CROATICA CHEMICA ACTA CCACAA **60** (3) 505—516 (1987)

CCA-1744

YU ISSN 0011-1643
UDC 577.352.2:541.13
Conference Paper (Invited)

Electrical Double Layer and Phospholipid Membranes. Aspects of Interface Water Structure*

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Received January 19, 1987

It is inferred that the formation of an electrical double layer in phospholipid membranes is affected by the modified water structure at the membrane/water interface. Theoretical evidence is presented indicating a decrease in the number density of water hydrogen bonds and the appearance of a layer of spontaneously polarized water at the solid/water interface which are the consequence of the orientational properties of the water structure and the asymmetric structure of the water molecule respectively. Consequences of such modifications of water structure are discussed on the basis of simple models regarding ion distribution at the interface, effect on the phospholipid chain melting phase transition temperature and the membrane-membrane interaction.

INTRODUCTION

Phospholipid membranes contain on their surfaces ionizable groups and therefore some of them are charged. The interaction between a charged membrane and the surrounding ionic solution leads to the formation of the electrical double layer. Many membrane phenomena such as binding of charged ligands to the membrane, membrane structural phase transitions, or membrane-membrane interactions depend on the properties of this electrical double layer and therefore its studies are of great theoretical and also practical interest.

The full theoretical description of the membrane/electrolyte solution interface and its effects on the membrane properties is at present unattainable. The system is constituted by three components, i. e. water, ions and membrane, and its behavior is in a complex manner governed by the interactions between these three components and also by the structure and the dynamic properties of the membrane. Even systems which comprise only some of the above constituents, i. e. water, ionic solutions, phospholipid membranes, cannot be treated comprehensively. Therefore it is still of interest to analyze the properties of the electrical double layer in membrane

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* Based on an invited lecture presented at the *7th »Ruđer Bošković« Institute's International Summer Conference on the Chemistry of Solid/Liquid Interfaces,* Red Island — Rovinj, Croatia, Yugoslavia, June 25—July 3, 1986.

systems by studying the behavior of simple models which include only certain features of the system.

A widely used model to describe the membrane electrical properties is the classical Gouy-Chapman model of the electrical double layer[1,2] in which the membrane surface is assumed to be a smooth surface with the membrane charges uniformly smeared on it and the water electrolyte solution is assumed to be a homogeneous dielectric medium embedding ions as point charges.

The purpose of this work is to describe an extension of the Gouy-Chapman theory of the electrical double layer which is based on the notions of the effect of solid surfaces on the structure of interface water and the finite size of ions. In the following section theoretical evidence will be presented indicating a decrease in the number of water hydrogen bonds and the appearance of a layer of spontaneously polarized water at the solid/water interface which are the consequence of the orientational properties of the water structure and the asymmetric structure of the water molecule respectively. In subsequent sections the consequences of such modifications of water structure will be discussed regarding (*i*) ion distributions at the interface, (*ii*) effect on the phospholipid chain melting phase transition temperature and (*iii*) the membrane-membrane interaction. All these topics except that of membrane-membrane interactions have been more extensively discussed earlier.[3-8]

MODELING OF WATER PROPERTIES AT SOLID/WATER INTERFACES

The model presented is based on the assumption that there are two properties of a water molecule which affect the behavior of water at the membrane/water interface, firstly, its ability to form hydrogen bonds and, secondly, its asymmetrical structure. It is assumed that a water molecule in the bulk may form up to four hydrogen bonds, two in the direction of its O—H bonds and two in the direction of its electron lone pairs. Thus, if an oxygen atom is placed in the center of the tetrahedron, the directions in which hydrogen bonds can be formed are approximately the four directions from the center of this tetrahedron to its corners. Because of this property a water molecule with its oxygen atom lying within an interface water layer of a thickness of the length of water hydrogen bond ($d_{\mathrm{O-H\ldots O}} \sim 0.3$ nm) can form all four hydrogen bonds only in some of its orientations. At other orientations it can form three, two or only a single hydrogen bond. Furthermore, water molecules which have their oxygen atom in the interface layer of the thickness of the water molecule O—H bond ($d_{\mathrm{O-H}} \sim 0.1$ nm) are restricted in their possible orientations because for steric reasons the orientations with the molecule protons lying outside the water region must be excluded.

