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LANDAU THEORY OF TWO-COMPONENT PHOSPHOLIPID BILAYERS

I. PHOSPHATIDYLCHOLINE/PHOSPHATIDYLETHANOLAMINE MIXTURES

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Priest's phenomenological model (Mol. Cryst. Liq. Cryst. 60 (1980) 167.) on one- and two-component PC bilayers is extended here. We constructed a new excess free energy term in the state function to describe the thermodynamic properties of the two-component phospholipid bilayers where the chain lengths and the polar heads of the components can be different simultaneously. By means of this generalized state function, we can calculate the phase diagrams of DPPC/DPPE, DMPC/DMPE, DMPC/DPPE, DPPC/DMPE and DSPC/DMPE mixtures. We obtained complete miscibility both in the liquid crystalline and in the gel phase if the chain lengths of the components were the same. If the chain length of the PE component was longer than that of the PC component, we obtained a peritectic system. A eutectic system was obtained in the reverse case. The results of the model were compared with the experimental data available. Applying the quasichemical approximation, we determined the molecular meaning of the phenomenological model parameters. Namely, σ and γ are proportional to the sublimation heat of the CH_2 group in the long-chain alkanes and to the hydrogen-bonding energy between the polar heads of the ethanolamines; otherwise the model resulted in -1.94 kcal/mol per CH_2 for the sublimation heat and -1.4 kcal/mol for the hydrogen-bond energy.

1. Introduction

Within the past few years, the approach of the complexity of the lipid matrix of biological membranes to the experimental work in model membranes has progressed from the investigation stage of one-component lipid bilayers to the study of two-component ones [1–8].

Statistical-mechanical and thermodynamic models have been constructed to give a theoretical basis for the experimentally obtained phase diagrams [3,9–13].

The main efforts were made to explain the experimentally well documented phase diagrams of the PC homologues when the lipid components have the same head groups but differ in chain length.

On the basis of the Landau phenomenological theory of phase transitions, Priest [12] has developed probably the simplest model of these binary mixtures. The model contains only two model parameters which can be fitted independently from each other and which results in all of the phase diagrams of PC mixtures in good agreement with the experimental data.

Abbreviations: DPPC, L-α-dipalmitoylphosphatidylcholine; DMPC, L-α-dimyristoylphosphatidylcholine, DSPC, L-α-distearoylphosphatidylcholine; DPPE, L-α-dipalmitoylphosphatidylethanolamine; DMPE, L-α-dimyristoylphosphatidylethanolamine; PC, phosphatidylcholine; PE, phosphatidylethanolamine.

In this paper, our aim is to extend the Priest model to cases where not only the chain lengths of the lipid components but also the type of the polar heads differ. First, we determine the parameters of the Priest model for one-component bilayers of PE homologues. Taking into consideration the hydrogen bonding between the polar heads of PE molecules, we construct a new excess free energy term in the state function of binary mixtures. By means of this generalized state function, we calculate the phase diagrams of binary mixtures of DPPC/DPPE DMPC/DMPE, DPPC/DMPE, DSPC/DMPE and DMPC/DPPE. In the appendix, applying the quasichemical approximation, we determine the molecular meaning of the phenomenological model parameters. The calculated phase diagrams and the experimental data available are compared.

2. The model

2.1. One-component bilayers of PE homologues

Recently, Priest [12] has worked out probably the simplest phenomenological model of one-component PC membranes describing the phase transition properties of these systems. According to this model, the free energy per mole of hydrocarbon chains (two hydrocarbon chains belong to one molecule and one chain consists of L CH_2 units) is given by:

$$\frac{F}{2RT} = \frac{E_0}{RT}(L-3)S-(L-L^*) \times \left[W(S-0.39)^2 - Z(S-0.39)^3 - W(0.39)^2 - Z(0.39)^3\right] / RT-(L-2)2\sqrt{2}\,(S-S^2) \quad \text{at } S \geq 0,$$

$$F/2RT = \infty \text{ at } S < 0. \qquad (1)$$

where S is the order parameter (the fraction of C–C bonds in the hydrocarbon chain tails which are in the *gauche* conformation), E_0 ($= 500$ cal/mol $= 2.1$ kJ/mol) the energy associated with the *trans-gauche* energy difference, R the universal gas constant and T the absolute temperature. L^*, W/R and Z/R are the fitted model parameters and 0.39 the value predicted for S at the melting point of extended chain conformation (ECC) polyethylene. The first term of eq. 1 is associated with the intramolecular conformation of molecules. The second contribution is due to the change in the optimal value of the density connected with the changes in S, i.e., to the change of intermolecular conformation. The third one is the entropy term.

