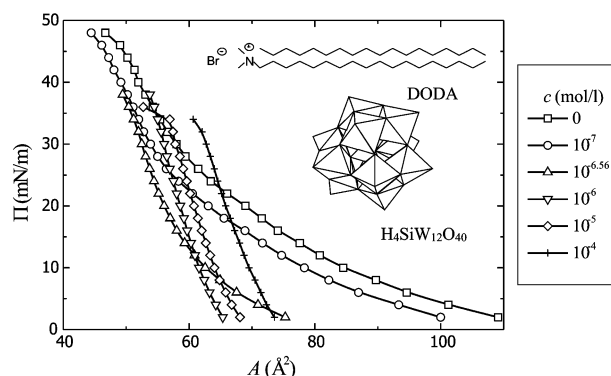


Fig. 1 Compression isotherms of DODA on aqueous subphase containing different concentrations of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ polyanion.

DODA film. In fact, for a given surface pressure the DODA monolayer becomes more and more dense when the polyanions concentration increases. However, if the concentration of the polyanions exceeds the critical value C_C corresponding to the highest density of the film, the further addition of the polyanions to the subphase leads to the re-expansion of the DODA monolayer. This “exotic” behavior was found in the presence of various polyanions whatever their exact chemical structure and effective charge might be. It is worth to notice that the pure inorganic polyanion is not *per se* a surfactant agent but it behaves like a strong electrolyte: it increases the surface tension of the subphase at sufficiently high concentrations, *i.e.*, the polyanions deplete from the interface if the positively charged insoluble monolayer of DODA is no present.

An increase of the density of the lipid layer with the concentration of Keggin polyanion can be easily understood in terms of a counter-balance of the head-group repulsion by the attractive interaction between the polyanions and DODA molecules. However, it is less obvious why the monolayer re-expands when the concentration of inorganic polyanion exceeds the critical value. A few hypotheses were put forward⁶ but only one was kept. Most probably, the inorganic layer becomes saturated at the C_C concentration, while the exchange between Br^- and the polyanion is total. Therefore above the critical concentration, the polyanions can be adsorbed only by formation of kind of a diffuse electric double layer by means of small cations present in the subphase. The thickening of the inorganic sublayer would weaken the interaction between polyanions and DODA monolayer and thus lower the density of the latter.

The main goal addressed in this paper is to verify this hypothesis by following directly the dependence of the monolayer thickness on the polyanion concentration. Ellipsometry seems to be the more adapted method for such a study.^{9,10} This technique is based on the principle that polarization state of the light changes after reflection at the interface between two continuous media. The ellipsometric angles Ψ and Δ obtained from the measurement are related to the variation of intensity and phase of electromagnetic field, respectively. The presence of a thin film at the interface modifies the ellipsometric angles and their variations $\delta\Psi = \Psi - \Psi_0$ and $\delta\Delta = \Delta - \Delta_0$, as compared to the bare interface values (denoted by the sub-index 0), can then be defined. These variations are directly related to the refractive index n , absorption coefficient κ and thickness d of the film. For non-absorbing ultrathin film, as it is in our molecular system, $\delta\Psi$ is sensitive only to the second order to the film thickness. Such variations are below the detection limit of a standard ellipsometer. Thus all the information is included in $\delta\Delta$, the only accurately measurable parameter. In order to obtain the film thickness, one has to know the refractive index of the monolayer or to deduce it from an appropriate optical model. Fortunately, in our case the final result does not depend much on the precision with which we estimate the refractive index. This allowed us to decide on the evolution of the film thickness as a function of the polyanion concentration.

2. Experimental techniques and data analysis

2.1. Materials and film preparation

Dimethyldioctadecylammonium bromide, DODA, (Kodak, purity higher than 99%) and the polyanion $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (Aldrich) were used as received. The Langmuir monolayers were formed by spreading the chloroform (Prolabo, spectroscopic grade) solutions of DODA on an aqueous subphase being pure Milli-Q water or polyanion solution. The resistivity of the Milli-Q water was 18.2 M Ω cm and the surface tension 73 mN m⁻¹ at 20 °C. The isotherms were recorded in a thermo-

stated trough ($70 \times 15 \times 1$ cm³) at 20.0 ± 0.5 °C, by compression with a continuous speed of *ca.* 6 Å² molecule⁻¹ min⁻¹. The details of the experiment are given in ref. 6. The ellipsometric measurements were performed in a circular vessel (10 cm in diameter) made of Teflon. The aqueous solutions of polyanion were filtered through a Teflon Millipore membrane with 1 μm pore diameter, to remove the residual dust which randomly perturb the ellipsometric measurements. The ellipsometric signals of the filtered polyanion solutions were comparable with those of pure water indicating the lack of surface activity of the anion. The concentration of DODA monolayer was increased by successive additions of the chloroform solution onto the subphase.