The formation of a hydrogen bond is an energetically favorable process and it can be expected that the orientations of water molecule with a larger number of hydrogen bonds are more favorable. In order to study the system described quantitatively a simple model of water was introduced[3,4] which emphasized both water hydrogen bonding and orientational degrees of freedom of interface water molecules. The free energy density of water ($g(x)$) is expressed in terms of the free energy of the subspace of the system encompassing a water molecule with its oxygen atom at the distance x from the surface ($x = 0$ is defined as the distance of closest approach to the surface of the oxygen atom) and the hydrogen bonds it can form ($F_1(x)$)

$$g(x) = {}^1/_2\, F_1(x)\, \varrho_w(x) \tag{1}$$

where $\rho_w(x)$ is the number density of water oxygen atoms and

$$F_1(x) = -1/\beta \ln Z_4(x) \tag{2}$$

with

$$Z_4(x) = \sum_{j=1}^{4} Z_o^{\,j}\, Y_j(x) \tag{3}$$

Here $\beta = 1/kT$, k is the Boltzmann constant and T the absolute temperature. Z_o denotes the partition function of a single hydrogen bond and is in the present model calculation expressed as a sum of two terms

$$Z_o = \frac{\alpha}{\alpha + 1} + \frac{\exp(-\beta E_H)}{\alpha + 1}. \tag{4}$$

The first term represents the non-bonded state of a hydrogen bond and the second term the bonded state. α is the non-bonded fraction of the phase space and E_H is the energy of the hydrogen bond. The two parameters were chosen[4] in such a way ($\alpha = 28$ and $E_H = -13.4$ kJ/mole) that the model applied for the bulk water gave a good fit to the spectroscopically obtained temperature dependence of the non-bonded water O—H groups.[9,10] $Y_j(x)$ are fractions of the orientational space of a water molecule with its oxygen atom at a distance x from the surface within which a molecule can form j ($j = 1, 2, 3, 4$) hydrogen bonds.[3,4] One half in the expression 1 appears in order that in the total free energy of the system the number of hydrogen bonds is counted properly.

The contribution of hydrogen bonding to the surface energy per unit area can be calculated as a difference between the integral over coordinate x of the free energy density (Eq. 1) in the interval from $x = 0$ to $x = d_{\mathrm{O-H\ldots O}}$ and the corresponding bulk integral.[3,4,7] The value obtained for $T = 298$ K is 0.035 J/m^2 which is about one half of the surface tension of water at this temperature.

The above model was utilized in order to estimate the mean number of hydrogen bonds in the interface region. It turned out[4] that the number of hydrogen bonds falls gradually from its bulk value at $x = 0.3$ nm to about three quarters of the bulk value at $x = 0$. This result essentially agrees with the result obtained by the molecular dynamics simulation of water.[11]

By employing the same simple water model it was also possible to determine the mean value of the electrical dipole moment.[4] It was shown to be nonzero for all water molecules with their oxygen atom lying within the layer $0 < x < d_{\mathrm{O-H}}$. It was concluded[4] that due to the asymmetric structure of the water molecule and the fact that its permanent dipole is located close to the oxygen atom, the water layer comprising water molecules with their oxygen atom within $0 < x < d_{\mathrm{O-H}}$ is polarized with the direction of polarization normal to the surface and towards the bulk. The response of the interface water to the external electric field has been estimated also[4] and it was shown that the effective dielectric constant drops within this layer to about one tenth of its bulk value. The appearance of the water spontaneous polarization leads to the decrease of the electrical potential at the membrane/water interface where the effect is enhanced due to the decreased value of the dielectric constant.[5,6]

SOLID/WATER INTERFACE ION DISTRIBUTION AND MEMBRANE SURFACE POTENTIAL

Phospholipid membranes, if charged, are as a rule negative, which in accordance with the electrical double layer phenomenon causes cations to be attracted into and anions to be expelled from the interface region. However, solution ions also feel the decrease of the electrical potential at the membrane/water interface arising due to water spontaneous polarization and the smaller value of the dielectric constant. Thus cations are additionally attracted to the surface and anions additionally expelled from it. These effects can be taken into consideration by the following generalized version of the Poisson-Boltzmann equation[6]

