*Biochimica et Biophysica Acta*, 552 (1979) 11—22

BBA 78312

# PHOSPHOLIPID MONOLAYERS AT THE HYDROCARBON-ELECTROLYTE INTERFACE

## THE INTERRELATION OF FILM POTENTIAL AND FILM PRESSURE

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(Received June 9th, 1978)
(Revised manuscript received November 8th, 1978)

*Key words: Surface potential; Surface pressure; Hydrocarbon-electrolyte interface; (Phospholipid monolayer)*

## Summary

Measurements of surface pressure and of surface potential are reported for films of distearoyl phosphatidylcholine (density range: $0.15–2.65 \cdot 10^{18}$ molecules/m$^2$) spread at the interface between 2,2,4-trimethylpentane and 100 mM NaCl. Low density behavior of the surface pressure is explained using classical virial theory. The behavior of the surface potential is qualitatively explained for all densities in terms of the dipole moments associated with the carboxyl groups and headgroups of the phosphatidylcholine.

## Introduction

There appear to be very few published data which permit correlation of the surface potential $\Delta V_s$ and surface pressure $\Pi$ of a monomolecular film spread over the interface between a liquid hydrocarbon and an aqueous electrolyte. And those data which do exist for phospholipid films [1,2] are sufficient primarily to show that $\Delta V_s > 0$ and that $\partial \Delta V_s/\partial n > 0$ and $\partial \Pi/\partial n > 0$, where $n$ is the surface density of film molecules. It is therefore not surprising that the

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interrelationship of the two is unclear, especially for films sufficiently dense to be classified as condensed.

Likewise, little firm information is available theoretically. State equations for various classes of monolayers have been reviewed by numerous authors [3—5] and it seems firstly that direct predictions of $\Pi(n)$ isotherms are inexact except perhaps for films of very low surface density and secondly that recent calculations for denser films [6,7] tend to neglect direct electrostatic ($\Delta V_s$ related) effects of favor of short range van der Waals effects of the London or Debye type [3]. The latter observation is not surprising since, in all but the simplest cases, it is very difficult to calculate direct Coulombic interactions [8] and emphasis has therefore been placed upon attractive interactions which promote the condensation phenomena of interest in dense films.

A monolayer may be thought of as a two-dimensional system, and, in direct analogy with three-dimensional systems, it is better understood in the rarified gas form. For phospholipid films in which $A$, the surface area per film molecule, is large (for example, above 2 $\text{nm}^2$), there are a number of contending approaches:

(i) Ideal gas. $\Pi A = kT$, where $k$ ($=1.38 \ldots \cdot 10^{-23}$ J/K) is Boltzmann's constant and $T$ is the absolute temperature. This is the two-dimensional analogue of the familiar three-dimensional ideal gas law and works poorly except perhaps at exceptionally high $A$. Some justification of this equation will be given in the next section.

(ii) Ideal gas with excluded area. $\Pi(A - A_0) = kT$, where $A_0$ is the excluded area occupied by a film molecule. This relation, commonly called the Volmer equation [9], may suffice at very high areas [1] but is commonly considered to be inadequate [2,4].

(iii) Ideal gas with excluded area and "excluded pressure". $(\Pi - \Pi_0)(A - A_0) = kT$, where $\Pi_0$ is a constant surface pressure excess. This form, now not much used, was introduced by Langmuir [10] who showed that it can work well at intermediate areas. It clearly will fail at high areas since the pressure does not tend asymptotically to zero.

(iv) Two-dimensional van der Waals. $(\Pi + \alpha/A^2)(A - A_0) = kT$. This relation, introduced by Magnus [11] on heuristic grounds is normally written so that it includes a coefficient $\alpha$ to take account of direct binary interactions; it gives a somewhat more reasonable, but by no means entirely satisfactory, fit of experimental data [2].

(v) Two-dimensional virial expansion. The idea of taking explicit account of the intermolecular forces in the film and of deriving a state equation using a direct virial calculation is due to Mitchell [12] and has been developed by Vrij [13]. It appears never to have been employed for the interpretation of specific monolayer data and never to have been explicitly worked out for the case where direct Coulombic dipolar repulsion is the dominant intermolecular force. None of the above approaches have yet been developed to yield a satisfactory fit of the experimental data.