In his original paper, Priest determined the model parameters for PC homologues, namely, $W_C/R = -1085$ K, $Z_C/R = -275.1$ K and $L_C^* = 6.4$ but the parameter-fitting procedure is applicable in the case of other lipid homologues as well.

Since we would like to determine the phase diagrams of PC/PE mixtures, as a first step, it is necessary to obtain the model parameters for one-component PE bilayers.

According to DSC measurements [14], the first-order phase transition of PE homologues turns into a second-order one where the chain length, L_E is about ten. Using $L = 10$ in eqs. 16 and 17 of ref. 12 and seeking the best fit to the L_E vs. T_{PE} (chain length vs. phase transition temperature) diagram, we obtain the following parameters for PE homologues: $Z_E/R = -188.31$ K, $W_E/R = -1117.76$ K and $L_E^* = 5.4$.

Substituting these model parameters into eq. 1, the free energy functions of PE homologues are determined. Similarly to the free energy functions of PC membranes, they have two local minima, a

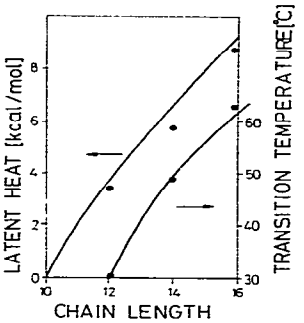

Fig. 1. Transition properties of one-component PE bilayers. Left hand scale: latent heat as a function of chain length. Right hand scale: transition temperature as a function of chain length. Solid curves are model results. Dots are experimental data from ref. 14.

cusp-like minimum at $S = 0$ and another one at higher S (< 0.39). The deeper minimum determines the equilibrium state of the membrane. When the global minimum belongs to $S = 0$, the membrane is in the gel phase; and when it belongs to $S < 0.39$, it is in the liquid crystalline phase.

At a given chain length (L_E) one can find a temperature, the phase transition temperature (T_{PE}), where the local minima of the free energy function become global ones, i.e., the gel and liquid crystalline phases coexist.

In fig. 1, the calculated phase transition temperatures and enthalpies of PE homologues are plotted as a function of chain length.

The enthalpy changes were calculated by means of eqn. 14 in ref. 12.

2.2. Two-component bilayers of PC / PE homologues

Similarly to the free energy function of two-component PC bilayers (see eq. 18 in ref. 12), the free energy function of PC/PE binary mixtures is:

$$\frac{G(X_E, S)}{2RT} = X_E \frac{F_E(S)}{2RT} + (1 - X_E)\frac{F_C(S)}{2RT} + \tfrac{1}{2} X_E \ln X_E + \tfrac{1}{2}(1 - X_E)\ln(1 - X_E) + \Delta U X_E + \frac{(\sigma|\Delta L| + \gamma)}{RT}\left(\tfrac{1}{2} - S\right) X_E (1 - X_E) \quad (2)$$

where X_E is the mole fraction of PE component and $\Delta L = L_E - L_C$. The first two terms are the free energy functions of the one-component PE and PC bilayers, respectively. The next two terms denote the mixing entropy. The fifth term is connected with the difference in the chemical potential (ΔU) between the two components of the mixture. These terms are practically identical with those of the Priest model.

The last term, the excess free energy representing the non-ideal effects, however, differs by a new γ term from the respective term of the PC mixtures. This is the simplest way to consider the experimental fact that PC/PE mixtures of the same chain length are not ideal, i.e., the excess free energy cannot vanish when $L_E - L_C = 0$.

According to the quasichemical approximation (see the appendix), the excess free energy reflects the difference of the nearest-neighbour interaction energies between the same and different components.