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[\varepsilon(x)\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}\right] = -\frac{\varrho(x)}{\varepsilon_o} + \frac{\mathrm{d}P(x)}{\mathrm{d}x} \tag{5}$$

with the boundary condition

$$\left.\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}\right|_{x=0} = -\frac{\sigma - P(0)}{\varepsilon_o\,\varepsilon(0)} \tag{6}$$

where $\psi(x)$ is electrical potential, $P(x)$ spontaneous polarization, $\varepsilon(x)$ the dielectric constant, ε_o the permittivity constant, σ the surface charge density, and $\rho(x)$ charge density of solutions ions

$$\varrho(x) = e_o\,[n_+(x) - n_-(x)] \tag{7}$$

where

$$n_+(x) = n_\infty \exp\,[-e_o\,\psi(x)/kT] \tag{8}$$

$$n_-(x) = n_\infty \exp\,[e_o\,\psi(x)/kT]. \tag{9}$$

e_o is unit charge and n_∞ salt concentration at infinity. Electrical potential is defined so that its value at infinity is zero.

Consequences of interface water spontaneous polarization can be visualized particularly well by replacing the actual spontaneous polarization curve $P(x)$ by a step function.[5] In such a case the spontaneous polarization is taken to be constant (P_d) within the layer $0 < x < a$ ($a \sim d_{O-H}$) and zero at $x > a$. Accordingly, a lower value of the dielectric constant (ε_2) can be attributed to the region $0 < x < a$. Then Eq. 5 reduces into the form of the ordinary Poisson-Boltzmann equation where two additional charged infinitely thin layers must be taken into consideration, one at $x = 0$ with a surface charge density $-P_d$ and another at $x = a$ with a surface charge density P_d. The boundary condition at $x = 0$ then reads

$$\left.\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}\right|_{x=0} = -\frac{\sigma - P_d}{\varepsilon_o\,\varepsilon_2}. \tag{10}$$

The two additional boundary conditions for the new boundary at $x = a$ are

$$\psi\,(a - 0) = \psi\,(a + 0) \tag{11}$$

and

$$\varepsilon_2 \frac{\mathrm{d}\psi\,(a - 0)}{\mathrm{d}x} - \frac{P_\mathrm{d}}{\varepsilon_\mathrm{o}} = \varepsilon_1 \frac{\mathrm{d}\psi\,(a + 0)}{\mathrm{d}x} \tag{12}$$

where ε_1 is the bulk value of the dielectric constant.

The set of the above equations represents a modification of the Gouy-Chapman theory of the electrical double layer and can be solved in a similar manner.[8]

It is of interest to compare the electrical potential profile obtained by the present model with that predicted by the Gouy-Chapman theory. Such a comparison is demonstrated in Figure 1. Inclusion of the interface water layer exhibiting spontaneous polarization and a lower value of the dielectric constant causes the membrane surface potential of the negatively charged membrane to be more negative than that predicted by the ordinary Gouy-Chapman theory. However, for the distance from the surface larger than the range of the spontaneusly polarized region the electrical potential is smaller than that predicted by the simple Gouy-Chapman theory. The behavior of the system described is fairly obvious. Due to the drop of the electrical potential in the region of polarized water additional cations are trapped in this region. They partially screen the effect of the surface charge towards the electrolyte solution further away from the surface.

The dependence $\psi\,(x)$ at $x > a$ obtained by the present model can not be distinguished from the prediction of the Gouy-Chapman theory obtained by assuming an appropriately smaller surface charge density (dotted line in Figure 1.). Therefore measurements of the electrophoretic ζ-potentials which are presumably[12] potentials at distances from the surface greater than 0.1 nm do not distinguish between the two possible models of cation behavior at the membrane interface, the model assuming their tight binding[12] and the model assuming their trapping within the layer of polarized water.[5,6] However, the two models differ in their prediction regarding the membrane surface potential. As can be seen in Figure 1 the membrane surface potential obtained by the present generalization of the Gouy-Chapman theory has a much more negative value than that obtained on the basis of the cation binding model.

