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Spectroscopic and Electrokinetic Study of the pH-Dependent Ionization of Langmuir-Blodgett Films. 2

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The pH titration of the spectroscopic probe molecule 4-octadecyl oxy-1-naphthoic acid (ONA) cast in Langmuir-Blodgett films with the neutral diluent molecules polyvinyl octadecyl ether (PVOE) and eicosan-1-ol, onto hydrophobic silica, has been examined via the technique of attenuated total internal reflection spectroscopy and streaming potential measurements. The ONA molecules exhibited pronounced pH-dependent aggregation when cast onto hydrophobic silica plates. Neutralization (titration from high to low pH) of charged ONA films was in agreement with the behavior predicted by the Gouy-Chapman equation. Reionization (titration from low to high pH) of the ONA molecules proceeded much more slowly than neutralization and the rate was also slower in the polymeric PVOE diluent. Marked hysteresis was evident between the neutralization and reionization curves, this being more pronounced at lower ionic strength and less pronounced in the polymeric PVOE diluent. The reionization results could be modeled using ONA dimers to represent the aggregation state of the probe molecules in the film at low pH.

Introduction

Lipoidal acid-base indicators, or spectroscopic probes as they will hereafter be referred to, have been shown to be useful for measuring the electrostatic surface potential, ψ_0 , of micelles,¹ vesicles,² and microemulsions.^{3,4} The procedure used to extract ψ_0 in such surfactant self-assembled structures using spectroscopic probes is also applicable to cast film interfaces, i.e., Langmuir-Blodgett (L-B) films. Unfortunately, previous attempts to make such measurements in this laboratory on L-B films have been troubled by the unusual titration behavior of the probes used.^{5,6}

In a recent study,⁷ we examined the pH titration characteristics of the well-studied⁸⁻¹⁰ spectroscopic probe 4-heptadecyl-7-hydroxycoumarin (HHC) embedded in L-B films. It was found that quite different titration results were obtained depending on whether the silica casting substrate was rendered hydrophobic by an established¹¹ silylation procedure or by esterification¹² with a long-chain alcohol. As a consequence of this work, we sought to resolve the question of whether or not the apparent pH-dependent aggregation of another previously used⁵ spectroscopic probe, 4-octadecyl oxy-1-naphthoic acid (ONA), was also affected by the method used to make the substrate hydrophobic. The ionization of the L-B films was

monitored via the techniques of streaming potential and attenuated total internal reflectance (ATR) spectroscopy, as follows.

Experimental Section

Materials. The 4-octadecyl oxy-1-naphthoic acid (ONA) was prepared by the Victorian Institute of Drug Technology by the method of Gray and Jones.¹³ Polyvinyl octadecyl ether (PVOE) was synthesized from glycerol tristearate (BDH reagent grade) and high-purity vinyl stearate as described previously;⁵ its molecular weight was $1.4 \pm 0.1 \times 10^6$. Analytical grade octadecyl-trichlorosilane (OTS) was obtained from Tokyo Kasei. The eicosan-1-ol was of ultrahigh purity obtained from the Hormel Institute. Dodecan-1-ol was Puriss grade from Fluka. All organic solvents used were of spectroscopic grade, all other reagents were of analytical grade. The water used throughout the study was from a Milli-Q system and had a conductivity of less than 10^{-4} S m⁻¹ and a surface tension of 72.0 mN m⁻¹ at 25.0 °C.

The silica substrate in both the ATR and streaming potential measurements was high-grade vitreous silica (Suprasil), polished to optical smoothness, obtained from H. R. Groiss Ltd., Melbourne, Australia.