In this paper it is our intention: First, to derive for phospholipid molecules at a hydrocarbon-electrolyte interface a new equation of state which is based upon the virial theorem of Clausius and which takes explicit account of variations in a surface dipole moment $\mu$ and then to present experimental data which support it strongly. Second, to present extensive $\Delta V_s$ and $\Pi$ isotherms for phospholipid films whose densities vary all the way from rarified gaseous to putatively solid. Third, to offer a qualitative explanation of the observed correlations between $\Delta V_s$ and $\Pi$.

## Theory

To obtain a suitable equation of state for a two-dimensional fluid, we proceed using the classical virial theorem of Clausius [14] which, in analogy with the three-dimensional case, yields

$$\frac{\Pi}{nkT} - 1 = \frac{1}{NkT}\overline{\left(\frac{1}{2}\sum_{\nu=1}^{N} \vec{F}_\nu^{(i)} \cdot \vec{r}_\nu\right)} \tag{1}$$

where $N$ is the number of molecules in the film, $\vec{r}_\nu$ is the $\nu$th molecule's position, the bar denotes a time average, and $F_\nu^{(i)}$ is the force acting on the $\nu$th molecule due to interactions with other film molecules. Since the left-hand side of Eqn. 1 is independent of $N$ and dimensionless, it follows that the remaining virial summation must be linear in $N$ and representable as $NkTG$ where $G$ is a specific (intensive) property of the film. In analogy with the classical gas technique, $G$ can be given a virial expansion in $n$ and Eqn. 1 expressed as

$$\frac{\Pi}{nkT} - 1 = \sum_{p=2}^{\infty} B_p n^{p-1} , \tag{2}$$

where the $B_p$ are the so-called virial coefficients. We shall approach the consideration of $G$ in two fashions.

First, an approach from dimensional analysis. Since the high area data to be presented (cf. ref. 15) all have $\Pi$ larger than would be expected on the basis of perfect gas theory (surface pressure excess), it is seemingly the case that repulsive intermolecular forces outweigh attractive ones at sufficiently low film densities. The most obvious repulsive force is that between dipoles and hence a dipole moment $\mu$ and a dielectric constant $\epsilon$ must be included. Since the measurable intermolecular interactions are net repulsive, no obvious means of determining the outweighed attractive forces exists; and they will, for simplicity, be neglected. In addition, it seems essential to include the effects of film density $n$ and of thermal kinetic energy $kT$. A straight-forward application of the Buckingham Π-Theorem [16] then reveals that $G$ must equal $f(\zeta)$, where

$$\zeta = (\mu)^{4/3} n/(\epsilon kT)^{2/3} \tag{3}$$

Thus, Eqn. 1 reduces to

$$\frac{\Pi}{nkT} - 1 = f(\zeta) \tag{4}$$

Aside from inferring from Eqn. 2 that $f(\zeta)$ may admit of a power series representation about the origin, little can be said about it.

Second, $B_2$ can be calculated directly from the expression [12]

$$B_2 = \pi \int_0^{\infty} 1 - e^{-E(r)/kT} r \, dr \tag{5}$$

where $E(r)$ is the potential energy between two film molecules a distance $r$ apart. Since the net intermolecular interaction is repulsive, $E(r)$ is presumably dominated by dipole-dipole Coulombic repulsion. For point dipoles this yields an energy $\mu^2/(4\pi\epsilon r^3)$, and Eqn. 5 then reduces to

$$B_2 = \frac{1}{n}\zeta\left[\frac{\pi}{2}\frac{1}{(4\pi)^{2/3}}\Gamma(1/3)\right] \tag{6}$$

where the term in brackets has the numerical value 0.77853 . . ..

The approach leading to Eqns. 4 and 6 is not without its difficulties, several of which will be elaborated here.

(a) No account has been taken of attractive forces between molecules, and therefore the state equation must involve variables other than $\zeta$; unfortunately, there seems to be no identifiable, unequivocal manifestation of their existence at densities below the first clear-cut phase transition. Moreover, since the phase changes of a real fluid are poorly understood theoretically, even for simpler and more intensively investigated systems than ours [17], it would seem excessively optimistic to attempt to account for them here.