$\sigma|\Delta L|(\frac{1}{2} - S)$ and $\gamma(\frac{1}{2} - S)$ represent the interaction energy differences as a consequence of the different chain lengths and that of the different polar heads, respectively. Namely σ relates to the sublimation heat of a CH_2 group of long-chain polyethylene, and γ to the energy of a hydrogen bond between the polar heads of the PE molecules (see the appendix). In both cases, the interaction energy differences vanish in a maximally disordered system (at $S = 1/2$ [12]) and they have a maximum in the gel state (at $S = 0$). We note here that Eibl and Woolley [15], according to their experimental results on PE bilayers, also concluded that during the phase transition (i.e., with increasing S) the loosening of the hydrogen bonds between the polar heads took place.

By means of this state function, similarly to the procedure in the Priest model [12], one can determine the phase diagrams of different PC/PE mixtures. Namely, one has to determine the value or values of ΔU where two or three minima of the state function become global ones to obtain the points of the solidus and liquidus curves at a given temperature, and the X_E values belonging to these minima determine the points of the phase diagram.

Considering the general physical meaning of model parameter σ, we can use $\sigma/R = 125$ K determined by Priest. The only model parameter to be fitted is γ/R. We obtained the best fit to the experimentally determined PC/PE phase diagrams at $\gamma/R = 500$ K.

3. Results

3.1. DPPC / DPPE and DMPC / DMPE mixtures

In the cases of DPPC/DPPE and DMPC/DMPE mixtures, i.e., when $L_E = L_C$, there are two important local minima of $G(X_E, S)$. One is at $S = 0$ and a larger value of X_E ($= X_g$): this is the PE-rich gel minimum. The other minimum is at a liquid crystalline value of $S (= S_{lc})$ and a smaller value of X_E ($= X_{lc}$): this is the PC-rich liquid

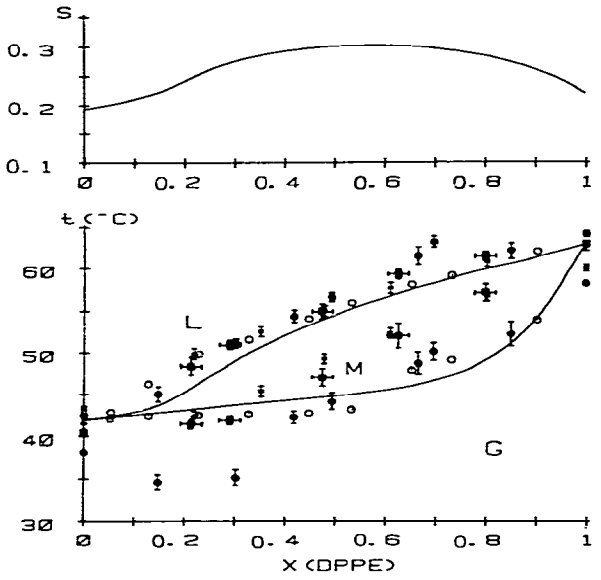

Fig. 2. Phase diagram for DPPC/DPPE mixture in the temperature-mole fraction of DPPE and in the order parameter-mole fraction planes. Solid curves are the model results. (⊙) DSC data from ref. 8. (■) ESR data from ref. 6. (×) fluorescence data from ref. 7. (●) DSC data from ref. 4.

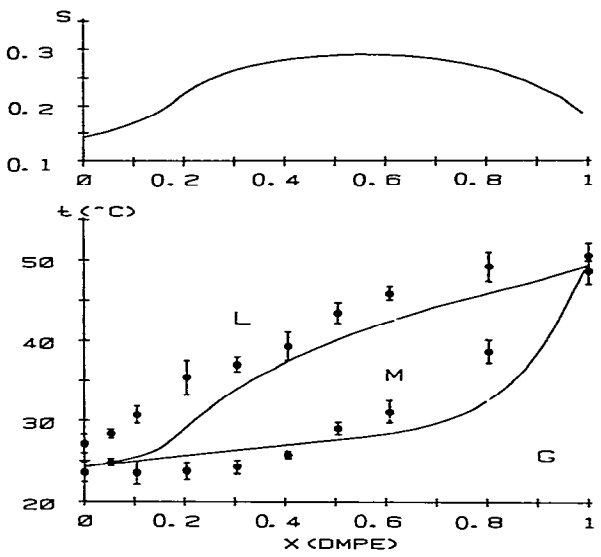

Fig. 3. Phase diagram for DMPC/DMPE mixture in the temperature-mole fraction of DMPE and in the order parameter-mole fraction planes. Solid curves are the model results. (●) DSC data from ref. 5.

crystalline minimum. (The global minimum of G is the free energy of the system for given ΔU and T.)

