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The Formation Dynamics of Cholesterol Films Prepared by Spontaneous Self-Assembly Method

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The dynamics of the process of formation of cholesterol films on a solid substrate prepared by the spontaneous self-assembly technique has been investigated. An expression for the coverage in a multilayer system was derived. Application of the equation to cholesterol multilayer film formation kinetics shows that the approach to equilibrium of the self-assembly process obeys first-order rate law. An observed adsorption free energy change of $-21..7\pm0.1$ kJ mol^{-1} was obtained for cholesterol on quartz slide and a mean lifetime of cholesterol on the slide surface during deposition of 78 ± 3 ks at 298.16 K. A mean lifetime for stearic acid adsorbed from hexadecane onto native aluminium oxide surface (data from elsewhere) was found to be 12.4 ± 0.3 ks. The results suggest dynamic processes which strongly depend on the formation constant of the amphiphile for coordination to the substrate.

The adsorption and spontaneous organization of amphiphilic molecules on solid substrates have been of great interest in the recent past.[1—4] Much of the interest in these organic films have generated from their industrial applications in wear prevention, lubrication, and catalysis;[1] and in their potential technological applications in the areas of surface-modified electrodes for electrochemical applications,[5] optics, and microelectronics.[6] It is also believed that if the process by which they can be prepared are well understood, spontaneous self-assembly method offers wider possibilities for large-scale applications of organic films, a limitation suffered by the Langmuir–Blodgett method.[7]

One handicap to a clear understanding of the processes (or process) involved in multilayer adsorption from solution is that theoretical developments lag behind experimentation. While theoretical developments in other aggregation processes in solution, such as micellization and flocculation[8] continued to receive attention, adsorption has largely been neglected. In many studies, Langmuir adsorption isotherm developed for monolayer gas adsorption,[9] or modified forms of it,[10,11] continued to be applied to multilayer adsorptions from solution.

The earliest theory of multilayer adsorption by deBoer and Zwikker[12a] and later Bradley[12b] assumes that adsorption of nonpolar molecules on ionic adsorbents is due to induced dipoles. The uppermost layer of the adsorbent induces dipoles in the first layer of adsorbed molecules which in turn induce dipoles in the next layer and so on until several layers are built up. According to Brunauer et al.,[13] the polarization of the second layer of adsorbed gas by the first is too small to constitute the major portion of the binding energy between the two adsorbed layers; particularly in cases where such molecules do not possess permanent dipoles.

In this contribution, it has been proposed that free-energy considerations which account, in large part, for micellization and flocculation[8] are also responsible for the aggregation at solid–liquid interfaces. An expression has been developed from a consideration of the dynamics of the adsorption involved in the formation of organic films by spontaneous self-assembly technique. The new expression obtained was applied to the adsorption of cholesterol onto quartz slide and to a similar study from literature.[1] The results suggest that a useful expression has been obtained.

Theory

Let S_0, S_1, $\cdots$, S_i, $\cdots$, represent the surface area covered by only, 0, 1, $\cdots$, i, $\cdots$, layers of adsorbed amphiphiles. Since at equilibrium, S_0 must remain constant, the rate of adsorption on the bare surface is equal to the rate of desorption from the first layer and thus,

$$k_+CS_0 = k_-S_1\mathrm{e}^{-E_1/RT}, \tag{1}$$

where C (mol dm^{-3}), is the concentration of the adsorbate in an apolar solution of the surfactant, E_1 the heat of adsorption of the amphiphile to the first layer, k_+ the first-order rate constant for the entry of the adsorbate into the film and k_- the first-order rate constant for its exit from the film. This is essentially Langmuir's formulation for unimolecular adsorption and involves the assumption that k_+, k_-, and E_1 are independent of the number of adsorbed molecules already present in the first layer.