(b) A phospholipid molecule which (i) contains two carboxyl linkages, a phosphate group, a choline moiety, and which (ii) may be associated with a diffuse double layer can scarcely be considered to be a point dipole; nevertheless, it will be so treated since more sophisticated models involve still more unknown parameters and are analytically intractable.

(c) The dipole moment $\mu$, detected experimentally as a surface pressure excess, and the incremental surface dipole moment $\Delta\mu_s$, computed from measurements of the incremental surface potential $\Delta V_s$ (cf. ref. 15), bear no obvious relationship to each other; in particular, $\mu$ is inferred from phenomena taggential to the interface and $\Delta\mu_s$ from phenomena perpendicular to the interface.

Despite these shortcomings, the potential utility of our theoretical approach can be seen by defining, in analogy with Eqn. 3, a

$$\zeta_s = (\Delta\mu_s)^{4/3}n/(\epsilon_w kT)^{2/3} \tag{7}$$

and replotting the data of Fig. 3 of the preceding paper [15]. This is done in Fig. 1. The slope at low density is 0.61 rather than the 0.78 predicted by our crude theory. But note than the anomalously low values of $\Delta\mu_s$ encountered at very low film densities are now seen to be quite in keeping with the surface pressure data; whereas, without this development presented here, they would almost certainly be viewed with intense suspicion.

In view of the great uncertainties and simplications of the model, we regard this degree of agreement with experiment as a substantial confirmation of our underlying assumption that non-idealities in the pressure-area phenomena of the high area (low density/putatively gaseous) film are first and foremost a reflection of dipole-dipole repulsion.

If now the virial expansion of Eqn. 2 is rewritten as

$$\frac{\Pi}{nkT} - 1 = \sum_{p=2}^{\infty} C_p \zeta_s^{p-1} \tag{8}$$

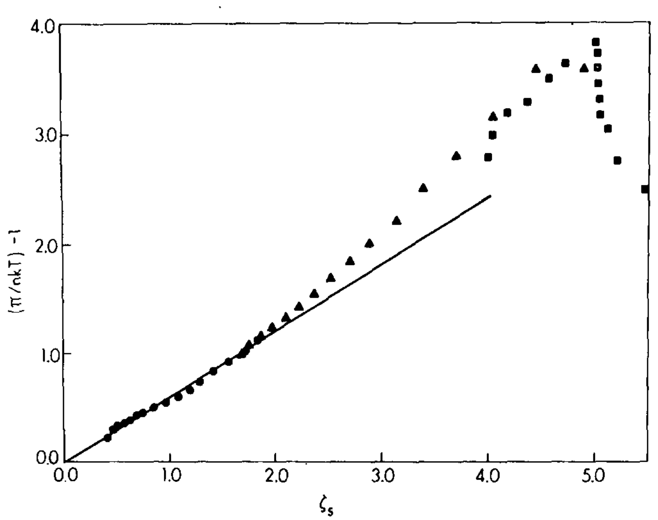

Fig. 1. Surface pressure excess ($\Pi/nkT - 1$) versus $\zeta_S$. The several symbols are: ●, first spread; ▲, second spread; ■, third spread. The solid line is the equation $0.61\zeta_S^{1.00}$ and was obtained by allometric regression over the interval (0,2); its correlation coefficient is 0.996. Note the phase transition beginning at $\zeta_S = 5.0$.

and if $C_2$ is known experimentally, then a plot of $(\Pi/nkT - 1 - C_2\zeta_s)$ vs. $\zeta_s$ should yield information about the next few virial coefficients if the data are sufficiently noise free.