Methods. In order for the film molecules to be cast onto silica plates with the hydrophilic moiety pointing out into the surrounding aqueous solution, hydrophobic silica plates were required. Plates were made hydrophobic either by using a 10% (v/v) solution of OTS in CCl₄ or by esterification with dodecan-1-ol according to the procedures described in detail previously.⁷

Film molecules were dissolved in the appropriate organic solvent and spread onto the aqueous subphase contained in a solid Teflon Langmuir trough of dimensions, 580 × 170 × 10 mm. The eicosan-1-ol was dissolved in hexane; other film components were dissolved in chloroform and/or methanol. The ONA dissolved with difficulty in most of the commonly used spreading solvents. It was found that ONA dissolved in chloroform after warming to ~80 °C. Details of the casting procedures used to obtain single L-B films on the hydrophobic silica substrates are given elsewhere.⁷ The temperature during casting was maintained at 25.0 ± 0.2 °C and the casting speed was 5.0 ± 0.5 mm min⁻¹. During casting, the surface pressure was maintained to within 0.3 mN m⁻¹ of the casting pressure. Plates with deposition ratios outside 1.00 ± 0.05 were rejected. After casting, the silica plates rested submerged in a well in the Langmuir trough and remained submerged during their subsequent transfer to either the ATR titration assembly or the

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streaming potential apparatus. The plates were therefore only passed through the air–aqueous solution interface once, during casting, to avoid exposing the hydrophilic headgroups to the air and thus risking stripping off and/or flipping of the film.

Full details of the ATR titration assembly^{5,7} and the streaming potential apparatus^{7,14} have been given previously. Briefly, in the ATR assembly the trapezoidal ATR plate (50 × 20 × 2 mm) was mounted in the cavity of a Cary 210 spectrophotometer with the exciting beam incident on one end of the plate while the attenuated beam emerging from the other end was directed into the detector by reflection off two mirrors. Aqueous phase was circulated against each side of the L–B film coated plate through to a reservoir containing a combined pH electrode (Triton Instruments) connected to a pH meter (Orion Ionalyzer 901) to monitor the pH. In the streaming potential apparatus, two rectangular, L–B film coated plates (75 × 25 × 1 mm) were used to form a narrow capillary 0.12 mm wide. The capillary connected two Teflon reservoirs across which a pressure difference, ΔP , could be applied and the resulting streaming potential, ΔE , measured via two platinum black electrodes. The bulk conductivity and pH of the liquid flowing through the capillary were monitored via a Triton conductivity electrode plus meter (Phillips Model PW9526) and a pH electrode (as above) placed in one of the reservoirs.

All measurements were conducted at $25.0 \pm 0.2^\circ\text{C}$. The pH of the aqueous phase was adjusted by the addition of small volumes of HCl and NaOH. All other details have been given elsewhere.^{5,7,14}

Calculation of the Surface Potential (ψ_0) and the ζ Potential

The theory behind the use of spectroscopic probes to determine ψ_0 has been discussed in great detail previously.^{9,15} Since the conjugate acid and base forms of the spectroscopic probe are spectroscopically distinct this allows the degree of dissociation, α , of the probe chromophore to be monitored as a function of pH in the ATR titration assembly. The measured pK_a for the dissociation of the conjugate acid form of the probe, pK_a^{obs} , is given by

$$pK_a^{\text{obs}} = \text{pH} - \log(\alpha/1 - \alpha) \quad (1)$$

and it can be shown that^{9,15}

$$pK_a^{\text{obs}} = pK_a^0 - (e\psi/2.303kT) \quad (2)$$

where ψ is the electrostatic potential at the time-averaged location of the prototropic moiety of the probe chromophore at the interface, e the charge on an electron, k the Boltzmann constant, and T the absolute temperature. The term pK_a^0 is the pK_a in the absence of any electrostatic potential ($\psi = 0$) and may be obtained by (a) extrapolating the same chromophore in a neutral surfactant interface, such as a nonionic micelle, (b) titrating the chromophore in a bulk solution with the same chemical environment as the neutral interface, or (c) extrapolating pK_a^{obs} to $\alpha = 0$ in an ionizable interface, such as an L–B film. In L–B films, if the probe chromophore is the only ionizable group, ψ in eq 2 may be unambiguously assigned as ψ_0 . The restrictions on the applicability of eq 2 are that there should be no specific molecular interactions between the chromophore and any surrounding molecules/ions which interfere with its acid–base equilibrium.

