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Interaction Free Energies in Langmuir–Blodgett Multilayers of Docosylammonium Phosphate

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The influence of pH and the ionic composition of phosphate subsolution on the static contact angles after upward and downward Langmuir–Blodgett (LB) deposition of docosylamine is studied. The corresponding free energies of interaction, ΔG_R and ΔG_A , are evaluated and compared with theoretical estimates of the van der Waals, electrostatic, and structural components of ΔG . The analysis shows that the sum of ΔG_{VW} , ΔG_E , and ΔG_S is positive, while the experimental interaction free energy is negative. This discrepancy leads to the conclusion that some strong attraction component should be included in the energetic balance. In the present case the lacking component might be attributed either to double layer ion correlation forces, which are strongly attractive in presence of divalent counterions, or to hydrogen bonds between the ammonium head groups of the opposite monolayers and the phosphate counterions included between them. These bonds, probably causing dehydration of the groups involved and ensuring the head to head adhesion in the LB multilayer, were experimentally proven in our previous IR study of the same system. The free energy of interaction of the hydrocarbon chains, ΔG_A , also depends on pH, obviously due to changes of the hydrophilic groups of the monolayer being transferred. This dependence reflects the presence of a nondispersive contribution to ΔG_A , which has been neglected in previous studies.

Introduction

Langmuir–Blodgett multilayers may be formally seen as an assembly of Newton soap films—bilayers of amphiphilic molecules contacting with their hydrophilic functional groups—Figure 1a. The free energy of interaction of adjacent surfactant monolayers, ΔG , is related to the contact angle, θ_0 , formed between the Newton film and the meniscus by

$$\Delta G = 2\gamma(\cos \theta_0 - 1) \quad (1)$$

and can be evaluated theoretically^{1–6} from the disjoining pressure isotherm $\Pi(h)$

$$\Delta G = - \int_{\infty}^{h_0} \Pi(h) dh \quad (2)$$

Here γ is the surface tension, Π is the disjoining pressure, h is the film thickness, and h_0 is the value of h corresponding to θ_0 .

Equations 1 and 2 should be applicable also to Langmuir–Blodgett films. However, while for soap films θ_0 has a unique value, in Langmuir–Blodgett systems two static contact angles, θ_A and θ_R , obtained after dipping or withdrawal of the solid substrate, are usually observed. Their difference is often referred to as contact angle hysteresis. Alternatively, Clint and Walker⁷ have assigned θ_A and θ_R to the different specific energies of the terminal groups, contacting during the downward and upward stroke—parts b and c of Figure 1. On the basis of this assumption they derived for the dipping mode a formula analogous to eq 1

$$\Delta G_A = -\gamma(\cos \theta_A + 1) \quad (3)$$

and compared the experimental interaction energy of alkyl

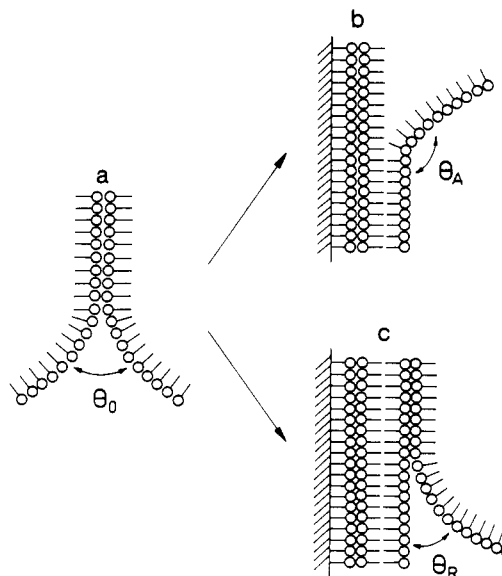


Figure 1. Static contact angle in Newton black soap films, θ_0 , and in Langmuir–Blodgett multilayers after dipping, θ_A , and after withdrawal, θ_R .

and partially fluorinated alkyl chains with theoretical estimates based on the dispersion theory.

For the withdrawal mode similar considerations yield

$$\Delta G_R = \gamma(\cos \theta_R - 1) \quad (4)$$

Langmuir⁸ has called θ_R “zipper” contact angle, thus highlighting the difference from the case of a drop of pure liquid resting atop of the multilayer. He noted that “dry” deposition during withdrawal of the solid substrate (without entrainment of an aqueous film) occurs only at large “zipper” contact angles.⁸ Later Bikermann⁹ found that different dynamic contact angles during dipping and withdrawal result in a different, Y or X, deposition mode. However, although rather important, these findings did not receive much attention and very few papers dealt with this problem later.

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(3) Huisman, F.; Mysels, K. J. *J. Phys. Chem.* 1969, 73, 489.

(4) de Feijter, J. A.; Rijnbout, J. B.; Vrij, A. *J. Colloid Interface Sci.* 1978, 64, 258.

(5) Scheludko, A.; Radoev, B.; Kolarov, T. *Trans. Faraday Soc.* 1968, 64, 2213.