As a function of ΔU and T, the equilibrium values of X_E and S correspond to the global minimum of $G(X_E, S)$. At a given temperature, between the melting temperatures of the pure PE and PC membranes, one can find a critical value of ΔU ($= \Delta U_c$) where both local minima are global minima of $G(X_E, S)$. On the phase diagrams (see figs. 2 and 3), the pairs of X_E values belonging to these double global minima are plotted against the temperature. On the upper part of these figures, the order parameters belonging to one of these double minima, namely, to the PC-rich liquid crystalline minimum, are plotted as a function of the mixing rate, X_E. The upper curves of the phase diagrams are the so-called liquidus and the lower ones the solidus curves. The liquid crystalline phase (L) is above the liquidus curve and the gel phase (G) below the solidus curve. Between these curves there is the mixed-phase region (M) where the PC-rich liquid crystalline phase coexists in equilibrium with the PE-rich gel phase.

Comparisons with the experimentally determined phase diagrams [3–8] show that the theoretical liquidus curve fits quite well, but a large discrepancy is shown in the case of the solidus curves. The results of the calorimetric measurements come closest to the calculated solidus curve. At the same time, we note that the solidus curves themselves are subjected to the greatest experimental uncertainty [1].

The calculated phase diagrams of DPPC/DPPE and DMPC/DMPE systems show that a complete miscibility occurs both in the liquid crystalline and in the gel phase.

3.2. DMPC/DPPE mixture

The situation for the DMPC/DPPE mixture is more complex. For $L_E > L_C$, there are three important local minima of G in the X_E-S plane. These can be classified as a liquid crystalline minimum, a PC-rich gel minimum and a PE-rich

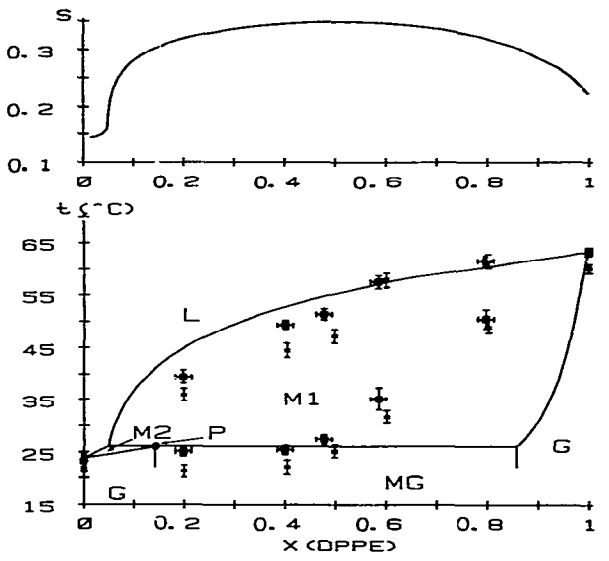

Fig. 4. Phase diagram for DMPC/DPPE mixture in the temperature-mole fraction of DPPE and in the order parameter-mole fraction planes. Solid curves are the model results. (■) ESR data from ref. 6, (×) fluorescence data from ref. 7.

gel minimum. At a certain value of T ($= T_p =$ 27°C – peritectic temperature) and ΔU, all the three local minima are global minima of G. Here all the three phases coexist in equilibrium (see fig. 4). At a given temperature, T, between T_p and T_{PE}, similarly to the DPPC/DPPE system, there is only one critical value of ΔU when two of the local minima are global. In the T_{PC}-T_p temperature interval, however, at a given temperature there are two critical values of $\Delta U(\Delta U_1, \Delta U_2)$. At ΔU_1 the PE-rich gel minimum and PC-rich gel minimum are global minima of G and, at ΔU_2, the PC-rich liquid crystalline and PC-rich gel minima are global. In the region labelled MG (mixed gel) the two gel phases coexist in equilibrium. In the region labelled M_1 a PC-rich liquid crystalline phase coexists with a PE-rich gel phase. The region labelled M2 is quite small and may be difficult to detect experimentally. In this region a PC-rich liquid crystalline phase coexists with a PC-rich gel phase. In fig. 4 the ESR data are also shown [5]. Similarly to the case of the DPPC/DPPE mixture, the agreement with the theoretical results is quite good for the liquidus curve but there is again a discrepancy for the solidus curve from $X_E = 0.5$.

