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ON THE STABILITY OF THE LIQUID–CRYSTALLINE LAMELLAR LECITHIN–WATER SYSTEM

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SUMMARY

The equilibrium distances in the lamellar arrangement of the lecithin–water system are accounted for in terms of the free energy contribution of fluctuations in the dipole moments of the phosphocholine groups of the lecithin molecules. The X-ray long spacing as a function of water content may be fitted with a reasonable choice of parameters, using a phenomenological approach for the free energy of a single bilayer.

INTRODUCTION

Phospholipids like lecithin are important compounds and lecithin–water forms a simple model system of biological membranes. Over a wide range of temperature and composition lecithin–water mixtures form lamellar smectic liquid crystals in which phospholipid bilayers alternate with water layers (Fig. 1). This system has been studied extensively by means of low-angle X-ray diffraction, which has been reviewed by Luzzati [1]. The X-ray measurements give us the repeat distance, that is, the water thickness plus lipid thickness, as a function of water content. Assuming the lipid bilayer thickness is proportional to the lipid volume fraction the data show that the lipid bilayer thickness increases with reduced water content. In this paper we

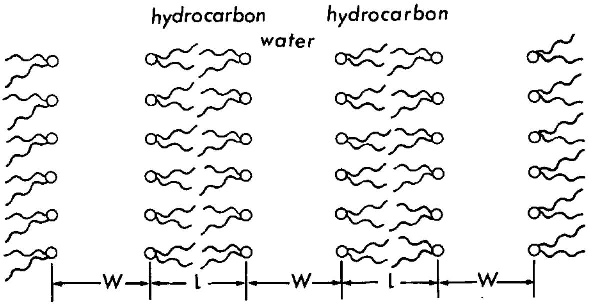

Fig. 1. Simplified version of the lecithin–water system. (○) polar group; (~~) hydrocarbon chain.

are presenting a quantitative theory explaining these results. We shall concentrate on the data for egg lecithin in pure water [2–5], neglecting the influence of electrolytes on the bilayer thickness [6]. To put the experimental data into a form suitable for comparison with our theory we want the lipid bilayer thickness rather than the repeat distance as a function of lipid volume fraction.

Little is known about the conformation of the zwitterionic phosphocholine group of the lecithin molecule relative to the water–lipid interface [7]. However, following previous workers [2, 4, 6] we shall assume that the entire phosphocholine group is part of the aqueous interbilayer region. The lipid thickness (l) may then be obtained from the measured lipid volume fraction (ϕ) and the measured repeat distance ($\delta = w+l$) through the Eqn [6]

$$l = \Phi\delta, \quad \Phi = 0.85\,\phi \qquad (1)$$

This lipid thickness has been plotted in Fig. 2 as a function of lipid volume fraction for the three sets of data [2–5]. The different sets of data show considerable variation particularly at high water content, where a separate low lipid phase may be expected to form [2].

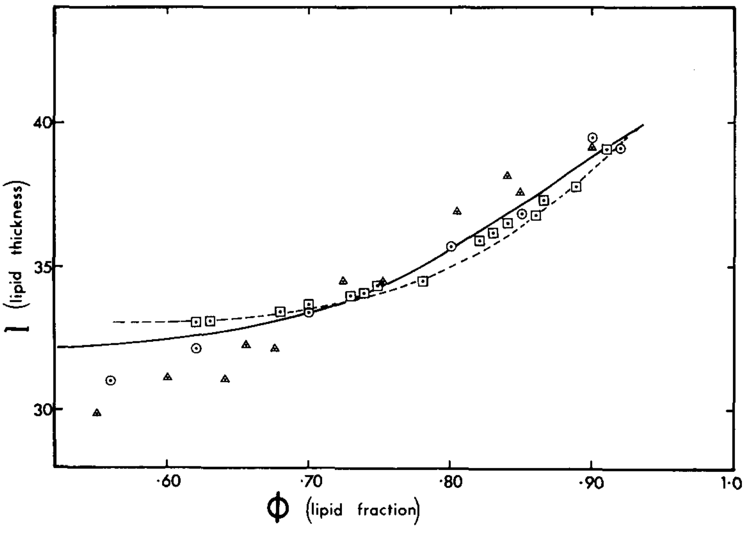

Fig. 2. Lipid thickness as a function of lipid fraction. Experimental data of refs 2 and 3 (○), 4 (☐) and 5 (△). The theoretical curve was calculated using Eqn 19 with $a_1 = 24$, $b_1 = 10$ Å, $l_0 = 32$ Å (—) and $a_1 = 100$, $b_1 = 14$ Å, $l_0 = 33$ Å (- - -).