(6) Ivanov, I. B.; Toshev, B. V.; Radoev, B. P. *Wetting, Spreading and Adhesion*; Padday, J. F., Ed.; Academic Press: London, 1978; p 37.

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(9) Bikerman, J. J. *Proc. R. Soc. London, Ser. A* 1939, 170, 130.

It should be stressed that the "zipper" contact angle characterizes the interactions in the three-phase contact zone, which is precisely the place where the elementary act of Langmuir-Blodgett deposition occurs. Therefore it can be expected that for LB systems of weak fatty acids or bases, θ_R will depend on pH because of transition between the charged and neutral form of the monolayer functional groups. θ_R should be also affected by adsorption of counterions from the aqueous subsolution. In fact, Neuman¹⁰ and Neuman and Swanson¹¹ have observed such correlations for stearic acid multilayers: the monotonous trend of θ_R vs pH changed when water was replaced by subsolutions containing Ca^{2+} . This change was related to adsorption of Ca^{2+} and formation of two-dimensional calcium stearate micelles in the monolayer. Similar pH and counterion effects might be anticipated for deposition of monolayers of long chain fatty amines from subsolutions containing divalent anions.

Assuming that the interaction between the alkyl chains, taking place during the dipping mode of a Y deposition, is purely dispersive, Clint and Walker⁷ postulated that ΔG_A should be independent on pH and the aqueous phase composition. The opposite was shown in the experimental study of Gaines,¹² who found a pH-induced variation of ΔG_A for cadmium arachidate multilayers.

The purpose of the present investigation is to follow the dependence of the static contact angles after withdrawal, θ_R , and after dipping, θ_A , on the ionic equilibria of docosylamine monolayers and phosphate subsolutions. The experimental values of ΔG_R and ΔG_A thus obtained will be compared with theoretical estimations based on eq 2 and theoretical disjoining pressure isotherms. Our previous neutron-activation analysis¹³ and IR spectroscopy¹⁴ data about the HPO_4^{2-} content and hydrogen bonding in docosylammonium phosphate multilayers are also invoked. Thus the interaction between opposite head groups will be analyzed in order to determine the predominant free energy component of ΔG_R —van der Waals, electrostatic, or structural. The presumably dispersive character of the interaction between the hydrocarbon chains contacting during dipping will be tested by studying the dependence of ΔG_A on pH and comparing the values obtained for docosylammonium phosphate multilayers with those found for different fatty acid soaps in refs 7 and 12.

Methods and Materials

The spread monolayers were characterized by their surface pressure/area isotherms, recorded on an automatic Langmuir film balance. ΔV potentials were also monitored using a ²⁴¹Am radioactive electrode and an AgCl reference electrode.

The deposition was carried out at a constant surface pressure of 30 dyn/cm. Glass cylinders (1.6 cm diameter) made hydrophobic¹⁵ by dip-coating with polystyrene dissolved in xylene were employed as solid substrates. The solid substrate velocity during the monolayer deposition (0.2 cm/s) was well below the speed of aqueous film entrainment for the system studied.¹⁶

The ratio of the area per monolayer molecule on the liquid surface, F_L , to that on the solid substrate, F_S , i.e. the so-called

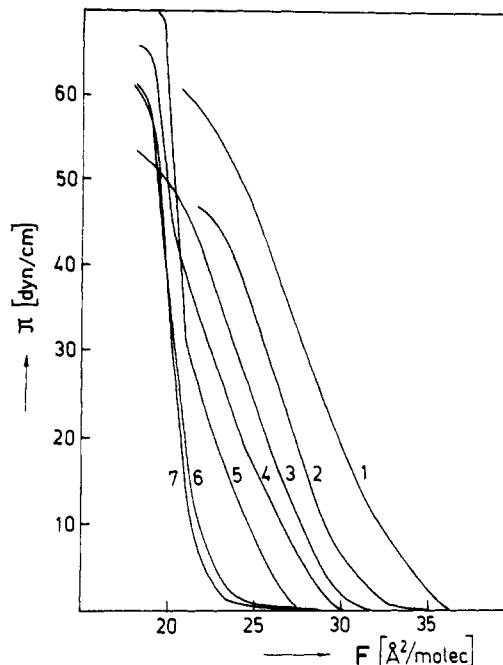


Figure 2. Surface pressure–area isotherms of docosylamine monolayers spread on 1×10^{-2} M phosphate solutions of different pH: 3.0 (1); 4.0 (2); 5.1 (3); 6.0 (4); 7.0 (5); 8.3 (6); 9.0 (7).