2.2. Ellipsometry: measurements and modeling

We have used a Plasmos SD2300 ellipsometer (Germany) operating at the He–Ne wavelength ($\lambda = 632.8$ nm) and equipped with an automatic rotating analyzer system. The laser beam spot was about 1 mm² in size. In order to maximize sensitivity of reflected light toward interfacial structure, we have fixed an incidence angle at $\theta = 55^\circ$, value close to the Brewster angle at the air/water interface ($\sim 53.1^\circ$). The two measured angles Δ and Ψ are related through the fundamental equation of ellipsometry:⁹

$$e^{i\Delta} \tan \Psi = \frac{r_p}{r_s} \quad (1)$$

where r_p and r_s represent the reflection coefficients for the polarization parallel and perpendicular to the plane of incidence, respectively. These coefficients can be calculated from the continuity condition for the tangential component of electromagnetic field. For a perfectly plane and infinitely thin interface between two isotropic and transparent media characterized by refraction indices n_i and n_j , one obtains the following expressions:^{9,10}

$$\begin{aligned} r_{ij}^p &= \frac{n_j \cos \theta_i - n_i \cos \theta_j}{n_j \cos \theta_i + n_i \cos \theta_j} \\ r_{ij}^s &= \frac{n_i \cos \theta_i - n_j \cos \theta_j}{n_i \cos \theta_i + n_j \cos \theta_j} \end{aligned} \quad (2)$$

where the incident θ_i and refracted θ_j angles are related through the Snell–Descartes law:

$$n_i \sin \theta_i = n_j \sin \theta_j \quad (3)$$

If we consider a thin film adsorbed at the air/water interface, the reflection coefficients can be calculated by summation of the electromagnetic waves refracted and reflected from the successive interfaces involved now, *i.e.* air/film (A/F) and film/water (F/W):

$$\begin{aligned} r^p &= \frac{r_{AF}^p + r_{FW}^p e^{-2i\beta}}{1 + r_{AF}^p r_{FW}^p e^{-2i\beta}} \\ r^s &= \frac{r_{AF}^s + r_{FW}^s e^{-2i\beta}}{1 + r_{AF}^s r_{FW}^s e^{-2i\beta}} \end{aligned} \quad (4)$$

where β is a phase shift introduced by the presence of the film:

$$\beta = \frac{d}{\lambda} n \cos \theta_F \quad (5)$$

n and d being the refractive index and thickness of the film respectively, and θ_F the refraction angle in the film. In our case, the film itself consists of two layers: the DODA organic monolayer and the inorganic polyanion sublayer, each characterized by its thickness (respectively d_{org} and d_{inorg}) and refractive index (respectively n_{org} and n_{inorg}). This gives four unknown parameters, while the only quantity obtained from the ellipsometric measurements is the Δ angle. However, the two refractive indices can be modeled or evaluated (see below)

and the thickness of the organic layer can be estimated from the ellipsometric measurements of DODA on pure water. Then, the ellipsometric angle Δ can be calculated from eqn. (1), where r_s and r_p are obtained from eqns. (4) and (5) applied to consecutive interfaces encountered by the electromagnetic waves. The final equation represents Δ as a function of the one unknown, *i.e.* the thickness of the inorganic sublayer d_{inorg} . It is impossible to obtain a simple analytical expression to calculate d_{inorg} , therefore we were varying numerically the thickness d_{inorg} in a continuous way until we found the only value for which the Δ angle equals the one obtained from ellipsometric measurements.