A previous theory by Parsegian [8, 9] was based on the assumption that the positively charged quaternary ammonium groups of the lecithin molecules may be considered as free ions in formulating the electrostatic free energy of the system. The justification for this was sought in the flexibility of the $-O-CH_2-CH_2-$ chain connecting the ammonium group to the negatively charged phosphoryl group. We believe the assumption of a free ion is not justified, and while Parsegian's theory gives a reasonably straight line fit [9] to the data of Small and Bourges [2], it provides a much poorer fit to the data by Reiss-Husson [4]. In our model the effective repulsion between two lipid bilayers arises from the variation of the surface dipole moments due to the zwitterionic phosphocholine groups.

THEORY

In equilibrium the lipid–water system may be characterized by its Helmholtz free energy $F(l, \phi)$. Assuming non-compressible fluids at a given lipid volume fraction ϕ and constant volume, the system assumes a value of lipid bilayer thickness l and thus of interlayer water spacing $w = l(1-\Phi)/\Phi$, $\Phi = 0.85\phi$ such that the free energy is a minimum. The condition for stability is thus

$$(\partial F/\partial l)_{\phi, v} = 0. \tag{2}$$

This gives the required relation between l and ϕ once the free energy is known. The latter may be written in the form

$$F(l, \phi) = F_0(l)+F_1(l, \phi) \tag{3}$$

where $F_0(l)$ is the sum of the free energies of the separate bilayers in the absence of interactions and $F_1(l, \phi)$ is the interaction free energy between the bilayers. $F_0(l)$ is independent of ϕ and includes the interactions between neighboring hydrocarbons, between phosphocholine dipoles within the same plane and the lecithin–water surface interactions. $F_1(l, \phi)$ should be mainly due to the interactions of the phosphocholine dipoles across the water-filled interbilayer spacing. In our model for F_1 we shall thus neglect any interactions of the hydrocarbon chains across the water and shall assume that the dipole–dipole interactions due to the phosphocholine molecules are only appreciable with the next nearest layer of dipoles. More distant layers are only effective through changing the effective dielectric constant (see Appendix). Since the interlayer water spacing is larger than 14 Å, the dipole approximation is expected to be valid for interactions across the water layer. The dipole–dipole interaction energy between two layers of dipoles (Fig. 3) is

$$U_d = \sum_{i,j} (P^2/\varepsilon R_{ij}^3)\{\hat{\mu}_i \cdot \hat{\zeta}_j - 3(\hat{\mu}_i \cdot \hat{R}_{ij})(\hat{\zeta}_j \cdot \hat{R}_{ij})\} \tag{4}$$

where the $\hat{\mu}_i$ and $\hat{\zeta}_j$ are unit vectors along the dipole directions in the two layers, P is the magnitude of the dipole moment, and $\hat{R}_{ij}$ the unit vector along the direction between the two dipoles. Due to image effects the effective dielectric constant ε of the interbilayer spacing is not just the dielectric constant of water (see Appendix).

The cylindrical symmetry permits now averaging Eqn 4 over ϕ_{ij}, the polar angle of $\vec{R}_{ij}$. The result is

$$H_1 = \bar{U}_d = 0.5 \sum_{i,j} v_{ij}(2\mu_{zi}\zeta_{zj} - \mu_{xi}\zeta_{xj} - \mu_{yi}\zeta_{yj}) \tag{5}$$

where

$$v_{ij} = (P^2/\varepsilon R_{ij}^3)(1-3\cos^2\alpha_{ij}),$$

$$\mu_{zi} = \cos\theta_i\,, \mu_{yi} = \sin\theta_i \cos\phi_i\,,$$

and $\mu_{xi} = \sin\theta_i \sin\phi_i$, with similar relations for ζ_j. If we define

$$\mu_i^{\pm} = \mu_{xi} \pm i\mu_{yi}\,, \zeta_j^{\pm} = \zeta_{xj} \pm i\zeta_{yj}\,, i = \sqrt{-1},$$