Furthermore, let the rate of adsorption of an amphiphile into an ith layer remain k_+ and rate of desorption of an amphiphile from a film containing i layers be ik_-. The latter assumption is consistent with the fact that there is incomplete coverage in the layers leading to the presence of S_0, S_1, $\cdots$, S_i, $\cdots$ surfaces, or put differently, the presence of defects in the layers. Thus, in a dynamic equilibria,

$$k_+CS_{i-1} = ik_-S_i\mathrm{e}^{-E_i/RT}, \tag{2}$$

Consequently, the number of layers are Poisson dis-

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tributed and the free energy of adsorption falls off with increase in the number of layers, a major defect suffered by the earlier BET theory of multilayer gas adsorption.[13] This defect gives rise to the physically implausible model of infinite adsorption.[14]

The heat of adsorption to the first layer, E_1 involves, in some cases, chemisorptive effects; but the crystallization - dissolution properties of the second and higher adsorbed layers are the same as those of the crystalline state. We may therefore make the simplifying assumption that, $E_2=E_3=\cdots=E_f$, the heat of fusion, and obtain from the set of Eqs. 1 and 2 that the surface area covered by a section of the film containing i layers,

$$S_i = \beta S_0 \frac{(kC\mathrm{e}^{E_f/RT})^i}{i!}, \tag{3}$$

where $\beta=\exp[(E_1-E_f)/RT]$ and $k=k_+/k_-$, the equilibrium constant for adsorption into the first layer. If we define an observed equilibrium constant, k_0 by $k\mathrm{e}^{E_f/RT}$ Eq. 3 becomes,

$$S_i = \beta S_0 \frac{(k_0C)^i}{i!}. \tag{4}$$

The total adsorbent surface area is given by the expression,

$$A = \sum_{i=0}^{\infty} S_i = \beta S_0 \sum_{i=0}^{\infty} \frac{(k_0C)^i}{i!} = \beta S_0 \mathrm{e}^{k_0C}. \tag{5}$$

The fraction of the surface covered by i layers, θ_i is obtained from Eqs. 4 and 5 as

$$\theta_i = \frac{(k_0C)^i/i!}{\mathrm{e}^{k_0C}}. \tag{6}$$

Eq. 6 , which refers to an equilibrium process, assumes the general form

$$\theta'_i \mathrm{e}^{k_0C} \leqslant (k_0C)^i/i!, \tag{7}$$

where equality and inequality signs refer to equilibrium and spontaneous processes, respectively and θ'_i the fraction of the surface covered by i layers at an instant, t before equilibrium. The rate of advancement to equilibrium is then given by,

$$\mathrm{d}\theta'_i/\mathrm{d}t + (N_0\mathrm{e}^{k_0C})\theta'_i = N_0 \frac{(k_0C)^i}{i!}. \tag{8}$$

N_0 is the number of moles of adsorbate per unit area at equilibrium. Equation 8 is a first-order differential equation. Given the boundary conditions: $t=0$, $\theta'_i=0$ and $t=\infty$, $\theta'_i=\theta_i$, the solution of the differential equation after rearrangement, is

$$\ln[\theta_i/(\theta_i-\theta'_i)] = (N_0\mathrm{e}^{k_0C})t. \tag{9}$$

The coefficient of t in Eq. 9 has the units of surface excess as expected of a multiple equilibria such as the one under consideration here.[15]

A plot of $\ln(\theta_i/[\theta_i-\theta'_i])$ against time, t is given in Fig. 3b. The slope represents the mean rate constant for the approach of the adsorption process towards equilibrium and the reciprocal yields the mean lifetime of all the molecules adsorbed on the adsorbent.

In this report our approach has been to equilibrate quartz slides in a solution of cholesterol in bromobenzene over a range of equilibration periods at constant temperature, withdraw the slides at various equilibration times and measure the thickness of the resulting films with ellipsometry. From the thicknesses, the coverages were computed as a function of time.

Bigelow et al.[16] in their pioneering spontaneous self-adsorption study from apolar solvents (including bromobenzene) observed that monomolecular films of cholesterol formed on platinium dippers from bicyclohexyl solvent in the concentration rage $(0.2—1.2)\times10^{-4}$ mol dm^{-3}. Since this study is focused on the dynamics of multilayer formation it was decided to work at a constant concentration 1.10^{-3} mol dm^{-3}. Other details on the experimentation are given in the next section.