Measurements of the electrophoretic mobility of phosphatidylserine (PS) vesicles in different cationic environments revealed[12] that the interaction between cations and PS membranes is cation specific. In terms of the cation binding model[12] this specificity can be described by assigning different values of the binding constant to different cations. The present model[5,6] offers the possibility that the ionic specificity may be attributed to different values of cationic radii. An inspection of the series of cations employed in the electrophoretic mobility studies mentioned above shows that cations with smaller radii exhibit smaller values of ζ-potentials. It is reasonable to expect that cations with smaller radii can approach the surface to a closer

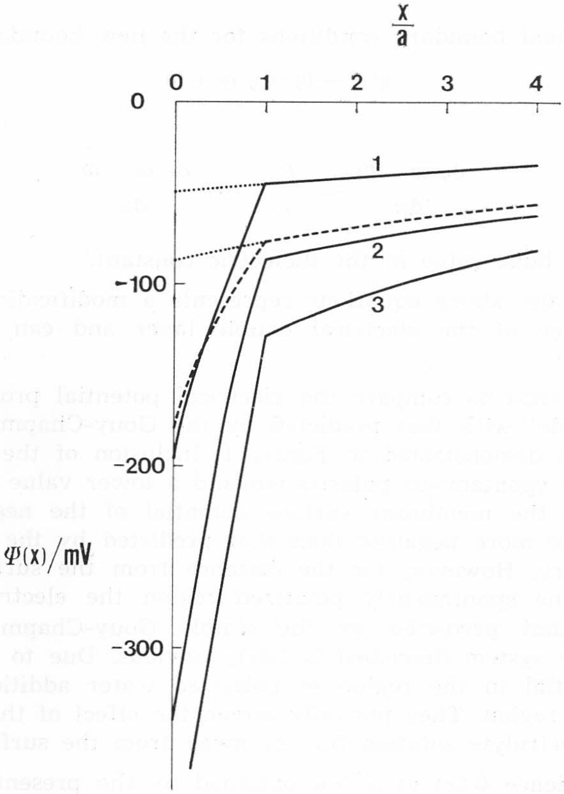

Figure 1. Calculated electrical potential as a function of the distance from the charged surface with the surface charge density $\sigma = -0.23$ As/m². The concentration of the univalent electrolyte solution is 0.1 mol/l. $a = 0.08$ nm. The broken line is the prediction of the Gouy-Chapman theory ($\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $T = 298$ K). The solid lines are predictions of the model considering the occurrence of spontaneous polarization ($P_d = 0.1$ As/m², $\varepsilon_1 = 80$, $\varepsilon_2 = 10$, $T = 298$ K) for $b = 0$ (1), $b = 0.5a$ (2) and $b = a$ (3). The obtained dependences $\psi(x)$ can be for distances $x > a$ also calculated on the basis of the cation binding model where the value of the surface charge density must be appropriately adjusted. The corresponding predictions of this model for distances $0 < x < a$ are shown for two of the above cases by dotted lines (here $\varepsilon_1 = \varepsilon_2 = 80$).

distance. Consequently, more of them are trapped in the layer of polarized water which causes more screening of membrane charges at larger distances and consequent lower values of the ζ-potentials. The distance of closest approach of a cation can be introduced as an additional parameter of the proposed modification of the Gouy-Chapman theory.[5,6] In Figure 1 the predictions of the model are presented for different values of this parameter. It should be pointed out that in order to predict a reasonable dependence of $\psi(a)$ on the distance of closest approach which would allow a comparison with the measured electrophoretic ζ-potentials to be made it is necessary to invoke the values of P_d (~ 0.1 As/m²) and ε_2 (~ 10) which are consistent with the theoretical estimates.[4]

MEMBRANE/WATER INTERFACE AND PHOSPHOLIPID CHAIN MELTING PHASE TRANSITION TEMPERATURE

A characteristic property of phospholipid membranes is the occurrence of the chain melting phase transition.[13] Below the transition temperature (T_t) of such a phase transition the hydrocarbon chains of phospholipid molecules are ordered and their C—C bonds are mostly in the *trans* conformation. Above T_t the chains are disordered with the fraction of C—C bonds in the *gauche* conformation drastically increased. An increase in the number of *gauche* conformations is accompanied by a shortening of phospholipid molecule chains and an increase of the area each molecule is occupying in the membrane. Therefore the high temperature (fluid) membrane phase has a larger membrane/water interface than the low temperature (ordered) membrane phase and the corresponding difference in the interface free energy affects the values of the transition temperature.