## Materials and Methods

These have been described elsewhere [15] except for the technique of preparing composite isotherms. The latter were prepared as follows: (i) For each experiment, the reduced data (cf. ref. 15) for both $\Pi$ vs. $n$ and $\Delta V_s$ vs. $n$ were plotted on full logarithmic tracing paper. (ii) Up to four experiments at a given temperature were overlaid on a light box; since $n$ was our least well known variable and could be in error by a constant multiplier in the range (0.98, 1.02), the sheets were translated slightly in the $n$-direction to obtain maximal overlap and the translations visually averaged to obtain a density reference value. (iii) An additional sheet was overlaid and composite isotherms drawn with the aid of French curves. (iv) Where necessary, these composites were themselves merged on the light box. (v) The final composites were then read to obtain the pressure and potential data in tabular form.

## Results

All data presented are taken from composite isotherms for distearoyl phosphatidylcholine ($C_{18}$) at the interface between 2,2,4-trimethylpentane and 100 mM NaCl. Much less extensive data for the di-$C_{20}$ homologue were qualitatively similar.

Fig. 2 shows the $\Pi(n)$ results at four temperatures. These are qualitatively what would be expected on the basis of previously published data at oil/water

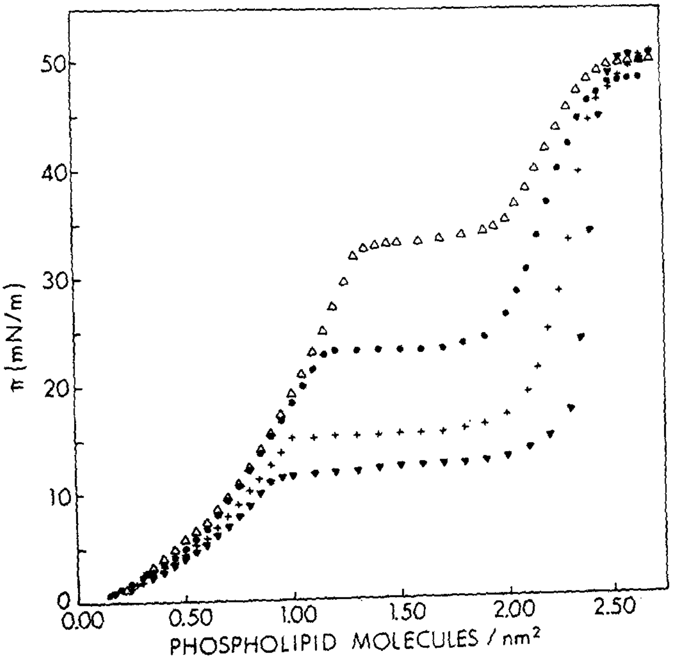

Fig. 2. Surface pressure (Π) versus film density (*n*) for films of distearoyl phosphatidylcholine at the interface between 2,2,4-trimethylpentane and 100 mM NaCl. The symbols for the several isotherms are: ▼, 4.5°C; +, 10°C; ●, 20°C; △, 30°C.

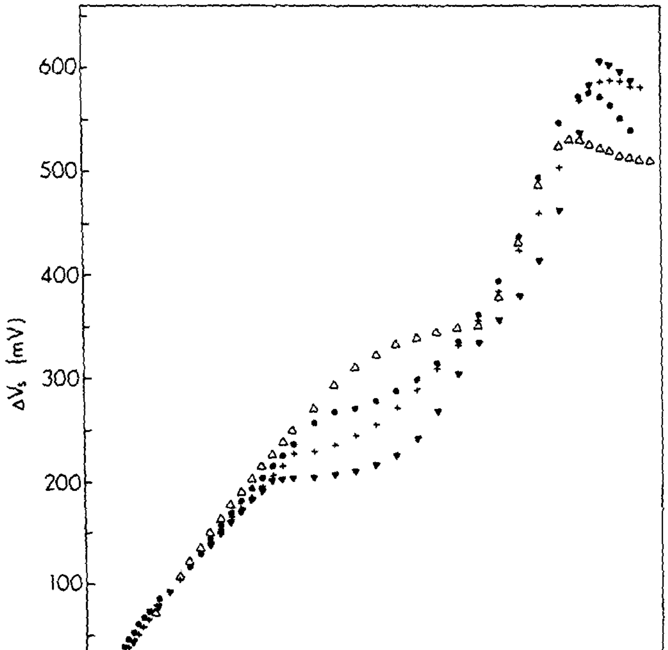

Fig. 3. Surface potential ($\Delta V_s$) versus film density (*n*). The symbols for the several isotherms are: ▼, 4.5°C; +, 10°C; ●, 20°C; △, 30°C.