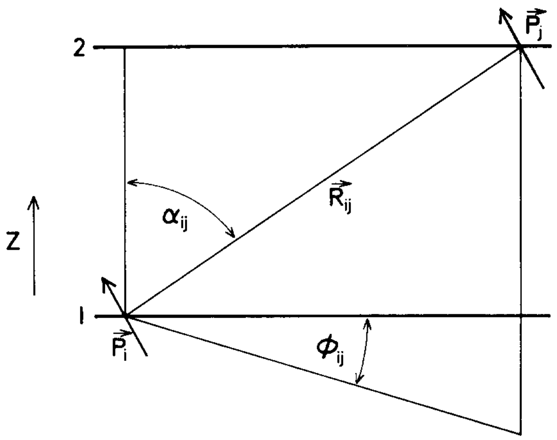

Fig. 3. Interaction of dipoles across two infinite planes.

H_1 is conveniently expressed as

$$H_1 = 0.5 \sum_{i,j} \nu_{ij}\{2\mu_{zi}\zeta_{zj} - \mu_i^+\zeta_j^-\} \tag{6}$$

The total energy for a neighboring pair of bilayers is $H = H_0 + H_1$, where H_0 is the sum of energies of the separate bilayers. The free energy for the bilayer system is given by

$$-\beta F = \ln Z,\ Z = \operatorname{tr} \exp(-\beta H) \tag{7}$$

where $\beta = 1/kT$, k being Boltzmann's constant and T the absolute temperature. Z is the partition function and tr refers to an integration over all dipole solid angles. We note that Eqn 7 can be put in the form of Eqn 3 by writting $Z = Z_0\langle\exp(-\beta H_1)\rangle$ where $Z_0 = \operatorname{tr}\exp(-\beta H_0)$ and we have introduced the notation for averages $\langle\ldots\rangle = \operatorname{tr}\{\exp[-\beta H_0](\ldots)\}/Z_0$. It follows that $F = F_0 + F_1$, where

$$-\beta F_0 = \ln Z_0,\ -\beta F_1 = \ln\langle\exp(-\beta H_1)\rangle$$

Since the interaction across the water is relatively weak, we expect that an expansion of F in terms of H_1 will be reasonable at sufficiently high temperatures (room temperature). To second order in H_1 we can write

$$F_1 = \{\langle H_1\rangle - (\beta/2)[\langle H_1^2\rangle - \langle H_1\rangle^2] + \ldots\} \tag{8}$$

Eqn 8 may be justified by examining each term in the expansion. The linear term $\langle H_1\rangle \propto \sum_{i,j}\nu_{ij}$ represents the mean interaction energy between two different dipole layers. Integration over the plane shows that this term is zero. This result is independent of the orientation of the dipoles, and comes from the factor $1-3\cos^2\alpha_{ij}$ in ν_{ij}. Thus the free energy associated with the interaction of the dipole layers arises from the fluctuations determined by the quadratic terms in lowest order. It can be seen that the next correction to Eqn 8 is fourth order in H_1 and gives a negligible contribution to the free energy at sufficiently high temperatures. Thus we are justified in keeping only the quadratic term in Eqn 8 and writing

$$F_1 \approx -0.5\beta\langle H_1^2\rangle \tag{9}$$

Using Eqn 6 for H_1 this becomes

$$\begin{aligned} F_1 = {} & 0.5\beta \sum_{\mathrm{j,j'}} \sum_{l,l'} v_{\mathrm{jj'}} v_{ll'} \{\langle \mu_{\mathrm{zj}} \mu_{\mathrm{z}l}\rangle\langle \zeta_{\mathrm{zj'}} \zeta_{\mathrm{z}l'}\rangle \\ & +0.25\langle \mu_{\mathrm{j}}^{+} \mu_{l}^{-}\rangle\langle \zeta_{\mathrm{j'}}^{-} \zeta_{l'}^{+}\rangle + \text{cross terms}\} \end{aligned} \tag{10}$$