Table I. Experimental Surface Potentials $\Delta V_{F_{30}}$ (Corresponding to Area per Molecule at 30 dyn/cm) of Docosylamine Monolayers Spread on 1×10^{-2} M Phosphate Subsolution of Different pH

	pH 3.4	pH 5.5	pH 7.5	pH 9.0
$\Delta V_{F_{30}}$, mV	735	845	785	715

deposition ratio or transfer coefficient, α , was obtained from the reduction of the spread monolayer area, ΔA_L , and the geometrical solid surface area, A_S

$$\alpha = F_L/F_S = \Delta A_L/A_S \quad (5)$$

Contact angles were measured goniometrically after drawing a tangent to the meniscus profile on photographs at 18-fold magnification. The data shown are an average of three values obtained with an accuracy of $\pm 2^\circ$. The static angles were determined after the solid substrate motion had been stopped and the contact angle relaxation was complete.

The docosylamine hydrochloride (its synthesis and purification are described in ref 17) was spread as 1×10^{-3} M solution in a mixture of spectroscopically pure chloroform and ethanol (4:1, v/v). The phosphate solutions were prepared by dissolving Na_2HPO_4 and NaH_2PO_4 of AR purity in doubly distilled water. pH was varied with NaOH or HNO_3 (Merck). All measurements were conducted at room temperature.

Results

Characterization of the Docosylamine Monolayers at the Liquid/Gas Interface. Information about the molecular packing of the DCA monolayers on 1×10^{-2} M phosphate subsolutions of different pH was obtained from the surface pressure/area isotherms shown in Figure 2. A gradual change from liquid condensed to solid condensed state is observed at the deposition pressure of 30 dyn/cm when pH increased from 3.0 to 9.0 (curve 1 to 7).

The pH variation of the surface potential, $\Delta V_{F_{30}}$, at an area per molecule corresponding to 30 dyn/cm, is presented in Table I. This quantity arises from the permanent dipoles and free charges of the surfactant molecules as

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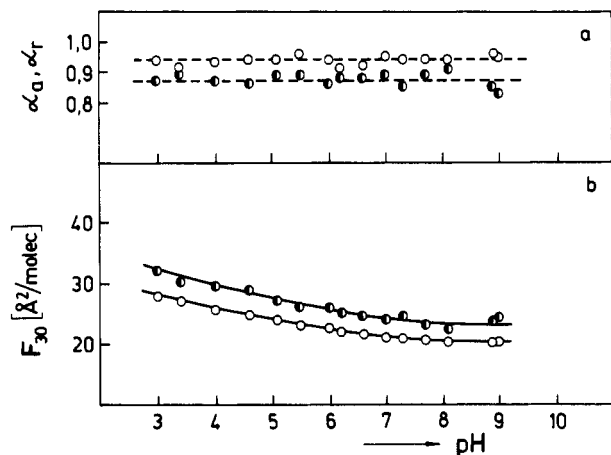


Figure 3. (a) Deposition ratios during dipping, α_d (●), and withdrawal, α_r (○), as a function of pH. The data refer to the ninth and tenth monolayer deposition. (b) pH dependence of the docosylamine area per molecule at 30 dyn/cm at the solid/liquid, $F_{S,30}$ (●), and the liquid/gas, $F_{L,30}$ (○), interface for the ninth monolayer deposition.

well as from the changed polarization and orientation of the water molecules near the water/air interface.

Transfer of the Monolayers onto the Solid Substrate and Characterization of the Solid/Liquid Interface. In a former study of the same system¹⁴ we have found that the deposition ratios do not depend on the number of transferred monolayers up to the 150th layer. Their values during dipping, α_d , and withdrawal, α_r , for the 9th and 10th monolayer, are presented in Figure 3a. Since they are close to unity, one may infer that the monolayers are transferred onto the solid substrate without significant change in their packing.

The area per molecule at the solid/liquid interface, $F_{S,30}$, evaluated from the deposition ratio during dipping, α_d , is compared with the one at the liquid/gas interface, $F_{L,30}$, in Figure 3b. Both $F_{L,30}/\text{pH}$ and $F_{S,30}/\text{pH}$ dependences have similar trends reflecting the symmetry of the pH variations of the gas/liquid and solid/liquid interfacial properties. The difference between $F_{L,30}$ and $F_{S,30}$ is about 16%.

Contact Angles and Interaction Free Energies. Contact angle relaxation is illustrated in Figure 4 for the first, fifth, and fifteenth deposition cycles. The static values of the contact angle after withdrawal, θ_R , were reached within 1–2 min, while those obtained after dipping, θ_A , were reached almost immediately after stopping the solid substrate. A much longer relaxation time of θ_R (10–15 min) was found after deposition of mixed monolayers of methyl arachidate and dimethyldioctadecylammonium bromide from NaCl subsolutions.¹⁸

Figure 4 also shows a significant difference between θ_A and θ_R and an independence of both values on the number of deposited layers.