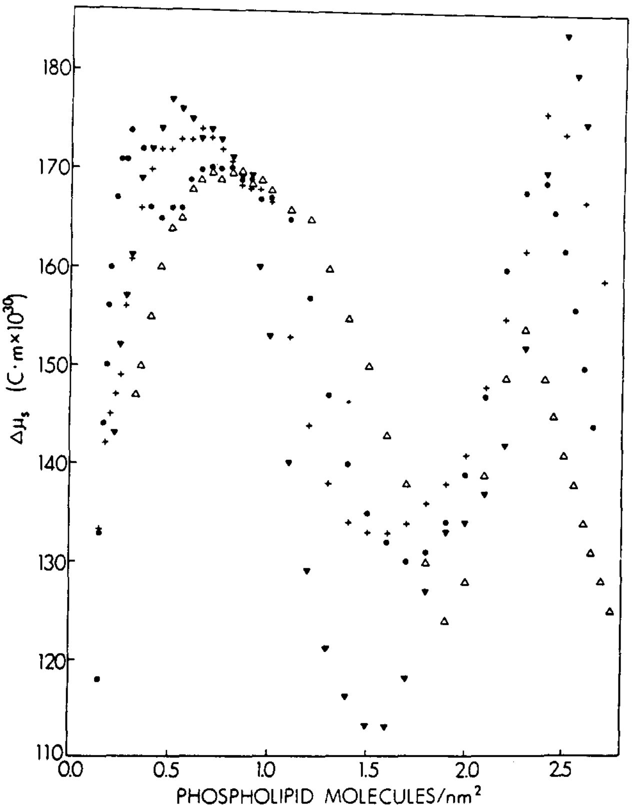

Fig. 4. Surface dipole moment ($\Delta\mu_s$) versus film density ($n$). The symbols for the several isotherms are: ▼, 4.5°C; +, 10°C; ●, 20°C; △, 30°C.

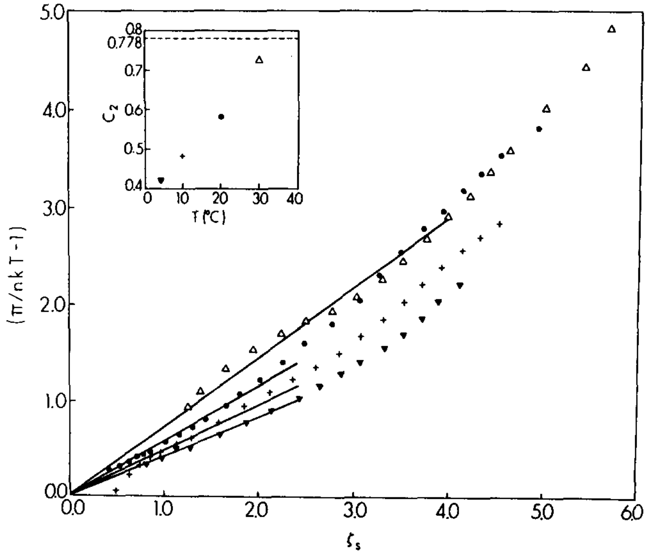

Fig. 5. Surface pressure excess ($\Pi/nkT - 1$) versus the dimensionless virial variable ($\zeta_s$). The low density straight line asymptotes were drawn by eye, and the inset shows their slopes ($C_2$) as a function of temperature ($T$). The symbols for the several isotherms are: ▼, 4.5°C; +, 10°C; ●, 20°C; △, 30°C.