Eqn 10 depends now on the correlation between dipoles in the same plane, and we shall use the mean field theory to evaluate these correlation. In the mean field approximation each dipole is assumed to move in an average molecular field due to all other dipoles. Under this assumption the orientation of a given dipole is governed only by the average molecular field. As a consequence the variables μ_{i} are statistically independent and we can replace the average of the products in Eqn 10 by the products of the averages. For example

$$\langle \mu_{\mathrm{zj}} \mu_{\mathrm{z}l}\rangle \approx \langle \mu_{\mathrm{zj}}\rangle\langle \mu_{\mathrm{z}l}\rangle,\ j \neq l \tag{11}$$

where $\langle \mu_{\mathrm{zj}}\rangle = \langle \cos\theta\rangle$ is independent of dipole site.

It is well known that the results of the mean field theory, for example in magnetism of crystals, are correct when the temperature is sufficiently above the transition temperature [10]. The approximation in Eqn 11 ignores fluctuations of short range order effects due to neighboring molecules. In the magnetic case these fluctuations become important near the critical temperature and the approximation fails to give quantitatively correct results in this region. In this paper we are not considering any type of phase transition and therefore expect that the mean field theory will give reasonable results. In the mean field approximation the cross terms in Eqn 10 vanish and

$$F_1 = -(\beta/8)\sum_{\mathrm{j,i}} |v_{\mathrm{ij}}|^2\{4\Delta^2 + \langle \sin^2\theta\rangle^2\}, \tag{12}$$

where $\Delta = \langle \cos^2\theta\rangle - \langle \cos\theta\rangle^2$. The angle θ is measured from the z-axis, which is normal to the bilayers (see Fig. 3). Assuming a uniform distribution of dipoles within a plane one obtains after integration

$$\left(\frac{F_1}{N}\right) = \left(\frac{3\pi\beta P^4}{32\varepsilon^2 w^4}\right)\left(\frac{N}{A}\right)(4\Delta^2 + \langle \sin^2\theta\rangle^2) \tag{13}$$

The number of dipoles (N) in a plane of area (A) is given by $N/A = l/2V$, where V is the volume per lipid molecule, excluding the dipolar part that forms part of the water layer. The water interlayer spacing is $w = l(1-\Phi)/\Phi$, and thus Eqn 13 becomes

$$(F_1/N) = -\alpha\Phi^4/l^3(1-\Phi)^4, \tag{14}$$

$$\alpha = (3\pi\beta P^4/64\varepsilon^2 V)(4\Delta^2 + \langle \sin^2\theta\rangle^2) \tag{15}$$

At room temperature, using a value of $V = 1063$ Å^3,

$$\alpha = 2.2\times10^{-3}(P^4/\varepsilon^2)(4\Delta^2 + \langle \sin^2\theta\rangle^2) \tag{16}$$

where P is in debye, l in Å and F_1/N in electron volt per molecule.

We next consider the free energy $F_0(l)$ of a single bilayer. $F_0(l)$ depends on the lipid thickness but not on the lipid fraction ϕ and includes all interactions of the molecules in the bilayer as well as the lecithin–water surface interaction. Thus an explicit calculation would be very difficult. However, we know F_0 must be a minimum at a thickness l_0 corresponding to no interaction between bilayers. The experimental data (Fig. 2) shows that the largest increase in bilayer thickness corresponding to maximum interaction is about 25%. Thus instead of trying to evaluate F_0 explicity we shall develop a model in which F_0 is first expanded about its minimum l_0 defined by $F_0'(l_0) = 0$, where the prime denotes differentiation with respect to l. To second order we then obtain

$$(1/N)F_0(l) = (1/N)F_0(l_0)+0.5(l-l_0)^2a \tag{17}$$

where $a = F_0''(l_0)$ may be seen tobe positive. The parameter α in Eqn (16) is a slowly increasing function of l as we shall show below. Thus we may write