Nevertheless, one certainly can reckon on a better agreement in the case of calorimetric data. In general, the calorimetrically determined solidus curves go to higher mixing rates than the solidus curves obtained by other methods, e.g., ESR, fluorescence spectroscopy (see experimental data in fig. 2).

According to the theoretical model, the DMPC/DPPE mixture is, after all, a peritectic system with a peritectic point, P, at $X_p = 0.13$ and $T_p = 27$°C.

3.3. DPPC / DMPE and DSPC / DMPE mixtures

For cases where $L_E < L_C$, there are three important local minima of G again. Their classification agrees with those of the minima in the $L_E > L_C$ case. At a certain value of T ($= T_E$ – eutectic temperature) and ΔU, all the three local minima are global minima of G (see figs. 5 and 6). At a given temperature below T_E one can find only one critical value of ΔU wnen two of local minima (the

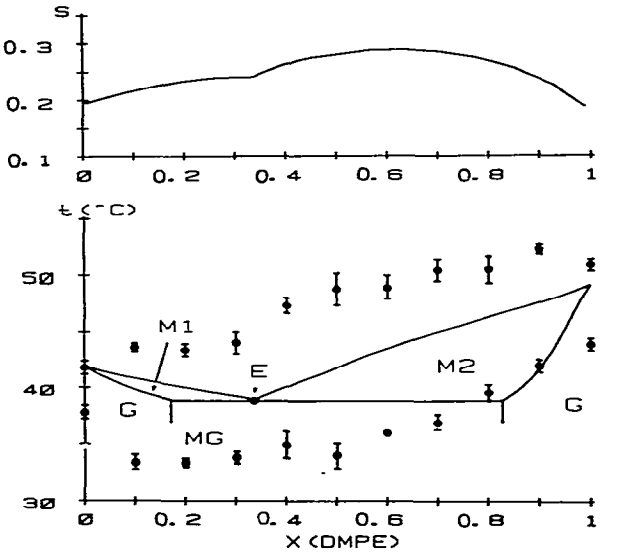

Fig. 5. Phase diagram for DPPC/DMPE mixture in the temperature-mole fraction of DMPE and in the order parameter-mole fraction planes. (●) DSC data from ref. 4.

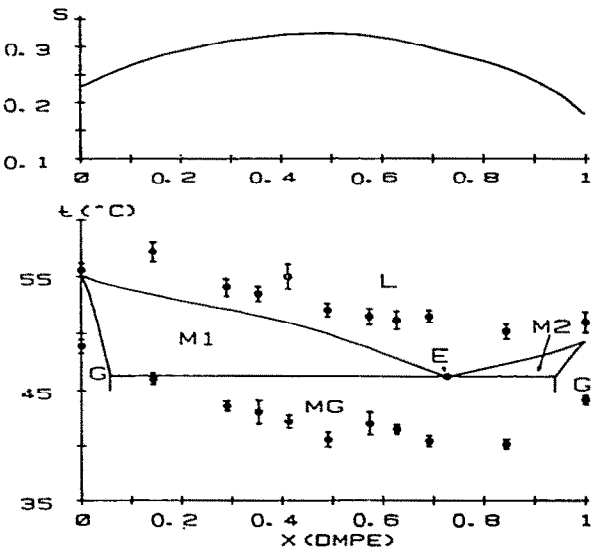

Fig. 6. Phase diagram for DSPC/DMPE mixture in the temperature-mole fraction of DMPE and in the order parameter-mole fraction planes. (●) DSC data from ref. 4.

PC-rich and PE-rich gel minima) become global. At a certain temperature above T_E, there are two critical values of ΔU. At ΔU_1, the PC-rich gel and the liquid crystalline minima are the global ones and, at ΔU_2, the PE-rich gel and the liquid crystalline minima are the global ones. At a given temperature in the T_{PC}-T_{PE} temperature interval, there is only one critical value of ΔU where the PE-rich gel and liquid crystalline minima are global. The coordinates of the eutectic points are $T_E = 38.6°C$ and $X_E = 0.33$ for the DPPC/DMPE system and $T_E = 46°C$ and $X_E = 0.73$ for the DSPC/DMPE system.