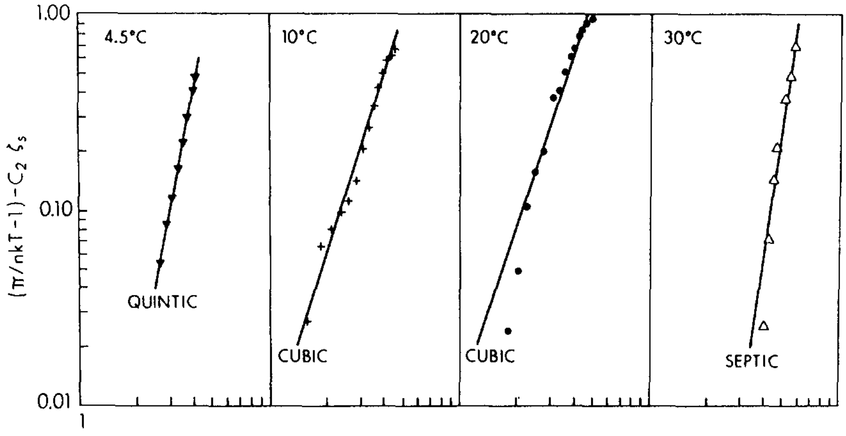

Fig. 6. Higher-order virial corrections ($\Pi/nkT - 1 - C_2\zeta_S$) versus $\zeta_S$. The straight lines of the powers indicated were drawn by eye.

interfaces [2]. The slight upward convexity near $n = 0.5 \cdot 10^{18}$ for the 30°C isotherm is believed to be artifactual and illustrates both the desirability of repeated replications and the difficulties of making measurements at high areas. Note that, in all cases, there seems to be a second phase transition occurring at densities above $2.5 \cdot 10^{18}$.

Fig. 3 shows the $\Delta V_s(n)$ results at four temperatures. Note that the putative phase transition at high density which was observed in Fig. 2 is very pronounced here. Note also the slight upward convexity in the 20°C isotherm near $n = 3.0 \cdot 10^{18}$. This is almost surely an artifact since it results in an uncharacteristic double hump in the rising phase of the $\Delta\mu_s(n)$ plot (Fig. 4); and it once again points up the problems of surface chemistry at moderately high areas.

Fig. 4 shows $\Delta\mu_s(n)$ as calculated from the equation [15] $\Delta\mu_s = (\epsilon_w \Delta V_s)/n$. Note that the film density at which $\Delta\mu_s$ begins to drop for the gas → liquid transition is a monotone increasing function of temperature as is the density at which the $\Delta\mu_s(n)$ isotherms bottom during the transition; conversely, the value of $n$ corresponding to the high density maximum of $\Delta\mu_s(n)$ is a monotone decreasing function of temperature.

Fig. 5 shows ($\Pi/nkT - 1$) as a function of $\zeta_s$. Note that the slopes of the low density asymptotes increase with temperature.

Fig. 6 shows the magnitude of the higher order virial terms. Note that the third order virial coefficient seems to be missing in all cases.

## Discussion

### *$\Pi$ and $\Delta V_s$ isotherms*

The $\Pi(n)$ data are qualitatively similar to those in the literature [2,18] for the *n*-heptane/aqueous NaCl interface. Here however the data extend to slightly higher film densities and reveal the onset of what appears to be a structural modification within the film. Since the surface pressures are so high at the onset of this putative transition, there is always the possibility that the rolloff of

$\partial\Pi/\partial n$ is due instead to a bulging of the interfacial film over the edges of the barriers which effectively increases the total film area and decreases the film density. We believe that this is probably not the case: For if the hypothesis that no transition is occurring is supplemented by the reasonable assumption that $\Pi$ increases monotonically with the true film density, we are then left with the untenable proposition that $\Delta V_s$ can, in the absence of film reconfiguration, actually decrease with increasing film density.

There exists no corpus of published data with which to compare our $\Delta V_s(n)$ results. But, they seem not to be at variance with qualitative expectations based (i) upon the behavior of $\Pi(n)$, (ii) upon those few data which have been published [1], and (iii) data at the air-water interface (cf. ref. 4).