There are two different contributions to the membrane/water interface free energy which depend on the area per phospholipid molecule in the membrane and which are the consequences of the phenomena described by the present model of the membrane/water or membrane/water ionic solution interface. The first contribution is due to the altered water hydrogen bonding in the interface region. Any increase in the membrane area requires the transfer of additional water molecules from the bulk to the interface region. In the case of the hydrophobic surface such a transfer is energetically not favorable, meaning that the described contribution to the interface free energy stabilizes the ordered membrane phase, which is expressed in the increase of T_t. The real membrane interfaces are much more complex than the hydrophobic plane/water interface; in particular they involve specific binding of water molecules to the membrane. It is therefore not possible to assess the contribution of water hydrogen bonding to T_t quantitatively. However, implications can be made in qualitative differences in the phase transition behavior of different phospholipids: the more hydrophobic the phospholipid headgroup region is, the larger T_t is. For instance, the transition temperatures of phosphatidylethanolamine (PE) are about 20 K larger than the transition temperatures of the corresponding phosphatidylcholines (PC).[13] PE head groups bind significantly fewer water molecules than do PC head groups, and head groups of PE are hydrogen bonded intermolecularly which also reduces the polarity of ethanolamine head groups.[14] The effect of chaotropic agents on the lamellar to hexagonal II phase transition of PE has been interpreted in an analogous manner.[14]

Another contribution to the interface free energy which depends on the membrane area arises from the free energy of the electrical double layer.[8,15] The free energy of the electrical double layer (F^{el}) consists of a term due to the electrostatic energy of the system (W^{el}) and the entropy term (TS^{el}) which arises due to the redistribution of the solution ions in the electrical double layer:

$$F^{el} = W^{el} - TS^{el} \tag{13}$$

The electrostatic energy per unit area of the membrane (w^{el}) can be obtained by the integral over coordinate x of the electrical energy density

$$w^{el} = {}^1/_2\, \varepsilon\, \varepsilon_o \int_0^\infty \left(\frac{d\psi}{dx} \right)^2 dx. \tag{14}$$

The entropy term can be estimated by considering each solution component as an ideal gas. In this approximation the entropy change per unit area (s^{el}) due to the redistribution of ions from the uniform distribution into the double layer distribution is given by

$$s^{el} = -k \sum_i \int_0^\infty \{ n_i(x) \ln \frac{n_i(x)}{n_\infty} - [n_i(x) - n_\infty] \}\, dx. \tag{15}$$

It can be shown[8,16] that the shift in the transition temperature due to the electrostatic free energy dependence on the membrane area can be expressed as

$$\Delta T_t^{el} = \frac{1}{\overline{S}_{o1} - \overline{S}_{o2}} [\overline{F_{1A}}^{el}\, \overline{\Delta A_o} + {}^1/_2\, (\overline{F_{1A}}^{el})^2\, (\overline{A}_{o1}\, \chi_1 - \overline{A}_{o2}\, \chi_2)] \tag{16}$$

where $\overline{S}_{o1}$ and $\overline{S}_{o2}$ are entropies per phospholipid molecule for the phase 1 (ordered) and 2 (fluid), $\overline{A}_{o1}$ and $\overline{A}_{o2}$ are the corresponding areas per phospholipid molecule, $F_{1A}{}^{el}$ is the first derivative of the electrostatic free energy by area, χ_1 and χ_2 are the compressibilities of the two phases, and

$$\overline{\Delta A_o} = \overline{A}_{o2} - \overline{A}_{o1}. \tag{17}$$

The electrostatic contribution to the free energy depends on the distance of closest approach b introduced in the previous chapter. Our preliminary determinations of the derivative $\overline{F_{1A}}^{el}$ predict the decrease of T_t by increasing b which is consistent with the observations on PS membranes that the salts with larger cations exhibit lower values of T_t.[17]

INTERFACE WATER STRUCTURE AND MEMBRANE-MEMBRANE INTERACTIONS

The phospholipid membranes interact with one another via several attractive and repulsive forces of different origin[18] which for instance leads to the establishment of stable multilamellar structures. These forces are either direct or act through the intermediate water solution. The latter forces may arise due to or are affected by the modified water structure at the two interfaces. Here we shall describe two examples. The first is the force due to altered density of water hydrogen bonds at the interface.[7] The second example is an effect of the modified water structure at the interface on the double layer repulsion between charged layers.