$$\alpha(l) = \alpha_0+\gamma(l-l_0),\ \gamma > 0 \tag{18}$$

The condition that the total free energy be a minimum

$$(\partial F_0/\partial l)_\phi+(\partial F_1/\partial l)_\phi = 0$$

then gives

$$b_1/(l-l_0) = 1+a_1\{l(1-\Phi)/l_0\Phi\}^4 \tag{19}$$

where

$$b_1 = (l_0/2)-(3\alpha_0/2\gamma) \text{ and } a_1 = al_0^4/2\gamma.$$

COMPARISON WITH EXPERIMENT

Eqn 19 relates the bilayer thickness l to the lipid volume fraction ϕ. For comparison of this theory with the data in Fig. 2 we need to find a reasonable set of the parameters l_0, a_1 and b_1. The quantity l_0 represents the bilayer thickness in the absence of interaction between bilayers, and thus should be obtainable from the multilayer data extrapolated to high water content, or from measurements on a single bilayer. The latter provides a value of $l_0 = 47$ Å from black film capacitance measurements [11], which is believed to be enlarged by the presence of hydrocarbon solvent [11]. A value of 33 Å from X-ray studies [2] has been quoted [11] as the most likely thickness of an isolated bilayer hydrocarbon region in an aqueous media. The Reiss-Husson [4] data in Fig. 2 flatten out for high water content at a lipid thickness of 33 Å. The other data in Fig. 2 indicates a somewhat lower value. As shown in Fig. 2, a reasonable fit to the data is obtained with $l_0 = 33$ Å, $a_1 = 100$ and $b_1 = 14$ Å (- - -) or with $l_0 = 32$ Å, $a_1 = 24$ and $b_1 = 10$ Å (———). The theory is quite sensitive to all three parameters, as well as the choice of 0.85 in Eqn 1 for the fraction of lipid volume that forms part of the bilayer thickness. We now want to see whether these values of a_1 and b_1 are reasonable. To estimate a_1, consider the following crude model of $F_0(l)$, similar to previous authors [8, 9, 12].

$$F_0(l) = g_0(l)+\gamma_{\mathrm{wp}}A_0+\gamma_{\mathrm{wh}}(A-A_0) \tag{20}$$

γ_{wp} and A_0/N are the surface tension and surface area per molecule of the bilayer for minimum surface area at low water content. γ_{wh} and $(A-A_0)/N$ are the surface tension and the area per molecule of the hydrocarbon–water interface created by the expansion of the surface area with increased water content. γ_{wp} of a lecithin bilayer is about [12, 13] 1 erg/cm^2, and A_0/N which is essentially the polar surface area should be nearly independent of lipid thickness. $\gamma_{wh} \approx 52$ erg/cm^2 for a pure hydrocarbon [17] (*n*-tetradecane) in contact with water. However, it is not clear that this value would be appropriate for the area of hydrocarbon–water contact in between the polar groups in an ordered bilayer. Parsegian [8, 9] calculated values of γ_{wp} of 18.5 and 9.85 erg/cm^2 based on theories that may be open to criticism. The surface area per molecule is $A/N = 2V/l$. $g_0(l)$ contains all other interactions within one bilayer, including the bulk hydrocarbon–hydrocarbon interaction. It is thought that the surface terms are more sensitive to variations in lipid thickness than the bulk term [8, 9, 12], although explicit calculations have not been performed. One might expect the surface contribution to $g_0(l)$ to be roughly proportional to the surface density of dipoles. This leads to a linear dependence of $g_0(l)$ on lipid thickness. Hence the second derivative $a = F_0''(l_0)$ would be dominated by the surface tension term. With this assumption $a \approx 4\gamma_{wh}\, V/l_0{}^3$ and

$$a_1 = al_0{}^4/2\gamma \approx 2\gamma_{wh} V l_0/\gamma \tag{21}$$

If we take $V = 1063$ Å^3, $\gamma_{wh} = 10$ erg/cm^2 and the values that fit the data in Fig. 2, of $\alpha_0 = 33$ Å, $b_1 \approx 14$ Å, $a_1 \approx 100$, then it follows from Eqns 19 and 21 that we require

$\gamma/\alpha_0 = 0.60$ Å^{-1} and $\gamma = 0.44$ ev Å^2 and thus $\alpha_0 = 0.73$ ev Å^3.