Since the area per probe molecule, A , is known at casting, ψ_0 may be calculated on purely theoretical grounds using the Gouy–Chapman equation,¹⁶ to give

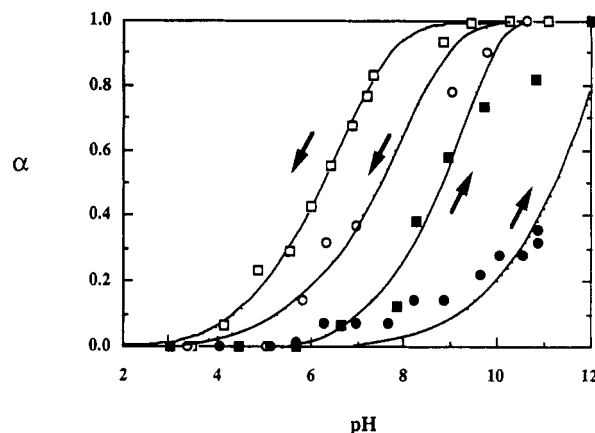


Figure 1. Degree of dissociation, α , versus pH for the neutralization of L–B films of 0.2 mol fraction ONA + 0.8 mol fraction PVOE, cast onto OTS-treated silica, in the presence of 10^{-1} mol dm^{-3} KCl (\square) followed by subsequent reionization (\blacksquare). Also shown are the neutralization (\circ) and reionization (\bullet) data for an identical film in the presence of 10^{-2} mol dm^{-3} KCl. The curves through the neutralization data are the trends predicted by eq 3 for $pK_a^0 = 4.9$ and 5.3 , respectively. The curves through the reionization data are the closest fits generated using the dimerization model with $pK_a^0 = 4.9$ and $pK_{\text{dim}} = 12.7$ and 16.0 for the 10^{-1} and 10^{-2} mol dm^{-3} KCl data, respectively. (The arrows on the figure indicate the direction of the titration.)

$$\psi_0 = (2kT/e) \operatorname{arsinh} [1.34\alpha/AC^{1/2}] \quad (3)$$

where A is expressed in nanometers squared and C is the bulk concentration of the 1:1 electrolyte. The corresponding values of α are given by

$$\alpha = \sigma_0/\sigma_{0\text{max}} \quad (4)$$

where $\sigma_{0\text{max}}$ is the maximum possible surface charge density, e/A .

In the streaming potential experiments the ζ potential was calculated via the Smoluchowski equation¹⁷

$$\zeta = \eta\lambda\Delta E/D\epsilon_0\Delta P \quad (5)$$

where η is the bulk viscosity, ϵ_0 is the permittivity of free space, D is the static dielectric constant, and λ is the conductivity of the solution in the capillary.

Results and Discussion

The ATR spectra of ONA cast in the L–B films studied showed main peaks at 315 (low pH) and 300 nm (high pH), corresponding to the un-ionized and ionized forms of ONA, respectively. In addition there was a shoulder at 344 nm, which has been attributed⁵ to the formation of aggregates of ONA—as observed with solid naphthoic acids.¹⁸ The ATR spectra obtained here were essentially the same as those obtained earlier.⁵

The fractional change in the absorbance at 315 nm due to the un-ionized form of the ONA was used to calculate the degree of ionization as the pH was changed. Any baseline drift in the absorbance was accounted for by monitoring the absorbance at 600 nm; at this wavelength the absorbance is independent of pH. Figure 1 shows the results of ATR titrations of L–B films of 0.2 mol fraction ONA + 0.8 mol fraction PVOE in the presence of 10^{-1} and 10^{-2} mol dm^{-3} KCl, respectively. The films were cast at a surface pressure of 27 mN m^{-1} from subphases containing the same concentrations of KCl and onto silica plates rendered hydrophobic with OTS. The subphase also