The force between the two membranes arises at distances between them where the corresponding interface regions with altered density of water hydrogen bonds overlap. The model introduced in the second section can be applied to study interaction between two hydrophobic surfaces. An additional contribution appears if the distance between the two surfaces, or in other words, the width of the water layer (d), is less than $2\, d_{O-H\ldots O}$ because a water molecule within such a layer may have »missing« partners for the formation of hydrogen bonds beyond both surfaces at some of its orientations. The difference in free energy per unit surface area (Δf) can be defined as the difference between the integral of Eq. 1 over x in the interval $0 < x < d$ and the corresponding bulk integral where the free energy F_1 depends now both on the oxygen atom position in the layer and the layer width

$$F_1(x, d) = -1/\beta \ln Z_4(x, d) \qquad (18)$$

with

$$Z_4(x, d) = \sum_{j=0}^{4} Z_0^{\,j}\, Y_j(x, d) \qquad (19)$$

where the fraction of water molecule orientations with no bonds formed is included. Fractions of orientations corresponding to the ability of a water molecule to form zero to four hydrogen bonds have been determined. Then it was possible to calculate the dependence of free energy difference on the water layer width.[7] For distances $d > 2\,d_{O-H\ldots O}$ the value of Δf is twice the value corresponding to a single interface. It is of interest to note that by decreasing d below $2\,d_{O-H\ldots O}$ the value of Δf first increases and reaches its maximum value at a certain distance between the surfaces. Then it falls to zero when all the layer water is expelled. If seems that the water hydrogen bonding contributes to the repulsive force at some, and to the attractive force at other distances between two hydrophobic surfaces. The dependence of the force on the width of the water layer is shown in Figure 2 (curve a). At $d = 0$ where there is no water between the two hydrophobic surfaces the force is attractive. This hydrophobic force is an obvious consequence of the fact that bulk is more favorable environment for water mole-

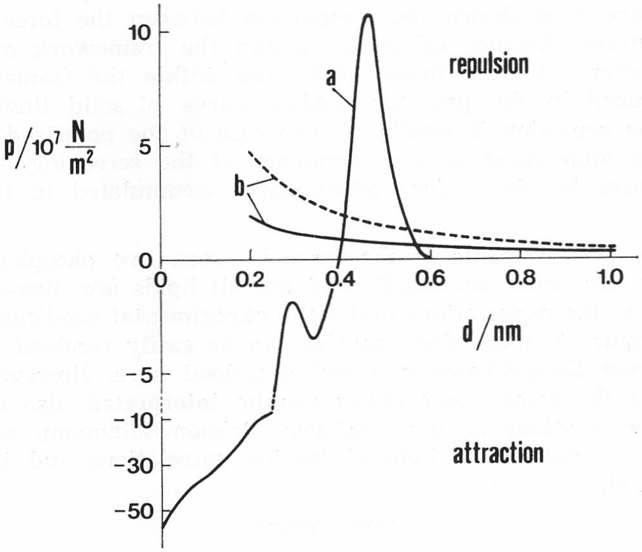

Figure 2. Force per unit area between two plane surfaces. (a) Hydrophobic force calculated on the basis of Eqs. 1, 18 and 19. (b) Electrostatic double layer force obtained from electrostatic free energy, Eq. 13, for the system of two charged layers at distance d. $\sigma = -0.23$ As/m², $a = 0.08$ nm, $b = 0$, $n_\infty = 0.1$ mol/l, $T = 298$ K. Solid line: $P_d = 0.1$ As/m², $\varepsilon_2 = 10$. Broken line: $P_d = 0$, $\varepsilon_2 = 80$.

cules than the intermembrane water layer. However, at larger membrane separations the force is found to be repulsive. This result can be understood in the sense that there, after certain infinitesimal decrease of the intermembrane distance, the gain in the free energy change of the molecules expelled from the intermembrane water layer is smaller than the free energy loss of the remaining water molecules.

As noted already in the previous section the real surfaces of phospholipid membranes are partly hydrophilic in nature where the degree of their hydrophilicity depends on the head group. It can be expected that depending on the strength of the membrane — water interaction the real force laws deviate from the hydrophobic as presented in Figure 2 in the sense that their attractive parts are lessened and the repulsive parts enlarged. These expectations can be related to the results of the direct measurements of the force between two membranes which show that the attraction between less hydrophilic PE membranes is much stronger than the attraction between more hydrophilic PC membranes.[19] It has been already inferred[7] that the repulsive part of the described hydrophobic law is a possible contribution to the so-called hydration force. It is speculated here that steeper separation dependence of the hydration force in PC than in PE membranes[20] may also be related to differences in force law shifts in membranes exhibiting different surface hydrophilicities.