To obtain an estimate of α_0 and of γ/α_0 let us assume the magnitudes of the dipole moment and the effective dielectric constant are nearly independent of lipid thickness in Eqn (16). If the dipoles are freely rotating within a cone of angle $\theta = \pi/2$ from the vertical one can estimate that $\Delta \approx 1/12$ and $\langle \sin^2\theta \rangle \approx 2/3$. Any restrictions on the dipole orientation reduces Δ even further. Thus neglecting $4\Delta^2$ in Eqn (16) and using Eqn (18) we find

$$\gamma/\alpha_0 = 2\langle \sin^2\theta\rangle'/\langle \sin^2\theta\rangle \text{Å}^{-1} \tag{22}$$

$$\alpha_0 = 2.2\cdot 10^{-3}(P^4/\varepsilon^2)\langle \sin^2\theta\rangle^2 \text{ ev Å}^3. \tag{23}$$

Since Δ is small and approximately constant, we have $\langle\cos\theta\rangle^2 \approx \langle\cos^2\theta\rangle$, and thus we may write $\langle \sin^2\theta\rangle' = 2[\langle\cos\theta\rangle'/\langle\cos\theta\rangle]\langle\cos\theta\rangle^2$. If we make a dipole calculation within the plane the mean field analysis gives

$$\langle\cos\theta\rangle'/\langle\cos\theta\rangle = -\frac{3\beta U_0/4l_0}{1+\beta U_0\Delta/2} \tag{24}$$

where

$$U_0 = \frac{1}{\varepsilon_s}\sum_j \frac{P^2}{|r_{ij}|^3} \approx \frac{2\pi}{\varepsilon_s}\,\frac{N}{A}\,\frac{P^2}{r_0}$$

is the dipole energy in the plane (cgs units), ε_s is the surface dielectric constant, and the mean distance r_0 between dipoles in a plane is given by $\pi(r_0/2)^2 = A/N = 2V/l_0$. At room temperature we thus have $\beta U_0 = 0.27(P^2/\varepsilon_s)$, with P in debye.

Table of bond lengths [15] suggest a maximum separation between the positive and negative charge of the phosphocholine group of 6.1 Å corresponding to a maximum value of $P = 29$ debye in the absence of hydration and counter-ion effects. A somewhat smaller value appears more likely, thus let us choose $P \approx 25$ debye.

In the Appendix we have estimated the effective dielectric constant across the interlayer water spacing as $\varepsilon \approx 14$. The surface dielectric constant at the lipid-water interface is expected to be [16] $\varepsilon_s \approx 40$. With these values for the dipole moment and the dielectric constants, and using Eqn 24, we obtain from Eqns 22 and 23

$$\gamma/\alpha_0 = 0.33\langle\cos\theta\rangle^2/\langle\sin^2\theta\rangle \text{ Å}^{-1} \tag{25}$$

$$\alpha_0 = 4.4\langle\sin^2\theta\rangle^2 \text{ ev Å}^3 \tag{26}$$

To evaluate these averages we should know more about the dipole surface interactions including steric hindrances. There are those [17–19] who believe the zwitterion is oriented with its axis in the plane of the bilayer, while others [20], think it is aligned perpendicular to the plane. An intermediate position [9] coming about as a result of the lowered electrostatic energy for the in-plane alignment, and out-of-plane alignment due to steric considerations, is probably not unreasonable. Phillips et al. [7] propose that the zwitterions of phosphatidylethanolamine are approximately tangential to the plane of the bilayer while the zwitterions of lecithin are approximately normal to the bilayer such that the end-group contribution to the X-ray long spacing is about 11 Å. The latter model is also supported by Kreutz [21].