The pH dependences of the static contact angles after withdrawal, θ_R , and after dipping, θ_A , are shown in Figures 5 and 6, respectively. The values of θ_A above 90° might have been underestimated because the concave profile of the meniscus formed after dipping was photographed with a slightly tilted camera. Both curves have extrema and thus are qualitatively different from the typical monotonous θ_0/pH curve of a monovalent base–acid titration.^{19,20}

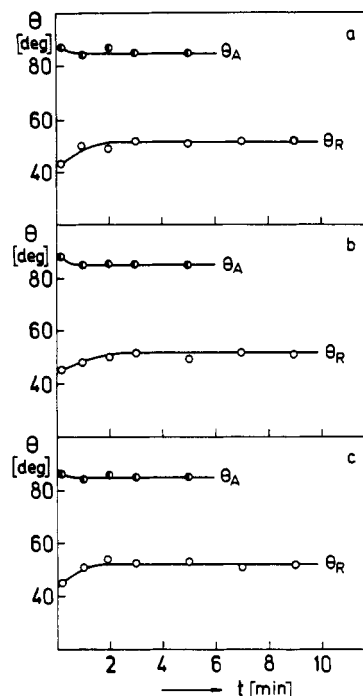


Figure 4. Relaxation of the contact angles after dipping (●) and withdrawal (○) of the solid substrate; deposition of (a) 1st and 2nd, (b) 9th and 10th, and (c) 29th and 30th monolayer. θ_A and θ_R are the static values established.

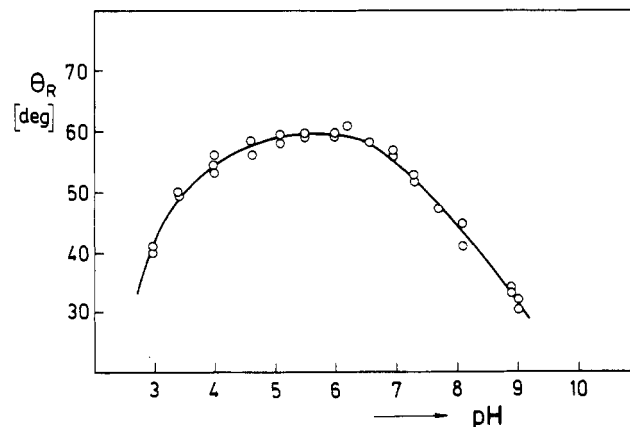


Figure 5. Dependence of the static contact angle after withdrawal, θ_R , on pH for the 10th monolayer deposition.

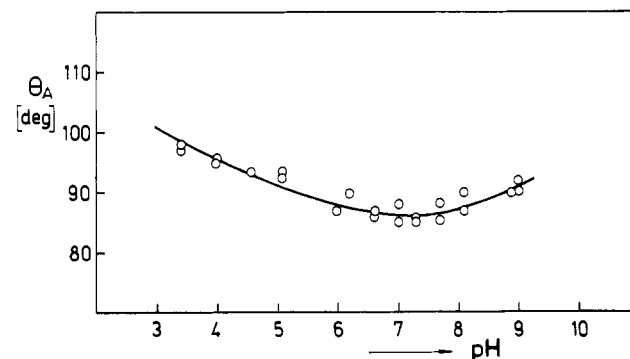


Figure 6. Dependence of the static contact angle after dipping, θ_A , on pH (deposition of ninth monolayer).

The fact that the contact angles after the first, fifth, and fifteenth deposition cycles have the same values (Figure 4) shows the absence of long range effects of the solid substrate. Therefore the experimental free energies obtained via eqs 3 and 4 from the data in Figures 5 and 6 are intrinsic properties of the LB films. The values of

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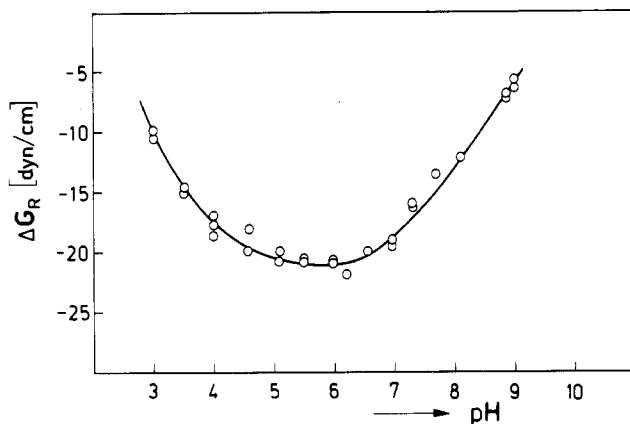


Figure 7. pH dependence of the free energy of interaction at withdrawal, ΔG_R , obtained from the experimental θ_R /pH dependence shown in Figure 5.

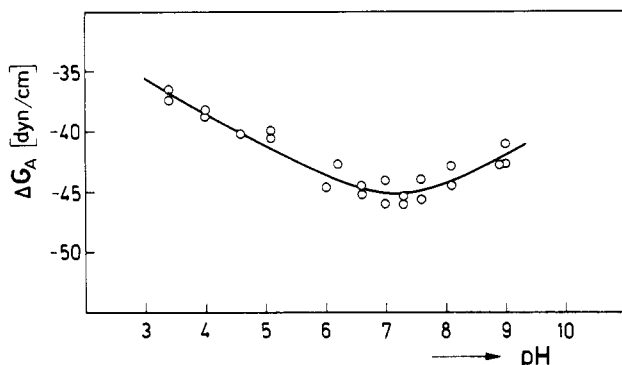


Figure 8. pH dependence of the free energy of interaction at dipping, ΔG_A , obtained from the experimental θ_A /pH dependence shown in Figure 6.