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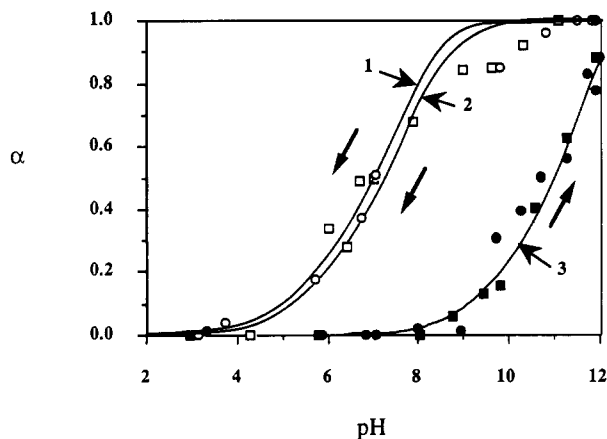


Figure 2. Degree of dissociation, α , versus pH for the neutralization of an L-B film of 0.2 mol fraction ONA + 0.8 mol fraction eicosan-1-ol, cast onto OTS-treated silica, in the presence of 10^{-1} mol dm^{-3} KCl (\square), and the same film composition cast onto esterified silica in the presence of 10^{-2} mol dm^{-3} NaCl (\bullet). Data for the reionization of these films are shown by \square and \bullet , respectively. Curves 1 and 2 are the theoretical neutralization results predicted by eq 2 (see text); curve 3 is the theoretical ionization behavior predicted by the dimerization model (see text). (The arrows on the figure indicate the direction of the titration.)

contained 10^{-4} mol dm^{-3} KOH. The corresponding values of A were 0.86 and 1.03 nm^2 , respectively. On Figure 1, the direction of the titration, from low to high pH, or vice versa, has been indicated; the considerable hysteresis in the ionization behavior is clearly evident. When films were left at low pH for several hours, a gradual increase in the height of the shoulder at 344 nm occurred. A rational explanation for the hysteresis seen in Figure 1 is therefore that once ONA molecules become neutralized they have tendency to aggregate—presumably involving lateral migration of the molecules in the film. Reionization then involves ionization of aggregated ONA molecules; i.e., the ONA molecules are in quite a different environmental state than the separated ONA molecules in the neutralization process.

Figure 2 shows the results of an ATR titration of an L-B film of 0.2 mol fraction ONA + 0.8 mol fraction eicosan-1-ol in the presence of 10^{-1} mol dm^{-3} KCl, cast in the same way as described above. The value of A for this film was 0.73 nm^2 . Similar hysteresis was observed in the ONA + eicosan-1-ol system, in agreement with the behavior observed earlier⁵ for this system on OTS-treated silica and confirming that the hysteresis is not specific to the second component of the L-B film. Comparison of Figures 1 and 2 reveals that the hysteresis in the ONA + eicosan-1-ol system was considerably more marked than in the ONA + PVOE system at the same ionic strength. In fact, the hysteresis in the ONA + PVOE system previously went unnoticed.⁵ This is probably because a lower mole fraction of ONA was employed in the earlier study, which will reduce the amount of aggregated ONA formed, and also because more time is required for the ONA molecules to aggregate in the PVOE matrix than in the eicosan-1-ol matrix, reflecting the polymeric nature of the former. The retarding effect on the aggregation-disaggregation kinetics of the polymeric PVOE film is illustrated in Figure 3, where α is plotted against the time from a sudden switch from low pH to high pH. It is seen that for ONA in the PVOE film longer time is required to reach full dissociation than in the eicosan-1-ol film. In contrast, the time for complete neutralization of each film was the same and complete within 10 min. The results in Figure 1 also indicate that