If the dipoles are freely rotating in a cone of maximum angle θ_0 with the vertical to the bilayer, then

$$\langle\cos\theta\rangle = \int_1^\delta \cos\theta \,\mathrm{d}\cos\theta \bigg/ \int_1^\delta \mathrm{d}\cos\theta = (1+\delta)/2$$

$$\langle\sin^2\theta\rangle = 1-(1-\delta^3)/3(1-\delta),\ \delta = \cos\theta_0$$

For $\theta_0 = \pi/2$ we find from Eqns 25 and 26 the values $\gamma/\alpha_0 = 0.12$ and $\alpha_0 = 2.0$. If the polar group contribution to the X-ray long spacing [7] indicates that $\delta \approx 0.9$, which is 11/2 Å divided by the polar length of 6.1 Å, then $\gamma/\alpha_0 = 3.1$ and $\alpha_0 = 0.04$. An in-between value of $\delta \approx 0.6$ gives $\gamma/\alpha_0 = 0.60$ and $\alpha_0 = 0.53$ which agrees best with the values $\gamma/\alpha_0 = 0.60$ Å^{-1} and $\alpha_0 = 0.73$ ev Å^3 as derived from a fit to the data in Fig. 2.

CONCLUSIONS

We have developed a theory to account for the increase in lipid thickness with decreasing water content in a lecithin–water mixture. The theory is to account for the change observed in the X-ray long specing through an interaction between neighboring bilayers caused by fluctuations in the phosphocholine groups. We cannot claim at present that our theory gives a good fit to the data since too many of the parameters are not well known. This applies particularly to the size of the phosphocholine dipole moment as well as to its freedom of motion, to the surface tension between water and the hydrocarbon region between polar groups, and to the effective dielectric constants at the lipid–water interface and across the interlayer water spacing. One may also question the use of the dipole approximation for the in-plane energy calculation, since the nearest neighbor dipole separation is about equal to the size of the dipoles. Nevertheless, we believe our theory captures the essentials of the problem and provides a good fit if we choose for the parameters those values which we presently believe to the most likely ones.

APPENDIX: DIELECTRIC CONSTANT EFFECTS

We shall now derive the effective dielectric constant to be used in the interaction free energy (Eqns 15, 16). Two cases are of interest: (A) Two dipole layers are separated by water ($w \simeq 30$ Å) and (B) they are separated by hydrocarbon ($l \simeq 30$ Å). We shall assume that the dipole motion is slow compared to the rotation of a water molecule or the polarization current on the hydrocarbon molecule respectively. Thus the static dielectric constants $\varepsilon_w \simeq 80$ for water and $\varepsilon_H \simeq 2.4$ for hydrocarbon are applicable. However, due to image effects these are not the proper values to use. To calculate the proper constants it will be sufficient to find the potential $V(R)$ at the point P (○) due to a charge q (⊕). To the desired approximation the effective dielectric constant will be the same as the ε in the dipole–dipole interaction energy. Both P and q are in the water a distance z' from the interface (see Fig. 4), and for mathematical simplicity we shall take the limit as z' approaches zero. This

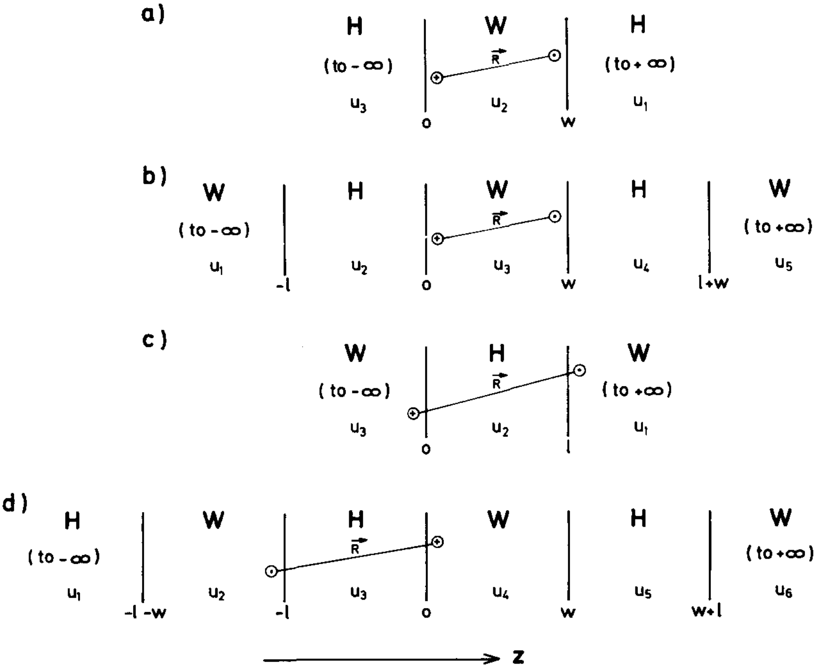

Fig. 4. The potential at a point P (⊙) due to a charge q (⊕), both inside water (W) near the water–hydrocarbon (H) interface.