ΔG_R , characterizing the interaction between the hydrophilic groups, are plotted versus pH in Figure 7, and Figure 8 gives the free energy of interaction of the hydrophobic chains, ΔG_A . Both ΔG_R and ΔG_A are negative and depend nonmonotonously on pH. Because of the uncertainty in the determination of θ_A , the particular values of ΔG_A should be considered with caution, but nevertheless, the pH-induced variation of ΔG_A is quite clearly expressed.

Discussion

It is usually assumed that the interaction free energy is a sum of van der Waals, ΔG_{vw} , electrostatic, ΔG_E , and structural, ΔG_S , components

$$\Delta G = \Delta G_{vw} + \Delta G_E + \Delta G_S \quad (6)$$

Neither pH nor the electrolyte composition of the subsolution have direct influence on the van der Waals component; it is predominantly determined by the hydrocarbon chain density. Indeed, the ionic equilibria in the docosylamine monolayer and the aqueous phase affect the area per hydrocarbon chain (see Figure 3b), but this change is relatively small. On the other hand, variations of the aqueous phase composition and the state of the hydrophilic head groups with pH should alter the interfacial potentials and the head groups hydration. Thus the electrostatic and structural components of the interaction free energy should be influenced.

Unfortunately the theoretical evaluation of the free energy components is questionable for systems with large contact angles. The relationship between ΔG and $\Pi(h)$ given by eq 2 holds for a shallow transition zone between film and meniscus, because only then disjoining pressure

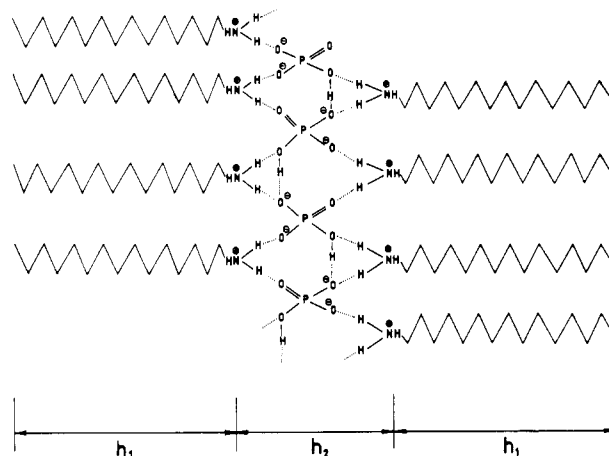


Figure 9. Structure of the docosylammonium phosphate multilayer assumed in the evaluation of the free energy of interaction: h_1 , thickness of the hydrocarbon layers; h_2 , thickness of the aqueous core, including the ammonium functional groups and the phosphate counterions. Data are from IR analysis of the same system.¹⁴

Table II. Theoretical Estimation of the van der Waals Component, ΔG_{vw} , of the Free Energy of Interaction

model	Hamaker constant, erg	ΔG_{vw} , dyn/cm
alkane/water/alkane (eq 7)	5.4×10^{-14}	-0.033
alkane/water/air (eq 7)	-2.0×10^{-14}	0.012
alkane/water/alkane (eq 8)		-0.093

isotherms for flat film can be used. According to ref 21 this requirement restricts the analysis to contact angles below 45° , but even this value seems to be rather optimistic. Nevertheless, in an absence of any rigorous specification of the upper applicability limit of the above relationship, we will apply eq 2 to the receding contact angle data, keeping in mind that the results obtained should be considered as estimates.

Free Energy of Interaction of the Hydrophilic Head Groups. ΔG_{vw} was evaluated from eq 7 which neglects the electromagnetic retardation and thus overestimates the van der Waals component of ΔG

$$\Delta G_{vw} = -A/12\pi h_0^2 \quad (7)$$

Several models were considered. ΔG_{vw} for two infinite phases interacting through a water core (alkane/water/alkane or alkane/water/air) can have opposite signs depending on the Hamaker constant used,²² Table II. To specify the water core thickness, use was made of the multilayer structure proposed in ref 14 on the basis of the IR analysis of the same system, Figure 9. This thickness, $h_2 \approx 20.7 \text{ \AA}$, was estimated from the dimensions of the ammonium groups and the phosphate counterions.²³ The empirical formula of Donners²⁴ for the alkane/water/alkane model

$$G_{vw}(h_2) = -\frac{1}{h_2^2} \left[\frac{b + ch_2}{1 + dh_2 + eh_2^2} + q \right] \quad (8)$$

with b , c , d , e , and q being numerical coefficients taken from ref 24, predicts greater attraction energy, but even then ΔG_{vw} is more than 2 orders of magnitude smaller

(21) Churaev, N. V. *Physical Chemistry of Mass-transport Processes in Porous Media*; Khimia: Moscow, 1990; p 227 (in Russian).