2.2.1. Model calculation of the n_{org} refractive index: the isotropic case. In principle, the organic film should be treated as a bi-axial optical medium. However, the small difference between the two principle refractive indices that we obtained from the anisotropic model (see appendix) suggests that a simplified model in which the DODA film is assumed to be optically isotropic would be sufficient. In this model, we assume that the molar refractivity of the film, R_F , is obtained by simple addition of the molar refractivities R_i of the film constituents: DODA molecules and water. The molar refractivity of the pure DODA, R_{DODA} , is calculated by summing the atomic and bond contributions,¹¹ which gives the value of 319.5 \AA^3 . The film and water refractivities are defined by the Lorentz–Lorenz formula:¹¹

$$R_i = \frac{M_i n_i^2 - 1}{\rho_i n_i^2 + 2} \quad (6)$$

where M_i and ρ_i are the molecular weight and density of the i component.

Though, the refractive index of the film, n_{org} , is finally obtained from the following equation:

$$R_F = \frac{n_{\text{org}}^2 - 1}{n_{\text{org}}^2 + 2} A d_{\text{org}} = R_{\text{DODA}} + x \frac{M_W n_W^2 - 1}{\rho_W n_W^2 + 2} \quad (7)$$

where A is the DODA molecular area and x is the average number of water molecules per one DODA molecule in the monolayer. This number is evaluated assuming that the water molecules (with an average molecular area of 9.65 \AA^2) occupy the area equal to the difference between the actual DODA molecular area and the cross section of this molecule in a stretched conformation ($\sim 40 \text{ \AA}^2$). It means that we consider only one layer of water molecules in the hydration shell. Such an approach is consistent with the typical monolayer image the people deduced from simultaneous ellipsometric and X-ray studies of fatty acids.^{12,13} The water is present only in the polar heads region with hydration shell which is approximately one water molecule thick. Calculations made on the assumption of two or three hydration layers lead to smaller refractive index n_{org} and film thickness higher than the maximum length of a DODA molecule.

Using eqn. (8) we calculated n_{org} for each molecular area A for which we measured the angle $\delta\Delta$. The variation of the refractive index with the surface concentration of DODA in the film was found of the same order of magnitude that the experimental uncertainty. Therefore for further calculations, we took the mean value of $n_{\text{org}} = 1.45$.

3. Experimental results and discussion

3.1. Effect of the $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ polyanions on the DODA compression isotherms

The concentration effect of polyoxometalates on the compression Π – A isotherms of DODA is depicted in Fig. 1 in the case

of the $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ polyanions. The isotherm of DODA spread onto a pure water surface (square symbols) is clearly the most expanded one. As it was already observed in ref. 6, the introduction of a small quantity of polyanions in the subphase results in a shift of the whole isotherm towards lower surface areas. In the same time, the isotherm becomes steeper and the surface area corresponding to the collapse of the monolayer slightly diminishes. These are clear indications of the higher density of the monolayer. However, the condensation effect on the monolayer stops when the critical concentration of polyanions $C_C \sim 0.4 \text{ \mu M}$ is reached. Above this value, further addition of polyanions to the subphase leads to a re-expansion of the organic film. The isotherms obtained above the critical concentration rest steep, but return to the higher molecular areas (inverse triangles, diamonds and crosses in Fig. 1).

3.2. Ellipsometric data

3.2.1. DODA monolayer on the pure water sub-phase. First, we performed measurements on a pure DODA monolayer in a function of its surface concentration (see Fig. 2a). The “raw” ellipsometric angle Δ varies about 2.5° over the range of molecular area between 120 \AA^2 and 60 \AA^2 , as it was already observed for the DODA film spread on a 10 mM NaCl solution.¹⁴ The experimental points were obtained in two series of measurements and are clearly scattered for areas above 80 \AA^2 . In particular, for some points in this range, Δ takes values corresponding to more condensed films. As revealed by BAM,⁵ phase coexistence is observed in this region, so this phenomenon might be explained by the presence of LC domains in the area illuminated by the laser beam.