has no appreciable effect on the effective dielectric constant. We compared 3 with 5 (or 6) regions in order to see the effect upon our answer. After integration over angle, Laplaces equation in cylindrical coordinates (cgs units) is

$$\frac{\partial^2 V}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial V}{\partial \rho} + \frac{\partial^2 V}{\partial z^2} = -(2q/\varepsilon)\frac{\delta(\rho)}{\rho}\delta(z-z')$$

Substituting a solution of the form

$$\phi(\rho, z) = \int_0^\infty Jo(k\rho)u(k, z)\mathrm{d}k, \ (Jo = \text{Bessel function})$$

we find

$$(\partial^2 u/\partial z^2)-k^2 u = -(2q/\varepsilon)k\delta(z-z')$$

After writing down the solutions corresponding to the four cases in Fig. 4, i.e. in case a) we have

$$u_1 = (a_1/\varepsilon_H)\exp[-k(z-w)]$$
$$u_2 = (1/\varepsilon_w)\{b\exp(-kz)+c\exp(kz)+q\exp(-k|z-z'|)\}$$
$$u_3 = (a_3/\varepsilon_H)\exp(kz)$$

we have to match u and ε $(\delta u/\delta z)$ at the interfaces. After letting z' go to zero, we neglect terms like λ^2, $\lambda \exp(-4kw)$, $\lambda\exp(-4kl)$, $\exp(-6kw)$, etc. compared to one, since $\lambda \equiv (\varepsilon_H/\varepsilon_w) \simeq 0.03$ and since the important k are of order $(1/k) \simeq w \simeq l$. After multiplying the relevant Bessel function and integrating

$$\left[\int_0^\infty Jo(k\rho)\exp(-\alpha k)\mathrm{d}k = (\rho^2+\alpha^2)^{-\frac{1}{2}}\right]$$

we obtain (a) Across water (3 regions):

$$V_2 = (q/\varepsilon_w)\{[(4-8\lambda)/R]+(4-10\lambda)(R^2+8w^2)^{-\frac{1}{2}}\}$$

(b) Across water (5 regions):

$$V_3 = (q/\varepsilon_w)\{[(4-8\lambda)/R]+[(4-16\lambda)(R^2+8w^2)^{-\frac{1}{2}}]$$
$$-16\lambda(R^2+4l^2+4lw)^{-\frac{1}{2}}+2(R^2+24w^2)^{-\frac{1}{2}}\}$$

(c) Across hydrocarbon (3 regions):

$$V_1 = (4\lambda q/\varepsilon_w)\{[(1-2\lambda)/R]+(1+2\lambda)(R^2+8l^2)^{-\frac{1}{2}}\}$$

(d) Across hydrocarbon (6 regions):

$$V_2 = (2q/\varepsilon_w)\{(\lambda/R)+(1+\lambda)[R^2+4w(l+w)]^{-\frac{1}{2}}$$
$$+[R^2+8l^2+12lw+4w^2]^{-\frac{1}{2}}+\lambda(R^2+8l^2)^{-\frac{1}{2}}+[R^2+8w(l+2w)]^{-\frac{1}{2}}\}$$

where $R^2 = \rho^2+w^2$ in cases a) and b) and $R^2 = \rho^2+l^2$ in Cases c and d. For the potential across the water one obtains nearly the same results for 3 and 5 regions, while for the potential across the hydrocarbon it is essential to consider 6 regions.

No further important changes are produced by considering more regions. For the dipole–dipole interaction the relevant distances are $R^2 \simeq \sqrt{2w} \simeq \sqrt{2l}$. Making this substitution and using $\lambda \simeq 0.03$, we may write to a reasonable approximation

$$V = q/\varepsilon R$$

where $\varepsilon = 14 \pm 2$ across the water, and $\varepsilon = 36 \pm 8$ across the hydrocarbon.

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