*Dipole moment isotherms*

As was explained in the previous paper [15], $\Delta\mu_s$ can be approximated by

$$\Delta\mu_s = \frac{\epsilon_w}{\epsilon_h}\mu_{carb} + \mu_{HG} - \mu_{BS} \tag{9}$$

where $\epsilon_w/\epsilon_h$ (~40) is the permittivity ratio of water and the hydrocarbon used, $\mu_{carb}$ is the dipole moment of the polar linkages between the glycerol backbone and the side chains and is probably dominated by the carboxyl dipoles, $\mu_{HG}$ is the dipole moment of the headgroup, and $\mu_{BS}$ is the dipole moment of the bare interface. The measured dipole moments of straight chain organic acids approximate $3$—$4 \cdot 10^{-30}$ C · m and seem fairly independent of chain length [19]; since two such linkages are involved, the net carboxyl contribution could be as much as $250 \cdot 10^{-30}$ C · m. The phosphorus and nitrogen ends of the choline headgroup are roughly 0.4 nm apart; thus the headgroup contribution could be of the order of $60 \cdot 10^{-30}$ C · m. If $\mu_{BS}$ per disturbed water molecule is bounded by the dipole moment of water ($\sim 6 \cdot 10^{-30}$ C · m), this term could easily yield $60 \cdot 10^{-30}$ C · m if a 1 nm diameter region were disturned by each phospholipid molecule.

There are five distinct regions to the $\Delta\mu_s$ vs. $n$ isotherms, and we shall now endeavor to account for them using these three contributions and their variations.

*Region (i):* $\partial\Delta\mu_s/\partial n > 0$. This is the very low density case. Since the hydrocarbon side chains will dissolve in the superphase, the carboxyl dipoles will tend to be held in a relatively fixed orientation. In the zero density limit, the headgroup dipoles should be held perpendicular to the interface by electrostatic forces but could, again for electrostatic reasons, incline toward one another in an effort to form quadrupoles as the density increases (cf. ref. 1); since the phosphate group is presumably pegged in the interface, $\mu_{HG}$ will oppose $\mu_{carb}$, and any deviation of the headgroup from a perpendicular orientation will increase $\Delta\mu_s$. Further, a moving phospholipid should produce a 'wake' of unknown size and disrupt the bare interface dipole arrangement over an unknown area; if $\mu_{BS} > 0$, it will oppose $\mu_{carb}$, but its absolute effect per film molecule should diminish as density increases and the wakes overlap.

*Region (ii):* $\Delta\partial\mu_s/\partial n \sim 0$. Here the processes of change active in Region (i) have ceased. If the headgroup reorientation were correct, we would expect the (i)/(ii) boundary to shift upwards with increasing temperature as the headgroups acquire more thermal energy and resist coordination. On the other hand, we would expect a wake to be larger at higher temperatures (where the surface waters are less strongly coordinated) with the result that the (i)/(ii) boundary should shift downwards with increasing temperature. The isotherms of Fig. 4 support the headgroup reorientation hypothesis.

*Region (iii):* $\Delta\partial\mu_s/\partial n < 0$. This is the initial portion of the first-order phase transition. By now there should be no undisturbed interface left, so $\mu_{BS}$ variations cannot be a factor. Hence, either (a) the carboxyl dipoles are being rearranged into a more quadrupolar pattern or (b) the headgroup dipoles, putatively more parallel to the interface in Region (ii) are being re-erected through steric hindrance. We prefer the latter explanation since we feel that the carboxyls will be fairly well constrained by the tendency of the hydrophobic side chains to dissolve in the hydrocarbon superphase and by side chain steric interactions during condensation. We note that the (ii)/(iii) boundary should shift upward with increasing temperature since the increase of $kT$ should inhibit condensation; and it does.

*Region (iv):* $\partial\Delta\mu_s/\partial n > 0$. This is the other end of the first-order phase transition. There are two obvious explanations. (a) Carboxyl dipoles which are tilted in Region (iii) are being re-erected by steric hindrance. (b) As the headgroups become more closely packed and water is progressively excluded, headgroup ionization is suppressed and $\mu_{HG}$ consequently reduced. We would expect the (iii)/(iv) boundary to have a negative temperature coefficient if (a) were true since increasing $kT$ should favor disarrangement of a quadrupolar pattern and work with steric hindrance. On the other hand, increasing $kT$ should promote headgroup ionization and give the (iii)/(iv) boundary a positive temperature coefficient, as observed.