As a qualitative comparison with the experimental results, we note that Blume and Ackermann [4], analysing their calorimetric data, also concluded that DPPC/DMPE and DSPC/DMPE systems are eutectic mixtures.

4. Discussion

The Landau theory of phase transitions of binary mixtures of PC/PE bilayers was constructed by simply extending the Priest model [12].

The results obtained indicate that, depending on the chain length differences, three types of PC/PE mixed systems can be differentiated.

At $L_E = L_C$, a complete miscibility occurs both in the liquid crystalline and in the gel phase. When $L_E > L_C$ and $L_E < L_C$, peritectic and eutectic systems are obtained, respectively.

The comparison with the available experimental data shows that the calculated liquidus curves fit quite well. In the case of the solidus curves, the agreement is acceptable only for calorimetric data.

The phase diagrams of PC/PE mixtures are calculated by means of a general free energy function $G(X_E, S)$, being the result of an extended version of the Priest phenomenological membrane model. Model parameters σ and γ introduced into the excess free energy term of the free energy function can be interpreted physically. For the difference of the interaction energies between PE-PE and PC-PC head groups we obtain from eq. A9:

$$U_E^h - U_C^h = -698 \text{ cal/mol} \tag{3}$$

The interaction energies differ basically due to the formation of intermolecular hydrogen bonds between the NH_3^+ protons of the PE head group and to the neighbouring phosphate oxygens [16].

Considering that in the gel phase three hydrogen bonds belong to one head group in a PE membrane, the hydrogen-bond energy is estimated to be:

$$E_H = \frac{Z}{3}(U_E^h - U_C^h) = -1.4 \text{ kcal/mol}, \tag{4}$$

where Z ($= 6$) is the coordinate number [20]. Kanehisa and Ikegami [17] obtained exactly the same value for hydrogen-bond energy in globular proteins.

Substituting eq. 4 into eq. A10 we obtain the following formula:

$$\gamma = 3(b - \tfrac{1}{2})E_H \tag{5}$$

i.e., the γ parameter is proportional to the hydrogen-bond energy between the polar heads of a pure one-component PE membrane in the gel phase. At the same time, according to eq. A11, the σ parameter is proportional to the sublimation

heat of the CH_2 group of long-chain polyethylene, ΔH_s. From eq. A12 the calculated value of ΔH_s is -1.94 kcal/mol per CH_2 group. Salem [18] obtained practically the same value. The given value was smaller than ours by 100 cal.

Using the fitted values of γ ($= 1000$ cal/mol) and σ ($= 250$ cal/mol) model parameters, eqs. 5 and A11 result in the following values for the asymmetry parameters of intermolecular potentials: $a = 0.43$ and $b = 0.26$. The deviations of these parameters from 0.5 show the degree of asymmetry. The large asymmetry at b reflects that, due to the lack of hydrogen bonds, the interaction of PE-PC polar heads is much closer to the PC-PC interaction than to the PE-PE one.

The order parameter curves in figs. 2–6 show that the order parameters (*gauche* number) of the two-component PC/PE bilayers are significantly higher than those of the one-component systems. Therefore, the mixing results in a more flexible and more permeable membrane. These are characteristic features for the biologically active membranes as well, making the very quick adaptation of the membrane function to the external conditions possible.

The advantage of our model as compared with the works of Lee [3,21] and Cheng [11] is that a series of the phase diagrams can be generated if we determine the parameters only for one kind of mixture. The different types of phase diagrams obtained (peritectic, eutectic, etc.) are direct consequences of the same model and not of the parameter-fitting procedure. Furthermore, by means of the quasichemical approximation the physical meanings of the model parameters are also determined.

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Appendix

Here we construct the excess free energy term (nonideality term) on the basis of a molecular theory, i.e., on the basis of the quasichemical approximation [19]. After this derivation we make a comparison between this result and the excess free energy of our phenomenological model (see the last term of eq. 2), giving molecular meaning to the phenomenological model parameters in eq. 2.