Methods

Materials, Deposition of Multilayer Films: Cholesterol, a BDH reagent, was purified by passing the ethanol solution through a silica gel column and then through an alumina column. The product obtained was further recrystallized from absolute ethanol and dried under vacuum (mp 149.5 °C). Bromobenzene (BDH reagent) was re-distilled twice.

The quartz slides on which the films were deposited (10 mm×50 mm) were cleaned[17] by heating for 3 h at 100 °C in chromic acid and repeatedly rinsed in triply-distilled water followed by soaking overnight in a 10^{-5} mol dm^{-3} NaOH solution made with triply-distilled water. The slides were thereafter removed and kept in triply-distilled water. They were later air-dried and used immediately. About 20.0 ml of 1×10^{-3} mol dm^{-3} solution of cholesterol in bromobenzene was carefully measured into pre-cleaned weighing bottle with polyvinyl cap. The quartz slides were carefully lowered into the solution and kept in a dessicator at 298 K for various lengths of time. After equilibration, the slides were removed with stainless-steel tweezers (they came out dried) and were kept in empty weighing bottles with caps and stored in a desiccator.

Ellipsometry Measurement: The method outlined by Vasicek,[18] Rotten and Hauson,[19] and Rotten[20] was used. Sodium and Mercury lines 589.3 and 546.1 nm were used respectively. The procedure outlined in the above references were employed except that Nakamura's double plate was not available for locating the exact minimum position in the dark field of view of the telescope, and for this reason, two positions of first appearance of brightness on either side for the minimum were read, averaged and taken as the minimum position. The only setback that this approach may suffer is that the minimum region may not be symmetrical around the real minimum position and this may lead to error in the location of the exact position of this minimum. However, the minima so determined, with practice, were quite reproducible. In a single set of experiments, both the refractive index of the film and its thickness were obtained. The refractive index was obtained from the following equation:[18—20]

$$n_0 = \frac{\lambda_1^2 \sin^2\varphi_2 - \lambda_2^2 \sin^2\varphi_1}{\lambda_1^2 - \lambda_2^2}, \tag{10}$$

where n_0 represents the refractive index of the film, φ_1 and φ_2 the angles of zero ellipticity for sodium light (λ_1) and mercury line (λ_2) respectively. The values of φ_1 and φ_2 were determined from the plots of γ, an ellipticity parameter, as a function of the angle of incidence φ. Both the sign and the magnitude of the parameter γ are comparable with those reported by Vasicek.[18] The thickness of the film, d was calculated from any of the equations:

$$d(n_0^2 - \sin^2\varphi_1)^{1/2} = \lambda_1/4,$$
$$d(n_0^2 - \sin^2\varphi_2)^{1/2} = \lambda_2/4. \qquad (11)$$

From the values of d, the number of layers of cholesterol in the film was calculated by assuming that the structure of cholesterol molecule in the film is as shown in Fig. 2 (see also Ref. 22).

Results and Discussion

A measure of ellipticity, γ has been plotted against the angles of incidence, φ in Fig. 1. The curves are similar to those reported by Vasicek[18] for various wavelengths of light; the absolute values are smaller but similar to those reported recently by us for 2-naphthol derivatives.[4] The smaller magnitudes have been explained by the difference in the film matrix. The measurements were made for the reflections of sodium line and mercury line (with green filter) from cholesterol films on quartz slide in the experiments reported here while those by Vasicek were produced from etching of glass.[18] The angles of incidence for zero ellipticity were obtained from plots similar to those in Fig. 1 at various equilibration times. The thicknesses, d, were computed with the aid of Eq. 11. From an estimated cholesterol monolayer thickness of 2.52 nm (Fig. 2) the