From these data, one can deduce the thickness of the DODA monolayer d_{org} . Indeed, since the length of the DODA chain in the extended conformation (*ca.* 23 \AA) is small compared to the wavelength λ of the incident light (6328 \AA), one can substitute the ellipsometric eqn. (4), by its

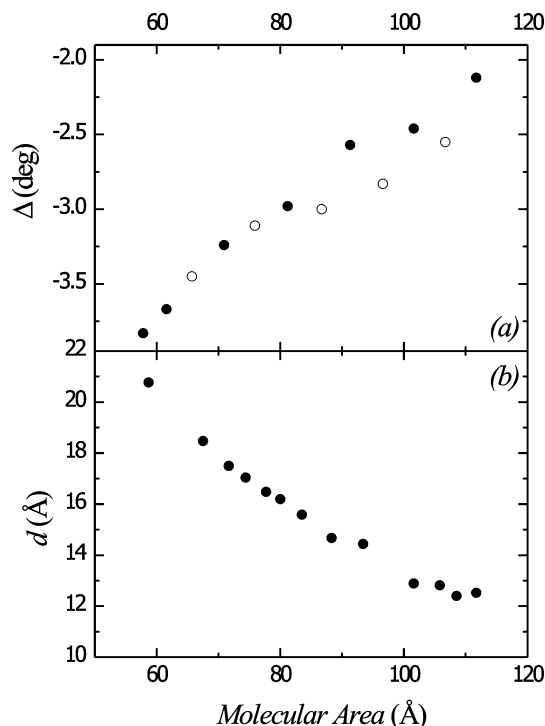


Fig. 2 Ellipsometric angle Δ (a) and film thickness (b) of pure DODA monolayer as a function of molecular area.

approximation of the first order in d/λ , the so-called Drude approximation:^{15,16}

$$\frac{\delta\Delta}{4\pi} = \frac{d}{\lambda} \frac{n_W^2 \cos \theta \tan^2 \theta}{(n_A^2 \tan^2 \theta - n_W^2)(n_W^2 - n_A^2)} \left(n_A^2 + n_W^2 - n_{\text{org}}^2 - \frac{n_A^2 n_W^2}{n_{\text{org}}^2} \right) \quad (8)$$

where, n_A and n_W are respectively the refractive indices of air and water.

The only missing parameter is the refractive index of the monolayer n_{org} , which equals 1.45 as estimated from the isotropic model of the monolayer presented in 2.2.1. In Fig. 2b, we plotted the calculated monolayer thickness as a function of the molecular area. Its value increases monotonously from about 12.5 Å at low surface pressure to a limiting value of ca. 21 Å at molecular area $A \sim 58 \text{ Å}^2$, corresponding to a close packing state. It has been found by X-ray reflectivity studies¹⁷ that, for this state, the molecules of DODA are tilted by ca. 35° from the normal to the surface and that the layer thickness is ca. 20 Å, a value close to the one obtained from the ellipsometric data.

3.2.2. DODA monolayer on the subphase containing the polyanions. In Fig. 3a we show the variation of the angle $\delta\Delta$ as a function of the concentration of the polyanion dissolved in the subphase. Three different surface concentrations of the DODA monolayer, corresponding to the molecular area of 80, 65 and 50 Å² were studied. Since these data are a bit scattered, differences between the three series are no discernible. This is not astonishing, because in the three cases the morphology of the DODA monolayer seen with the BAM technique⁶ corresponds to the same biphasic state, where the LC domains appear in a LE continuum. As compared with the DODA monolayer on pure water, the domains are more numerous and denser and their reflectivity is stronger, because of the pre-

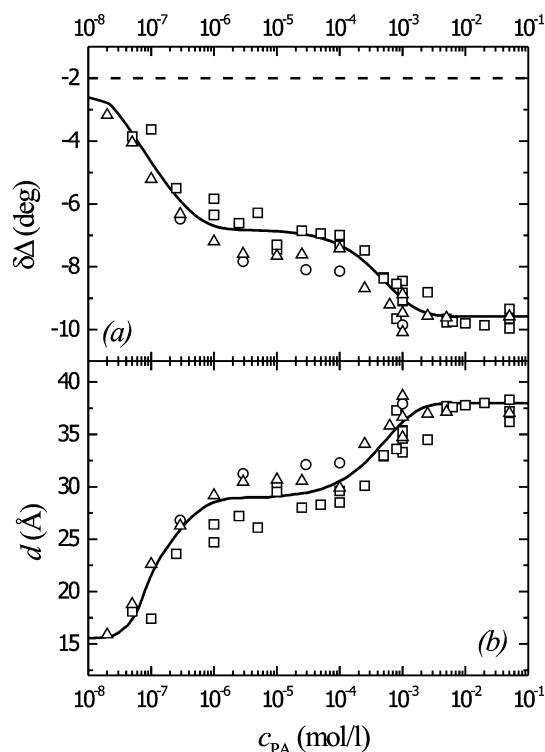


Fig. 3 Plots of $\delta\Delta$ and film thickness d versus concentration of polyanion in the subphase. These plots are for three different surface concentrations of DODA in the monolayer: 3.3×10^{-6} , 2.6×10^{-6} and $2.1 \times 10^{-6} \text{ mol m}^{-2}$ corresponding to the triangles, circles and squares, respectively.