The overlapping of the electrical double layers of the two approaching charged membrane surfaces gives rise to the well known electrostatic repulsive force. The spontaneously polarized layer of water which affects the distribution of interface ions thus affects also the repulsive electrostatic force. In Figure 2. is shown the comparison between the force dependence on intermembrane distance calculated within the framework of the Gouy-Chapman theory (curve b, broken line) and within the framework of the model introduced in the previous section (curve b, solid line). It can be noted that the repulsion is smaller in the case of the polarized water layer which can be understood as a consequence of the screening of negatively charged surfaces by the cations additionally accumulated in the polarized water layer.

From the measurements of the force between two phosphatidylglycerol membranes it has been concluded[21] that not all lipids are dissociated, which was contrary to the expectations under the experimental conditions employed. As seen in Figure 2. these discrepancies can be easily resolved on the basis of the extended Gouy-Chapman model described here. However, it should be noted that the same observations can be interpreted also on the basis of other generalizations of the nonlinear Poisson-Boltzmann equation, i. e. inclusion of electrostatically induced ion-ion correlations and the effect of the finite ion size.[22]

CONCLUSIONS

Two characteristic properties of a water molecule, its tendency to form hydrogen bonds in a tetrahedral configuration, and its asymmetrical structure, seem to govern the behavior of water at solid/water interfaces. In particular they cause a reduction in the number density of water-water hydrogen bonds in the interface region and the establishment of a layer of spontaneously polarized water therein. The present discussion of different phenomena such as charged membrane-cations interaction, membrane structural phase transitions, and intermembrane interactions indicates a possible role of interface water structure also in the determination of the phospholipid membrane properties.

Some of the membrane phenomena described can be understood on the basis of qualitative considerations of possible consequences of modified water structure at the interface. For instance, the layer of spontaneously polarized water gives rise to the electrical potential drop in the interface region which causes more cations to be attracted into this region and anions to be pushed out of it. The cation specificity in the membrane-cation interaction can then be understood simply as a consequence of differences in cation radii.

An outcome of the presented approach in studying the effect of interface water structure on membrane phenomena which is also of general interest is the force law obtained for the interaction between two hydrophobic surfaces. It shows a strong attraction between two such surfaces. It also indicates that at some intermembrane separations even such surfaces repel each other.

It is of interest to follow effects of water structure modifications on interface phenomena also in a more quantitative manner. A model approach was adopted here in order, firstly, to estimate the consequences of diminished hydrogen bonding in the interface region, and secondly, to obtain an idea of the resulting ionic distributions at the interface. The model introduced to study the latter effects represents an extension of the Gouy--Chapman theory of the electrical double layer in the sense that it takes into consideration the consequences of the polarized layer of water at the interface and finite ion sizes. Such modeling is crude and involves many simplifications of the real system. For instance, the hydrogen bond is considered as the only water-water intermolecular interaction, the obvious alterations in the ion hydration in the interface region are ignored, and the membrane surface is taken as being a smooth uniformly charged plane, to name only some of the model deficiencies. Also calculations are approximate, a kind of mean field approach is employed in determination of the effect of water-water interactions and the Poisson-Boltzmann approximation in determination of ionic distributions. Consequently, some of the quantitative predictions presented are not entirely realistic. For instance, any inclusion of correlations between orientations of neighbouring water molecules would certainly lead to a larger range of the hydrophobic force law than twice the length of the hydrogen bond. It should be pointed out that the results presented are not meant to be directly compared to the corresponding experimental data but rather to illustrate the manner in which the interface water structure may modify the otherwise expected behavior of the membrane/water solution interface.

The present work emphasizes primarily the phospholipid membrane data indicating the role of interface water structure. It can be expected that properties of other systems involving water and the electrical double layer can be affected in a corresponding manner.

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Električna dvojna plast in fosfolipidne membrane. Vidiki strukture vode ob medfazi

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Pokažemo, da na lastnosti električne dvojne plasti pri fosfolipidnih membranah vpliva spremenjena struktura vode na medfazi membrana/voda. S teoretskim pristopom ugotovimo, da se zaradi orientacijskih omejitev v strukturi vode in nesimetrične strukture molekule vode na medfazi trdno/voda zmanjša številčna gostota vodikovih vezi ter nastane plast spontano polarizirane vode. S pomočjo preprostih modelov študiramo vplive opisanih sprememb v lastnostih vode ob medfazi na porazdelitev ionov ob medfazi, na temperaturo faznega prehoda iz urejene v tekočo fazo fosfolipidne membrane ter na medmembransko interakcijo.