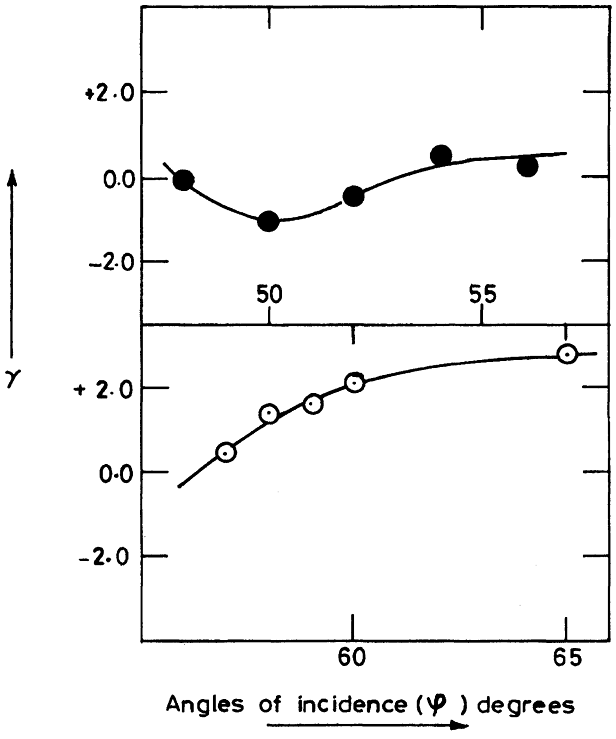

Fig. 1. Ellipsometric data showing the dependence of the ellipticity parameter γ on the angle of incidence, φ. (both in degrees): λ_{Na}=298.3 nm (•-•-•-•); λ_{Hg}=546.1 nm (o-o-o-o). Temperature=298±1 K.

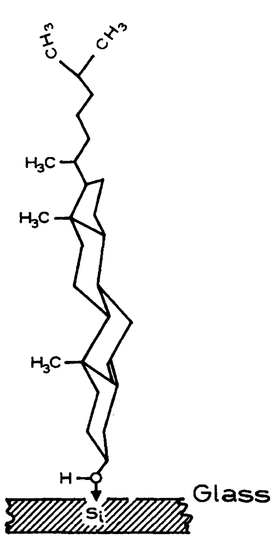

Fig. 2. Model structure on which the unimolecular layer thickness of cholesterol was based. Bond-lengths are taken from various sources. The model structure is based on published Electron Micrographs of cholesterol in Langmuir–Blodgett films (Ref. 22).

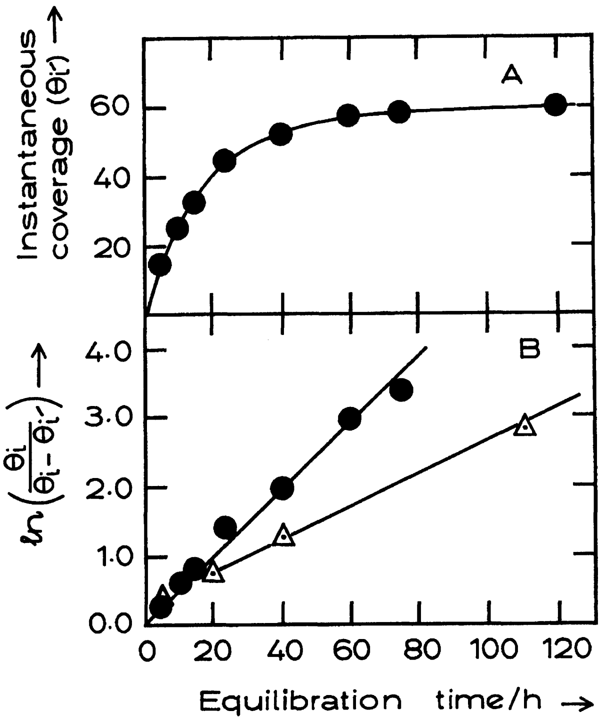

Fig. 3. a) Ellipsometric data showing the instantaneous coverage θ_i' as a function of equilibration time in hours. Temperature=298±1 K. b) First-order kinetic plot of a function of the coverage against time of equilibration: cholesterol data (•-•-•-•); stearic acid data from Ref. 1 (△-△-△-△).