sence of the polyanions under the lipid film. The differences between thickness of the DODA monolayer in the LE and LC states on one hand and between the content of both phases in the monolayer corresponding to three surface concentrations on the other hand are clearly not sufficient to be discerned by ellipsometry.

In all cases, in the high dilution limit, the experimental values of Δ are close to those measured for a pure DODA monolayer in the biphasic state, *i.e.*, $\sim 3\text{--}4^\circ$ (see Fig. 2a). With the increase of polyanion concentration, the angle Δ strongly diminishes and two plateaus can be clearly distinguished: one for the polyanion concentration between 10^{-6} and 10^{-4} M and the second between 10^{-3} and 10^{-1} M. Since the absolute value of $\delta\Delta$ grows monotonously with both, thickness d and refraction index n of the film, a thickening transition or/and a compacting of the polyanions could be the cause of such a behavior. If no adsorption of polyanion molecules is assumed, the only possibility is that the single film of DODA becomes highly compacted. However, from BAM experiments we know that for the three surface concentrations studied the monolayer remains in the biphasic state. Therefore if we use the eqn. (7) to estimate the refraction index of DODA film for the molecular area of 50 Å² (the smallest of three series) and considering that there is no water in the film, we obtain $n_{\text{org}} = 1.493$. In such a case the film thickness calculated from the Drude eqn. (8) with the maximal experimental value of Δ equals 50 Å, which is more than twice the length of a DODA molecule in the all-*trans* conformation! Obviously, such a thickness of a pure DODA film could be only explained if collapse occurs with 3D-growing, which is not compatible with the behavior observed in the Π - A isotherms. As a consequence, we have to admit that the adsorption of polyanions takes place, even at very low concentrations ($c_{\text{PA}} \leq 5 \text{ }\mu\text{M}$), where Δ has already diminished below the value corresponding to a single and compact layer of pure DODA. If the first plateau in Fig. 3a is related to the formation of an inorganic layer under the DODA organic monolayer, one may suppose that the second plateau is due to the thickening of this layer which may be described as the formation of a second layer of polyanions under the previous one. We therefore used the stratified model presented in 2.2 to check if this scenario of the thickness variations is sustained by the ellipsometric data.

From Fig. 3a it can be noticed that $\delta\Delta$ is strongly dependent on the concentration of Keggin polyanions and nearly independent on the concentration of DODA in the monolayer. Hence, in the model the thickness of the lipid layer d_{org} will be supposed equal to the one measured at the similar concentrations of DODA, but in the absence of inorganic sublayer. In particular, at three considered surface areas, the thickness of the DODA monolayer on pure water varies from 13 to 20 Å. Therefore in the calculations we took the average value of 16 Å. The average refractive index of the DODA film has already been estimated in 2.2.1 ($n_{\text{org}} = 1.45$). Moreover, the refractive index of a saturated aqueous solution of polyanions measured by means of the Abbe refractometer equals 1.6,⁵ and this value has been taken for n_{inorg} . The total thickness of the film $d = d_{\text{org}} + d_{\text{inorg}}$ as a function of polyanion concentration calculated with the ellipsometric data from Fig. 3a) is then presented in the Fig. 3b). To interpret this figure we calculated the ellipsometric angle $\delta\Delta$ of the whole film which is obtained if one or two polyanion layers are taken into account. The polyanion itself can be considered as a stiff sphere with diameter of ~ 10 Å. Therefore, if the sublayer is composed of only one layer of polyanions, the total thickness of the film equals to 26 Å (16 Å for organic + 10 Å for inorganic sublayer). This gives a value of $\delta\Delta$ close to -7° at the saturation state, which corresponds exactly to the first plateau. The second saturation plateau with $\delta\Delta \sim -10^\circ$ at $C_{\text{PA}} \geq 1 \text{ mM}$, is compatible with the formation of a second sublayer of polyanions, resulting in a total film thickness of about 36 Å.