(22) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press, Inc.: London and New York, 1985; p 149.

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(24) Donners, W. A. B.; Rijnbout, J. B.; Vrij, A. *J. Colloid Interface Sci.* 1977, 60, 540.

than the experimental values of ΔG_R (see Figure 7 and Table II). Therefore ΔG_{vw} plays a negligible role in the interaction between opposite head groups.

The overlapping of the opposite electric double layers should lead to an electrostatic interaction. To evaluate the corresponding ΔG_E , the diffuse double layer potentials at the liquid/gas, ψ_d^L , and solid/liquid interface, ψ_d^S , must be known. The Gouy-Chapman equation was used for this purpose—for 1-1 electrolyte between pH 3.0 and 6.0, where H_2PO_4^- is the main counterion, and for 1-2 electrolyte in the pH range 6.0–9.0, where HPO_4^{2-} prevails. The electroneutrality condition

$$\sigma_o = \sigma_1 + \sigma_d \quad (9)$$

was employed to find the diffuse layer charge per unit interfacial area, σ_d , from the charge density of the ammonium groups, σ_o , and the density of the adsorbed phosphate counterions, σ_1 . σ_o was extracted from the F_{30}/pH data (Figure 3b) and σ_1 was previously obtained by means of neutron activation analysis of the same LB system.¹³ The ψ_d^L/pH dependence thus obtained is shown in Figure 10a. Since the docosylamine monolayer is protonated almost in the entire pH range investigated,²⁵ the above variation of the diffuse layer potential with pH reflects the adsorption of the phosphate counterions in the Stern layer (see Figure 11b). Because of the small difference between $F_{S,30}$ and $F_{L,30}$, it was assumed that $\psi_d^S \approx \psi_d^L = \psi_d$. An estimation of this difference from the experimental ψ_o/σ_o dependence obtained by Frommertz and Masters²⁷ gives a reduction in ψ_d^L of less than 12%.

Following the approach employed by de Feijter and Vrij²⁸ to estimate ΔG_E in Newton black soap films, the expression for complete overlapping of the opposite diffuse double layers was applied

$$\Delta G_E = -2\Delta G_{dl} = \frac{16nkT}{\kappa} \left(\cosh \frac{ze\psi_d}{kT} + 1 \right) \quad (10)$$

ΔG_{dl} is the free energy of formation of a single double layer, n and z are counterion concentration and valence, and κ is the reciprocal of the Debye length. It was assumed that $z = 1$ between pH 3.0 and 6.0, and $z = 2$ between pH 6.0 and 9.0.

The $\Delta G_E/\text{pH}$ dependence obtained from the above equation is shown in Figure 10b. It can be seen that the absolute values of ΔG_E and ΔG_R are quite close (Figures 10b and 7). Moreover, the trend of $\Delta G_E/\text{pH}$ is similar to the $\Delta G_R/\text{pH}$ dependence but the experimental and theoretical interaction free energies have opposite signs. This difference persists even after summing ΔG_E and ΔG_{vw} because the contribution of ΔG_{vw} is negligible. Therefore, taking into account only the long range components of the classical DLVO theory, one cannot obtain reasonable theoretical estimate of ΔG , which is comparable with the experimentally found value of ΔG_R .

The structural component of the free energy of interaction between the opposite hydrophilic head groups has a repulsive character and decays exponentially with the film thickness h_o according the equation

$$\Delta G_S = Kl_o \exp(-h_o/l_o) \quad (11)$$

where l_o is a correlation length.

(25) Using the value of $\text{p}K = 10.1$ for nonadecylamine monolayers,²⁶ one finds that the molar part of the docosylammonium cation varies between 1.00 and 0.88 between pH 3.0 and 9.0.

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(27) Frommertz, P.; Masters, B. *Biochim. Biophys. Acta* 1974, 356, 270.

(28) de Feijter, J. A.; Vrij, A. *J. Colloid Interface Sci.* 1979, 70, 456.

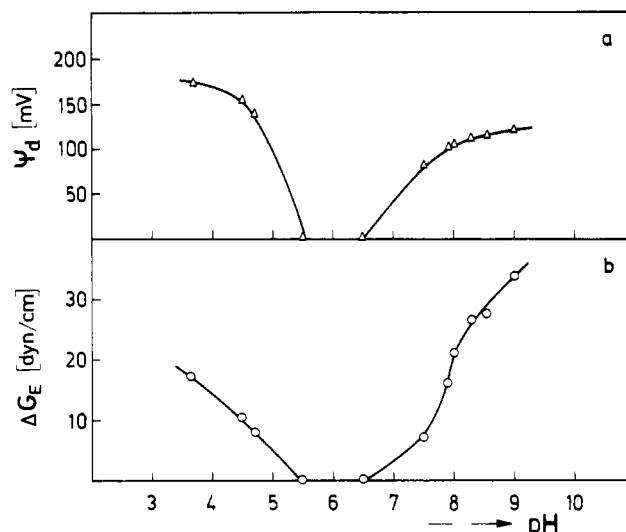


Figure 10. (a) pH dependence of the diffuse double layer potentials, ψ_d , determined from the Gouy-Chapman theory (see the text). (b) Electrostatic free energy of interaction, ΔG_E , as a function of pH, evaluated from eq 10 for complete overlapping of the diffuse double layers.