instantaneous average number of layers was obtained. Figure 3a shows a plot of the number of layers of cholesterol against equilibration time; from which the value of the number of layers adsorbed at infinite equilibration time was extrapolated. The instantaneous coverage θ'_i was obtained as a quotient of the average number of layers at time, t and at infinite time. Figure 3b shows a plot of $\ln[\theta_i/(\theta_i-\theta'_i)]$ against equilibration time for cholesterol and for the data extrapolated from the published results of Allara and Guzzo.[1] The graphs show linear plots suggesting good agreement with theory.

Application of Sterling's approximation to $\ln i!$ in a logarithmic form of Eq. 6 and rearrangement gives the linearized Eq. 12.

$$\ln\theta_i - i\ln C = b - k_0 C, \tag{12}$$

where $b=i(\ln k_0/i+1)$ is a constant for a given value of i. Plots of the left-hand-side of Eq. 12 against C are shown in Fig. 4 (data extrapolated from Refs. 10 and 11). It was observed that only one unique value of i gave a straight line with each data set. This appears to be diagnostic of the number of binding sites utilized per adsorbent particle. The Gibb's free-energy changes of film formation, given by $\Delta G_0^{\ominus}=\mathrm{RT}\ln k_0$, and the entropies of fusion are shown in Table 1. The entropies of fusion are of the right order of magnitude.[21] The values of the Gibb's free-energy changes accompanying adsorption onto the two classes of sites on graphitized furnace carbon black argue against simple layer formation in this system; and the data in Table 1 as a whole suggests that adsorption depends critically on the affinity of adsorbate for the adsorption site.