From Fig. 3b, we can highlight the strong dependence between the thickness of the adsorbed inorganic layer d_{inorg} and the concentration of the polyanions C_{PA} . Indeed, at low concentration a first inorganic sublayer is formed with the thickness equal to the Keggin polyanion diameter. This layer is fully formed at $C_{\text{PA}} \sim C_C = 4 \times 10^{-7}$ M. For higher concentrations, the ellipsometry data demonstrate the increase of the thickness of the adsorbed layer until a second plateau is reached. This behavior suggests the adsorption of a second but more diffuse layer. Indeed, the interactions between the polyanions and the second layer occurs at a distance larger than the Bjerrum length (~ 7 Å for water at 20 °C) indicating the diffuse character of this layer. The existence of this second layer has been hypothesized from the re-expansion of the isotherm and is now clearly visible from the growing of the film thickness until two complete layers of 10 Å each are formed.

4. Conclusion

We took advantage of the large (10 Å in diameter) size of inorganic polyanions as well as their refraction index (about 1.6) different enough from that of water, to follow their adsorption along the organic DODA monolayer by ellipsometric measurements. For this adsorption we demonstrated the two-step process: firstly, a highly packed anions layer is formed; secondly, above a critical concentration of polyanions in the subphase, a second more diffuse layer is formed under the previous one. The structure of the inorganic sublayer has therefore a diffuse character similar to that of electrical double layer.

Appendix: The anisotropic DODA monolayer model

In a bi-axial optical medium two principle refractive indices n_{\perp} and n_{\parallel} being perpendicular and parallel to the optic axis should be considered. To estimate their values in the case of fatty acid films, den Engelsen and Koning¹⁸ proposed a simplified model (a more complete one has been developed for the case of lipids by Ducharme *et al.*¹⁹). In this simple model, the molecules are considered as stiff rods of fixed dimensions associated to the stretched configuration L and with circular section equal to the molecular area A_0 corresponding to a saturated monolayer. Upon compression, these rod-shaped molecules reorient more and more vertically with the refractive index n_{\perp} growing at the expense of the parallel component, n_{\parallel} . The variation of the two principal refractive indices with respect to orientation of the rods is obtained from molecular refractive indices n_x and n_z through the following equation:

$$n_{\parallel}^2 = \frac{1}{2} [\varepsilon_x (1 + \cos^2 \theta) + \varepsilon_z \sin^2 \theta]$$

$$n_{\perp}^2 = \varepsilon_x \sin^2 \theta + \varepsilon_z \cos^2 \theta \quad (\text{A1})$$

where θ is a tilt angle and the dielectric constants are obtained from molecular refractive indices $\varepsilon_z = n_z^2$ and $\varepsilon_x = n_x^2$. Upon

compression the tilt angle and the molecular area A decreases, while the film thickness d proportionally increases following the equations:

$$d = L \cos \theta \quad \text{and} \quad A = A_0 / \cos \theta \quad (\text{A2})$$

The ellipsometric angle δA can then be estimated from the Drude equation for the bi-axial film:

$$\frac{\delta A}{4\pi} = \frac{d}{\lambda} \frac{n_w^2 \cos \phi \tan^2 \phi}{(n_a^2 \tan^2 \phi - n_w^2)(n_w^2 - n_a^2)} \left(n_a^2 + n_w^2 - n_{\parallel}^2 - \frac{n_w^2 n_a^2}{n_{\perp}^2} \right) \quad (\text{A3})$$

where the two refractive indices are then adjusted to give a measured value for a given molecular area. From this simulation we obtained $n_x = 1.4461 \pm 0.0005$ and $n_z = 1.459 \pm 0.002$ with the averaged value $n_{\text{ave}} = 1.453 \pm 0.002$ which agrees well with the value obtained from the model of an isotropic layer. Similar calculations performed by Tronin and Shapovalov¹⁴ for the monolayer of pure DODA spread on 10 mM NaCl solution gave a slightly higher values: $n_x = 1.48$ and $n_z = 1.51$. This difference can be explained by screening of electrostatic contribution to the molecular polarisabilities at a high ionic strength.

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