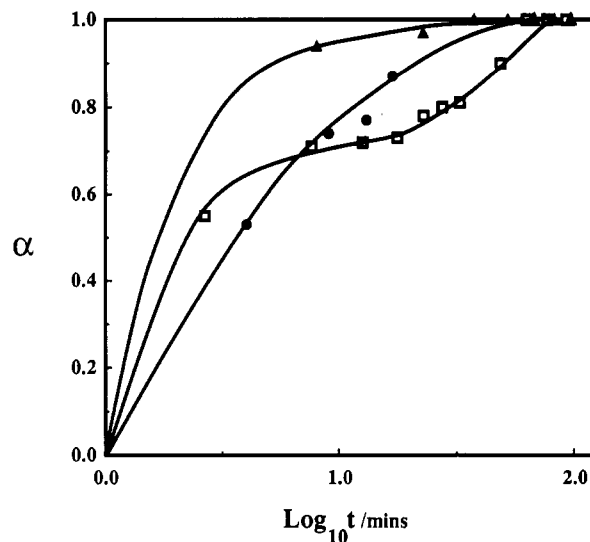


Figure 3. Degree of dissociation, α , versus the log of time, t , for a sudden change from pH 3 to pH 11 for films of 0.2 mol fraction ONA + 0.8 mol fraction PVOE (\square) and 0.2 mole fraction ONA + 0.8 mol fraction eicosan-1-ol (\triangle) in the presence of 10^{-1} mol dm^{-3} KCl, cast onto OTS-treated silica. A plot is also shown for 0.2 mol fraction ONA + 0.8 mol fraction eicosan-1-ol in the presence of 10^{-2} mol dm^{-3} NaCl, cast onto esterified silica (\bullet).

the hysteresis was more pronounced at the lower ionic strength. The reasons for this are not clear but it is likely to be some secondary affect of the polymer matrix, judging from the quite different electrolyte influences seen in the eicosanol system.

The Gouy-Chapman equation (eq 3) was used to try and predict the neutralization titration data by choosing an appropriate value for $\text{p}K_a^0$. The values of $\text{p}K_a^0$ which give a reasonable fit to the experimental results in the presence of 10^{-1} and 10^{-2} mol dm^{-3} KCl are 4.9 and 5.3, respectively, with the theoretical curves shown in Figure 1. The corresponding $\text{p}K_a^0$ value for the ONA + eicosan-1-ol system was 5.5. Following the procedure of Lovelock et al.,⁵ it is possible to obtain a fit to the ionization curves by nominally introducing aggregation effects through a dimerization model, where the constant

$$K_{\text{dim}} = [\text{HA}]_s^2 / [\text{H}_2\text{A}_2]_s \quad (6)$$

describes the equilibrium between the concentration of un-ionized ONA in the surface, $[\text{HA}]_s$, and the concentration of dimers in the surface, $[\text{H}_2\text{A}_2]_s$ (representative of aggregated ONA). It can then be shown that

$$a(\text{H}^+)_s^2 \left[\frac{(2/A)\alpha^2}{(K_a^0)^2 K_{\text{dim}}} \right] + a(\text{H}^+)_s (\alpha/K_a^0) + (\alpha - 1) = 0 \quad (7)$$

where $a(\text{H}^+)_s$ is the activity of H^+ in the surface. Given values of $\text{p}K_a^0$ and $\text{p}K_{\text{dim}}$, solution of the quadratic gives $a(\text{H}^+)_s$. The value of ψ_s is calculated from the Gouy-Chapman equation (eq 3) and then the corresponding activity of H^+ in the bulk, $a(\text{H}^+)_b$ (via the pH), is calculated from the Boltzmann equation

$$a(\text{H}^+)_s = a(\text{H}^+)_b \exp(-e\psi_s/kT) \quad (8)$$

This procedure leads to the theoretical α versus pH ionization curves shown in Figures 1 and 2. The corresponding values of $\text{p}K_a^0$ and $\text{p}K_{\text{dim}}$ which gave a reasonable fit to the reionization data were $\text{p}K_a^0 = 4.9$ and $\text{p}K_{\text{dim}} = 12.7$ and 16.0 for the ONA-PVOE films at 10^{-1} and 10^{-2} mol dm^{-3} KCl, respectively; $\text{p}K_a^0 = 5.5$ and $\text{p}K_{\text{dim}} = 15.5$ for the ONA-eicosan-1-ol film at 10^{-1} mol dm^{-3} KCl.