*Region (v):* $\partial\Delta\mu_s/\partial n < 0$. The simplest explanation here is that occasional film molecules are being 'popped' part way out of the interface to form a quadrupoles, thus lowering the interfacial charge density and $\Delta\mu_s$. Popping should be favored by increased $kT$. And the observed negative temperature coefficient of the (iv)/(v) boundary therefore supports this explanation.

We believe that the variations of $\Delta\mu_s$ with film density and temperature are most readily explained in terms of: (a) Carboxyl dipoles whose orientations remain fixed but which depth of penetration in the hydrocarbon can vary; and (b) headgroups whose negative ends remain near the interface but whose orientation and ionization can vary.

We note that this explanation, if correct, could imply a five state picture of the film: First, at densities below those measured, a rare gas characterized by headgroup dipoles perpendicular to the interface. Second, following a transition through Region (i) a dense gas having the properties ascribed to Region (ii). Third, following a transition through Region (iii), a putative liquid which exists only near the (iii)/(iv) boundary and is characterized by erect, strongly ionized headgroups. Fourth, following a transition through Region (iv), a putative solid which exists only near the (iv)/(v) boundary and is characterized by condensed side chains and by erect, weakly ionized headgroups. Fifth, following a transition through Region (v) and existing only at densities above those measured, a popped solid; this state should be exceedingly unstable as a result of the tendency of the film to undergo macroscopic buckling.

*Surface equation of state for the gaseous film*

As was demonstrated by Figs. 1 and 5, the second-order virial expansion represented by Eqn. 8 produced good qualitative agreement between the low density $\Pi$ and $\Delta V_s$ results when $\Delta\mu_s$ was substituted for $\mu$. And in fact, experimental plots like Fig. 1 tended to produce better linearity than did the composite curves employed for Fig. 5. We conclude that, at the very least, plots of $(\Pi/nkT - 1)$ vs. $\zeta_s$ will prove a useful adjunct to the traditional $\Pi/n$ vs. $\Pi$ plots in the analysis of low density isotherms. The nearly linear increase of $C_2$ with temperature should not be accorded great significance since the slopes from which $C_2$ was computed were drawn by eye and are subjective; however, the data are such that virtually any reasonable choice of the $C_2$ would reveal a fairly smooth and monotone increase with temperature, thereby lending credence to the assumption that we may be examining a real temperature dependence of a second virial coefficient and not experimental noise.

The apparently uniform unimportance (cf. Fig. 6) of the third virial coefficient $C_3$ cannot reasonably be ascribed to arbitrariness in the choice of $C_2$ (cf. Fig. 5) since it occurs also at both 4.5°C and 20°C where $C_2$ is unequivocal. Neither should it be deemed an artifact of using $\zeta_s$ instead of $n$ since $\Delta\mu_s$ (cf. Eqn. 7) is nearly constant over the film densities of interest. Rather, the expectation of a significant $C_3$ should probably be viewed as an unwarrented extrapolation from the behavior [17] of a two-dimensional gas of hard discs: where many body interactions are relatively unimportant (a three dipole collision is energetically unfavorable) such behavior is not unexpected [20]. Virial expansions sometimes display poor asymptotic convergence (cf. ref. 21), and the magnitude of $C_3$ could betoken such a problem. On the other hand, the surface pressure excess of so relatively simple a system as a two-dimensional electron gas [22] behaves fully as strangely. And in any event, even divergent asymptotic expansions can, if suitably truncated, provide excellent approximations for suitably restricted arguments: certainly the data of Figs. 1 and 5 support the use of a one term expansion at low densities.

## Conclusions

The use (i) of simultaneous surface pressure and potential measurement and (ii) of classical virial theory in the investigation of uncharged films at a hydrocarbon-water interface has enabled us to offer an explanation of the observed behavior of the film in terms of side chain interactions and the behavior of the carboxyl and headgroup dipoles. The complexities of the picture which emerges suggest the desirability of additional measurements to determine surface viscosity and diffusion.

## Acknowledgements

We wish to thank Drs. Brian Pethica and Barbara Abraham-Shrauner for helpful discussions and the United States Public Service for continued support under Grant HL14147.

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