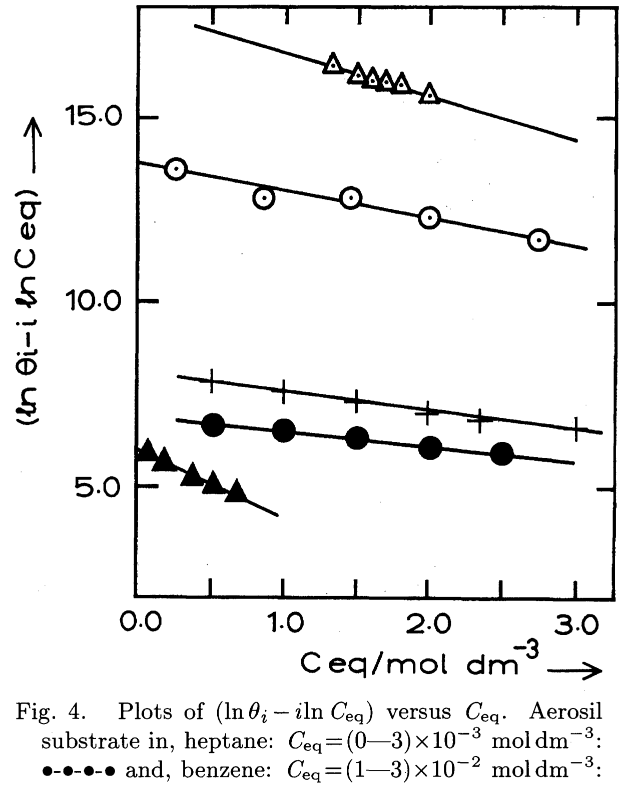

Fig. 4. Plots of $(\ln\theta_i - i\ln C_{\mathrm{eq}})$ versus C_{eq}. Aerosil substrate in, heptane: $C_{\mathrm{eq}}=(0\text{—}3)\times10^{-3}$ mol dm^{-3}: ●-●-●-● and, benzene: $C_{\mathrm{eq}}=(1\text{—}3)\times10^{-2}$ mol dm^{-3}: +-+-+-+. Graphitized furnace carbon black in heptane: $C_{\mathrm{eq}}=(0\text{—}3)\times10^{-3}$ mol dm^{-3}: ○-○-○-○, and $(1\text{—}3)\times10^{-2}$ mol dm^{-3}: △-△-△-△. Temperature= 293 K. Data from Ref. 11. Alumina substrate in benzene: $C_{\mathrm{eq}}=(0\text{—}2)\times10^{-3}$ mol dm^{-3}: ▲-▲-▲-▲. Temperature=298 K. Data from Ref. 10. The lines were fitted with least-square method with correlation coefficients better than 0.967.

Aerosil ($s=158$ m^2 g^{-1}) in heptane adsorbed only one cholesterol molecule, whereas in benzene two molecules were adsorbed onto each adsorbent particle. Graphitized furnace carbon black ($s=22$ m^2 g^{-1}), with much larger particle size than aerosil, adsorbed two molecules of the lipid per particle in the concentration range $(0\text{—}3)\times10^{-3}$ mol dm^{-3}, and at another concentration range an order of magnitude higher, four molecules. Thus, it seems as if there is an interplay between adsorbent size and solvent polarity: higher polarity favouring the formation of condensed film onto aerosil in benzene but dilute or less condensed monolayer in the lower polarity heptane. Large particle size of graphitized furnace carbon black leads to adsorption of two lipid molecules at a lower concentration region and four cholesterol molecules at higher concentration. This is broadly in consonance with the interpretation given in the original publication that at high concentrations of the lipid there takes place a re-orientation of the molecules in the adsorption layer accompanied by compaction of the monolayer.[11]

From Benko et al.[11] the area reportedly taken up by a cholesterol molecule in monolayers on aerosil was found to be 0.66 nm^2; the area was found to be independent of the nature of the apolar solvents used in their experiments. Ries et al.[22] found 0.39 nm^2 per molecule on air/water interface. Benko and his colleagues contended that the difference in these figures arose from screening off of the combined hydroxyl groups on aerosil surface. The concentration of silanol groups on aerosil surface of about one silanol group per 0.20 nm^2 has been reported.[23] A closer examination of these information suggests that it is possible to fit two cholesterol molecules per 0.81 nm^2 on a planar surface; in good agreement with a surface area of 0.39 nm^2 per molecule reported for air/water interface. The submicroscopic nature of aerosil and the relatively large size of the cholesterol molecule may account for the difficulty to fully utilize the available surface area of aerosil rather than the screening argument. Inspite of the close chemical similarity between aerosil and quartz slides, we are led to conclude from these arguments that cholesterol probably takes up an area of 0.39 nm^2/molecule in our system in agreement with the value observed for air/water interface.

From a value of 0.39 nm^2/molecule the average number of molecules adsorbed per cm^2 of film surface (using a limiting value of 60 layers observed experi-

Table 1. Thermodynamic and Kinetic Parameters of Spontaneous Self-Adsorption in Various Solvents and Adsorbents

Amphiphile	Adsorbent	Solvent	$\Delta G_0^{\ominus}$ kJ mol^{-1}	$\Delta S_0^{\ominus}$ J K^{-1} mol^{-1}	Mean lifetime τ (ks)
Cholesterol	Aerosil	Heptane[a]	-15.9 ± 0.7	-25.6 ± 2.1	—
		Benzene[a,c]	-9.9 ± 0.8	-10.2 ± 0.5	—
Cholesterol	Quartz slide	Bromobenzene	-21.7 ± 0.1	—	78 ± 3
Cholesterol	Graphitized furnace carbon black	Heptane[a,c]	-16.1 ± 1.2	—	—
Cholesterol		Heptane[a,d]	-11.9 ± 0.9	—	—
Cholesterol	Alumina	Benzene[e]	-13.0 ± 0.7	—	—
Steric acid	Alumina	Hexadecane[b]	—	—	12.4 ± 0.3

a) Ref. 11, $T=293$ K; b) Ref. 1, $T=298$ K; c) Number of cholesterol molecules adsorbed per substrate particle, $i=2$; d) $i=4$; e) Ref. 10, $T=298$ K.