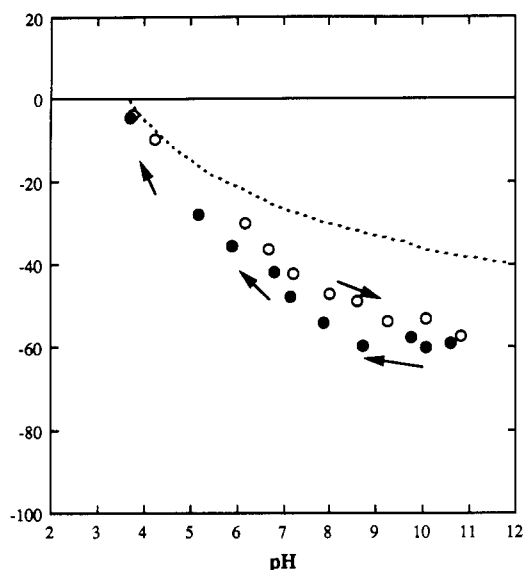


Figure 4. ζ potential versus pH for a film of 0.2 mol fraction ONA + 0.8 mol fraction PVOE, cast onto OTS-treated silica, in the presence of $5 \times 10^{-2} \text{ mol dm}^{-3} \text{ KCl}$: neutralization (\bullet); reionization (\circ). Dotted line is the uncoated OTS-treated silica.

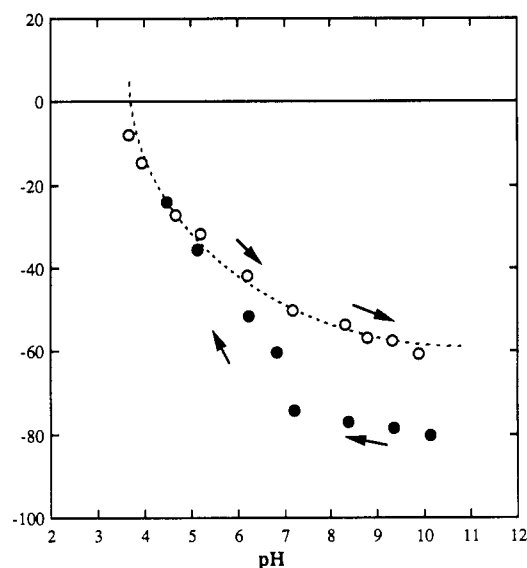


Figure 5. ζ potential versus pH for a film of 0.2 mol fraction ONA + 0.8 mol fraction PVOE, cast onto OTS-treated silica, in the presence of $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ KCl}$: neutralization (\bullet); reionization (\circ). Dotted line is the uncoated OTS-treated silica.

To confirm the hysteresis behavior observed in the ATR titrations, complementary measurements were performed on the same L-B films in the streaming potential apparatus in order to monitor the variation in the double-layer potentials directly. Figures 4 and 5 show the resultant ζ -pH curves obtained in the presence of 5×10^{-2} and $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ KCl}$ for L-B films of 0.2 mol fraction ONA + 0.8 mol fraction PVOE, respectively. Apart from the salt concentrations, the films were cast under the same conditions as stated above for the ATR titrations. The ζ -pH curves can only be sensibly compared when each are at constant background electrolyte concentration, and above $\sim 0.1 \text{ mol dm}^{-3} \text{ KCl}$, streaming potentials become too small to measure accurately. This therefore excluded the eicosan-1-ol + ONA system from examination in the streaming potential apparatus since it is seen that, particularly during reionization (Figure 2), the pH must be raised to very high values to obtain full ionization (α

$= 1$) and then the OH^- ions begin to make a significant contribution to the total ionic strength.