Table III. Preexponential Constant, K , and Free Energy of Structural Interaction, ΔG_s , Estimated on the Basis of Equations 11–13

	pH 3.4	pH 5.5	pH 7.5	pH 9.0
$10^{-9}K$, dyn/cm ²	1.1	1.5	1.9	1.5
ΔG_s , dyn/cm	1.3	1.9	2.3	1.9

The nonlocal electrostatic theory of the structural forces²⁹ relates the preexponential constant, K , to the normal component of the specific interfacial dipole moment μ_{\perp}

$$K = \frac{8\pi\eta}{\epsilon_i l^2} \mu_{\perp}^2 \quad (12)$$

For the order parameter, η , and the interfacial dielectric constant, ϵ_i , the theory²⁹ takes the values $\eta = 0.6$ and $\epsilon_i = 5$, respectively. The values of μ_{\perp} can be estimated³⁰ from the surface potential $\Delta V_{F_{30}}$, and the area per molecule F_{30} , at 30 dyn/cm

$$\mu_{\perp} = \mu/F_{30} = (\Delta V - \psi_o)/12\pi \quad (13)$$

μ is the vertical component of the molecular dipole moment and ψ_o the Gouy-Chapman potential in the plane of the ammonium groups.

Evaluating ψ_o from the Gouy-Chapman theory and using the $\Delta V/\text{pH}$ data from Table I, we have estimated the change of K with pH (Table III). The obtained values are close to those observed for lipid bilayers.²⁹ The value of $l_o = 2.5$ Å, characteristic for lipid bilayers, was taken and the structural component of ΔG was estimated (Table III).

Including the repulsive structural component in the sum of the ΔG components leads to an even more unrealistic picture—the total theoretical interaction free energy becomes even larger and positive, while the experimental values of ΔG_R are negative. The only way out of this contradiction is to assume that a strong attractive component has been neglected in the energetic balance presented by eq 5. Unfortunately this component cannot

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(30) Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; Wiley: New York, 1982; p 167.

be estimated from the difference between ΔG_R and ΔG_{TH} , since its additivity with ΔG_{VW} , ΔG_E , and ΔG_S cannot be postulated a priori.³¹

Similar discrepancy was found by Huisman and Mysels³ and de Feijter and Vrij²⁸ for Newton soap films of sodium dodecyl sulfate. The explanation proposed in the later study includes an electrostatic attraction caused by a discrete periodic surface charge distributions,^{32,33} which takes place when counterions penetrate between the charged surfactant head groups. Thus, two-dimensional lattices of alternatively arranged opposite charges are created on both film surfaces, and, due to their spatial correlation, attract each other.

While such a penetration of Na^+ between the dodecyl sulfate molecules, occupying an area of $40 \text{ \AA}^2/\text{molecule}$ (ref 28), might be possible, it seems rather unrealistic for the condensed monolayer of docosylammonium phosphate; $F_{L,30}$ varies from 28 to $20 \text{ \AA}^2/\text{molecule}$ and the phosphate counterions have a cross sectional area of about 44 \AA^2 , when hydrated, and 28 \AA^2 , when dehydrated.

Developments of the theory of the electrostatic surface forces emphasized the role of the ion correlation effects in the diffuse parts of the interacting opposite double electric layers.^{34,35} Between surfaces of high charge densities as ours these effects give rise to an attractive force, which can reverse the sign of the total interaction force if divalent counterions are present in the aqueous phase.^{35,36} Kjellander, Marčelja, Pashley, and Quirk³⁵ evaluated this effect theoretically and found a close agreement between the predicted force-distance dependence and the experimental one obtained via the surface force apparatus for mica surfaces interacting in 0.15 M CaCl_2 solution. According to them the strong attractive force arising in the presence of divalent counterions is responsible for the fact that Ca^{2+} prevents the swelling of clays.