mentally), N_0 in the expression for the slope ($N_0 e_0^{kC}$) comes to 2.43×10^{-8} mol cm^{-2}; this yields an equilibrium solute concentration of 9.88×10^{-4} mol dm^{-3}, an observed equilibrium constant for the formation of the first layer, k_0 of $(6.3\pm0.3)\times10^{3}$ dm^{-3} mol^{-1} and $\Delta G_0^{\ominus}=-21.7\pm0.1$ kJ mol^{-1}. If we combine the heat of fusion of cholesterol film from benzene onto aerosil of -2.97 ± 0.14 kJ mol^{-1} with the observed free-energy of formation of the first layer by cholesterol from bromobenzene in this work (ignoring temperature effect) an effective free-energy of formation, $\Delta G_{\text{eff}}^{\ominus}=-24.7\pm0.3$ kJ is obtained. This leads to the important conclusion that cholesterol self-adsorption onto silica from bromobenzene is almost exclusively free-energy driven.

The mean lifetime of cholesterol on quartz slide surface and stearic acid on active aluminium oxide during equilibration were also computed as reciprocals of the slopes. The results are shown in Table 1. From the values reported in the Table 1, it appears quite clear that the kinetics of layer formation by cholesterol by the spontaneous self-assembly method is slow with a mean rate constant of $(1.28\pm0.05)\times10^{-5}$ s^{-1}. The slow kinetics has been noted by other workers[1] for the adsorption of stearic acid onto active aluminium oxide surface. Although there is no direct correspondence between the two systems: cholesterol assemblage on quartz slide and stearic acid on native aluminium oxide, the magnitude of the mean-lifetimes underscores the importance of the dynamic nature of adsorption from solution where solvent molecules are constantly justling to exchange places with adsorbate molecules. The lifetime of 78 ± 3 ks for cholesterol is also to be compared with 12.4 ± 0.3 ks obtained from the data of Allara and Nuzzo[1] for stearic acid referred to above; the comparison should be done with caution in view of the differences in the two systems. It appears that the mean lifetimes depend on the solubility of the solutes in the solvent as well as the formation constants of the amphiphilic substances for coordination to the surface. Benko et al.[1] described this as the partitioning of the solute between the solvent and the adsorption site. This is in agreement with the fact that the pk_a of stearic acid is lower than that of cholesterol and that adsorption must be critically dependent upon the formation constant of the amphiphile to its coordination site.

The mechanism proposed by Allara and Nuzzo[1] for surface exchange reactions in monolayers of stearic acid, A and its perdeuterated analogue, B,

$$\mathrm{A}+\mathrm{B}\cdot\mathrm{X} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{A}\cdot\mathrm{X}+\mathrm{B}, \tag{13}$$

where X is the substrate, was reported to have demonstrated that the exchange reaction on native aluminium oxide substrates was not kinetically simple. If the heterogeneous nature of the adsorption process is taken into consideration, Eq. 14 is readily obtained.

$$\ln\left[\theta_i/(\theta_i-\theta_i')\right]=(k_-[\mathrm{B}]+k_+)t, \tag{14}$$

where θ_i and θ_i' have the same definitions as before and k_+ is a second-order rate constant for adsorption and k_- is a first-order rate constant for desorption. As suggested earlier, the plots shown in Fig. 3 are perfectly linear (although in the case of stearic acid, a nonzero intercept was obtained) showing that the procedure adopted is valid. The non-zero intercept may result from the low precision of the data as suggested by the authors.

In summary, these results confirm that the rate of advancement of an adsorption process to equilibrium follows a first-order rate law irrespective of whether the film obtained by the spontaneous process is a mono- or multi-layer type. A new adsorption equation has been proposed. It may also be concluded for this study that adsorption from solution, is critically dependent on the Gibb's free-energy of adsorption to the adsorption site.

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