Figures 4 and 5 demonstrate that hysteresis was indeed evident in the ζ -pH curves for PVOE + ONA, the hysteresis being far more pronounced in the lower KCl concentration case ($5 \times 10^{-3} \text{ mol dm}^{-3}$). On neutralization ζ is of greater magnitude than its magnitude on reionization, at a given pH. Since a higher value of ζ suggests a correspondingly higher value of α , this indicates a higher value of pK_a^0 on reionization, at a given pH. This is fully in accord with the trends found in the ATR titrations.

The explanation of the results presented so far is essentially the same as that put forward earlier,⁵ that the neutralization process appears to follow Gouy-Chapman theory whilst the ionization process does not, but it may be qualitatively explained by the dimerization model. It will be noted, however, that the fit of theory to experiment is by no means perfect and the values of pK_a^0 required to explain the data seem to vary. All the above L-B films had been cast onto silica made hydrophobic using OTS in organic solution. Our previous work^{7,19} has shown that this produces a fairly thick, porous hydrophobic layer which can result in anomalous titration behavior. In particular, there was evidence that the spectroscopic probe 4-heptadecyl-7-hydroxycoumarin was capable of migrating through the hydrophobic layer toward the underlying silica, which changed the environment of the probe and thus its pK_a^0 value. This therefore raises the question as to whether or not the apparent aggregation behavior of ONA was partly or wholly a consequence of the nature of the OTS-silica surface. In this respect several other points on Figures 4 and 5 should be noted. The dashed curves on the figures indicate the ζ -pH behavior obtained for the OTS-treated silica surfaces before deposition of the L-B films. Particularly in the $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ KCl}$ case, there is very little difference between the ionization profiles with and without the deposited L-B film over much of the pH range. The L-B film is expected to at least cause a change in ζ because of a shift in the plane of shear outward from the silica surface. This indicates that the un-ionized ONA film may indeed be partially buried in the OTS layer on the silica before subsequent ionization. Starting with the film in the ionized state, the results with $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ KCl}$ indicate a transition from one ζ -pH curve to another ζ -pH curve with a lower maximum $|\zeta|$ as the pH is lowered. This is reminiscent of the behavior of L-B films of HHC on OTS-treated silica,⁷ where detailed modeling of silica-OTS/L-B film interface suggested a transition between two different environments as the pH was changed.

The above observations complicate the analysis of the ONA results greatly. Not only is there the possibility of migration and aggregation of the probe within the plane of the surface, but also the possibility of migration toward/away from the silica, perhaps also accompanied by a change in the degree of aggregation. Figure 2 shows the results of an ATR titration of a L-B film consisting of 0.2 mol fraction ONA + 0.8 mol fraction eicosan-1-ol cast onto silica made hydrophobic by esterification with dodecan-1-ol. The film was cast from a substrate of $10^{-2} \text{ mol dm}^{-3} \text{ NaCl}$ plus $10^{-2} \text{ mol dm}^{-3} \text{ NaOH}$ to, as far as possible, ensure that the ONA molecules were completely ionized during casting. The aqueous phase in contact with the cast L-B film was maintained at this high pH until the first titration, to pH 3. This procedure was followed to try and ensure that there was no preaggregation of neutral ONA

(19) Trau, M.; Murray, B. S.; Grant, K.; Grieser, F. J. *Colloid Interface Sci.*, in press.

molecules in the L-B film before the first ATR titration. The film was cast at a surface pressure of 30.0 mN m^{-1} , corresponding to a value of $A = 1.25 \text{ nm}^2$.

The results in Figure 2 for the film cast onto the esterified silica clearly show the same type of hysteresis observed in the films cast onto OTS-silica—in fact, quantitatively the results are very close. The quantitative similarity may seem surprising since the films were titrated in the presence of different electrolyte concentrations— 10^{-1} and $10^{-2} \text{ mol dm}^{-3}$, respectively. However, for the film cast onto OTS-silica, $A = 0.73 \text{ nm}^2$ on casting, whereas for the film cast onto esterified silica, $A = 1.25 \text{ nm}^2$. (The higher value of A in the latter case was a consequence of the higher pH and lower salt concentration of the subphase during casting.) For the film cast onto the esterified silica, the higher value of A (hence lower $\sigma_{0\text{max}}$) compensates for the lower value of the screening electrolyte during the titration: curves 1 and 2 on Figure 2 show the theoretical neutralization behavior predicted by eq 3 for both cases using $\text{p}K_a^0 = 5.5$; the two curves are almost identical.