The striking similarity of the pH dependences of ΔG_R and of the degree of conversion, Q , of docosylamine in docosylammonium phosphate (parts a and b of Figure 11) could be due to the same double layer ion correlation attraction, which might be responsible for the observed difference between the experimental and theoretical values of ΔG . This hypothesis is supported by the experimental finding that divalent and trivalent counterions strongly facilitate formation of Langmuir-Blodgett multilayers of cationic and anionic surfactants probably ensuring enough strong attraction between the hydrophilic head groups.^{14,17,37} Moreover, if integrating the theoretical dependence in Figure 1 of ref 35, which shows the calculated double layer interaction (including the ion correlation effects) versus the separation distance between the surfaces, one finds that $\Delta G_E = -5 \text{ dyn/cm}$. This value, obtained for a system with a surface charge density of $0.6 \text{ nm}^2/\text{charge}$ (twice smaller than ours) and 2:1 electrolyte solution, is negative and greater than the positive sum of the ΔG_{VW} , and ΔG_S , estimated in this study.

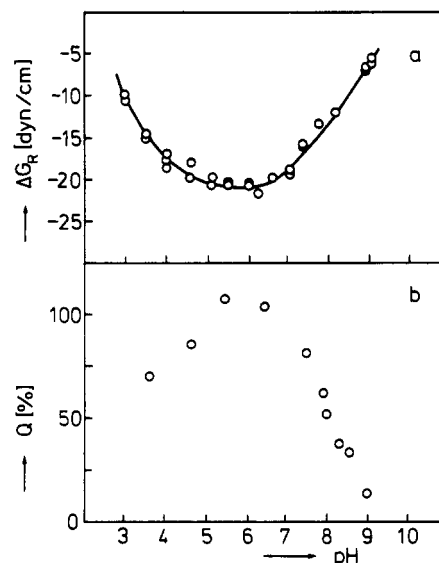


Figure 11. Comparison of $\Delta G_R/\text{pH}$ and the pH dependence of the degree of conversion, Q , of docosylamine in docosylammonium phosphate in the multilayers: subsolution, $1 \times 10^{-2} \text{ M}$ phosphate. Data are from neutron activation analysis.¹³

However, the lacking attractive free energy component might also be related to the hydrogen bonds between the docosylammonium head groups and the divalent phosphate counterions included in the multilayer. These bonds were experimentally proven in our previous IR spectroscopic study of the same system.¹⁴ Such an explanation also coincides with the correlation shown in Figure 11, since the pH-variation of the degree of conversion of docosylamine in docosylammonium phosphate (Figure 11b) reflects the change of the two-dimensional density of the hydrogen bonds with pH. We are not aware of any theoretical description of a hydrogen bond component of the surface forces and its contribution to the total value of ΔG cannot be estimated at present.

It seems interesting and worth mentioning that a difference of more than 1 order of magnitude is observed between the experimental values of ΔG_R for docosylamine LB films and these for Newton soap films of sodium dodecyl sulfate and 1:1 electrolyte solution of the same ionic strength as in our experiments.^{28,39,40} This difference could be due to the effect of the divalent counterions in the former case, probably leading to a more complete dehydration of the surfactant head groups during the LB deposition. This speculation is supported by our IR spectroscopic study, where the absence of hydration water was directly shown.¹⁴ It is also in agreement with the correlation between the decreasing solubility of different divalent long chain ammonium salts and their tendency to form stable Newton black films, commented on by Ibbotson and Jones.⁴¹ All these similarities are intriguing but still unclear and should be a matter of further investigations.

Free Energy of Interaction between the Hydrocarbon Chains. The values of the interaction free energy at dipping, ΔG_A , obtained in this study for docosylammonium phosphate multilayers, are close to the value of $\Delta G_A = -39 \text{ dyn/cm}$, found by Clint and Walker⁷ for cadmium behenate multilayers, and to the results of Gaines,¹² which show a monotonous change of ΔG_A with pH from -41.2 to -35.6 dyn/cm . The small differences

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observed show that the nature of the hydrophilic head group (acid or base) and the nature of counterion (metal cation or polyvalent anion) do not play a significant role in the interaction between the hydrocarbon chains.

On the other hand, Figure 8 demonstrates that ΔG_A , characterizing the interlayer interaction of the hydrocarbon chains in the docosylamine multilayers, depends on pH to a greater extent than the values obtained by Gaines¹² for cadmium arachidate built up films and that this dependence is a nonmonotonous one. Therefore the observed influence of pH is obviously due to the specific changes of the hydrophilic functional groups and to the counterion adsorption at the multilayer/water interface, located at 30 Å apart from the contacting terminal methyl groups. Recently, similar remote effects have been observed in an entirely different type of experiment. It was

shown that free charges located at the solid/multilayer interface⁴² or bulk free charges⁴³ and dipoles,⁴⁴ deeply located in the multilayer structure, influence quite strongly the acid-base equilibrium of the interfacial pH-indicator 4-heptadecyl-7-hydroxycoumarin embedded at the multilayer/water interface. In order to understand these results and their mutual relationship, additional systematic studies of the influence of the hydrophilic and the hydrophobic terminal groups on the contact angles and the interaction free energy in Langmuir-Blodgett multilayers are necessary.

Registry No. Phosphate, 14265-44-2; docosylamine, 14130-06-4; polystyrene, 9003-53-6.

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