The L-B film was left at pH ~ 3 for 14 h before beginning the back-titration to ca. pH 12. The long period left between neutralization and reionization was to ensure that any possible aggregation would reach equilibrium. The drift and noise in the spectrum over this period did not make it possible to clearly ascertain whether or not this was so simply from the absorbance at 344 nm (due to the aggregate species). In Figure 2 it is seen that the reionization results obtained on esterified silica were also very similar to those obtained on OTS-silica. Again, the higher value of A for the L-B film cast onto the esterified silica compensates for the lower concentration of salt so that the same dimerization model (curve 3) gives a reasonable fit to both sets of results. The value of $\text{p}K_a^0$ used was 5.5 (i.e., the same as for ionization) and the value of $\text{p}K_{\text{dim}}$ used was 15.5.

The parallel with the earlier results on OTS-silica is also revealed in the kinetics of reionization, shown on Figure 3. The reionization of the ONA + eicosan-1-ol film on the esterified silica appeared to be slower than on the OTS-silica, but this may have been a result of the 4 times longer period between neutralization and reionization for the experiment on esterified silica, resulting in a slightly more aggregated state. Clearly the aggregation of ONA in the L-B films cast onto both esterified and OTS-silica is not a function of the nature of the hydrophobic substrate.

With regard to the absolute values of ψ_0 determined via the ONA probe on neutralization, it can be seen that there is not complete agreement with the Gouy-Chapman predicted trend, particularly at $\alpha > \sim 0.6$. This lack of complete agreement may in part be due to the problem

of electrostatic interaction of the L-B film with the underlying silica, which for OTS-treated silica clearly retains appreciable negative charge—see Figures 4 and 5. Similarly, streaming potential measurements on the esterified silica indicate that this surface has ζ -pH characteristics almost identical to the bare silica.²⁰

Thus, electrostatic interaction with the silica substrate can be expected to make some contribution to the $\text{p}K_a^0$ value for a ONA film cast onto OTS and esterified silica substrates. However, for esterified silica, the magnitude of the effect of such an interaction would appear to be constant over the most of the pH range of the titrations, since a constant value of $\text{p}K_a^0$ seems to give a reasonable fit to each titration curve up to $\alpha = 0.7$. This is despite the fact that this range of α corresponds to the pH range where most of the change in the ζ potential for the silica substrate occurs—note that up to the pH where the L-B film begins to ionize the ζ -pH curve for the substrate plus L-B film seems to be almost identical to the curve for the substrate alone (see Figures 4 and 5). In order to model the electrostatics of the substrate plus L-B film, the detailed dielectric structure of the layer must be known, and this information is not yet available.

Conclusions

We have strengthened the conclusion that meaningful ionization behavior in L-B films cast onto silica substrates rendered hydrophobic via esterification can be obtained by using a spectroscopic probe embedded in the film. The spectroscopic probe ONA exhibits hysteresis on neutralization-ionization cycles, indicative of aggregation of the neutral ONA molecules within the film. This may allow analysis of diffusion kinetics within such L-B films. On neutralization, where the ONA molecules start in a non-aggregated state, the ionization behavior seems to follow a simple surface charge-surface potential relationship, i.e., Gouy-Chapman theory.

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(20) Esterification with dodecanol is likely to remove only about half of the surface hydroxyl groups,²¹ which should not greatly affect ψ_0 .²² The film may be expected to shift the plane of shear and hence affect the streaming potential. That this effect is not seen suggests the film has a low dielectric constant while still being permeable to protons.

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