According to the quasichemical approximation, the excess free energy can be written as

$$G_{ex} = Z[U_{E,C} - (U_E + U_C)/2] X_E X_C \qquad (A1)$$

where U_E, U_C and $U_{E,C}$ are the PE-PE, PC-PC and PE-PC nearest-neighbour interaction energies, respectively. Z is the value of the first coordinate number. For a one-component lipid bilayer, $Z = 6$ [20]. A mixture of two kinds of molecules can also be packed in the same way as each of the single components, since we are concerned with the mixtures of two very similar lipids. X_E and X_C ($= 1 - X_E$) are the respective mixing rates. One can separate each interaction energy into the following terms:

$$U_i = U_i^c + U_i^h + U_i^c(S) + U_i^h(S) \qquad (A2)$$

where U_i^c is the interaction energy between the hydrocarbon chains of i components, U_i^h the interaction energy between the polar heads of i components in the gel state (i.e., $S = 0$), and $U_i^c(S)$ and $U_i^h(S)$ denote the respective chain conformation-dependent parts of the interaction energies.

The interaction energies in the gel state are:

$$U_E^c = \frac{2L_E}{Z}\Delta H_s \qquad U_C^c = \frac{2L_C}{Z}\Delta H_s \qquad (A3)$$

where ΔH_s is the sublimation heat of a CH_2 group of long-chain polyethylene.

We use the intermolecular energy term of the free energy function of the one-component system (see second term of eq. 1): to determine the conformation-dependent part of the interaction energies:

$$U_E(S) = \frac{2}{Z} 2L_E \{W_E(S - S_0)^2 - Z_E(S - S_0)^3 - W_E S_0^2 - Z_E S_0^3\} - \frac{2}{Z} 2L_E^*$$

$$\times \{W_E(S-S_0)^2 - Z_E(S-S_0)^3 - W_E S_0^2 - Z_E S_0^3\}$$
$$= U_E^c(S) + U_E^h(S)$$

$$U_C(S)$$
$$= \frac{2}{Z} 2L_C \{W_C(S-S_0)^2 - Z_C(S-S_0)^3 - W_C S_0^2 - Z_C S_0^3\}$$
$$- \frac{2}{Z} 2L_C^* \{W_C(S-S_0)^2 - Z_C(S-S_0)^3 - W_C S_0^2 - Z_C S_0^3\}$$
$$= U_C^c(S) + U_C^h(S) \qquad \text{(A4)}$$

where the intermolecular energies are separated into chain-chain and head-head interaction parts.

Obviously, terms in eqs. A4, being proportional to the chain lengths, are connected with the chain-chain interaction and the others with the head-head interaction.

In order to construct the U_{EC} interaction term we assume that it also can be separated into head-head and chain-chain interaction terms:

$$U_{EC} = U_{EC}^h + U_{EC}^c. \qquad \text{(A5)}$$

Considering that the energy term of the lateral interaction is proportional to the membrane density [12], U_{EC} can be estimated by the following formula:

$$U_{EC} \propto (M_E + M_C)/(V_E + V_C)$$

where M and V are the specific mass and volume, respectively. In our case $V_E \approx V_C$, therefore

$$(M_E + M_C)/(V_E + V_C) \cong M_E(0.5+\epsilon_1)/V_E + M_C(0.5-\epsilon_2)/V_C$$

and consequently

$$U_{EC} \cong U_E(0.5+\epsilon) + U_C(0.5-\epsilon)$$

where

$$\epsilon_1 = (V_C - V_E)/V_E \approx \epsilon_2 = (V_C - V_E)/V_C \approx \epsilon \approx 0.$$

This formula can be used well especially for determining U_{EC}^c. U_{EC}^h, however, deviates strongly from the mean value of U_E^h and U_C^h, reflecting the asymmetry in the interactions, i.e., in contrast with the PE-PE interaction neither PC-PC nor PE-PC interactions contain hydrogen bonds. After all, we can assume that U_{EC}^c and U_{EC}^h interaction terms are the linear combinations of the U_E^c and U_C^c, and U_E^h and U_C^h terms, respectively:

$$U_{EC} = bU_E^h + (1-b)U_C^h + aU_E^c + (1-a)U_C^c, \quad \text{where}$$
$$0 < a, b < 1. \qquad \text{(A6)}$$

Substituting eqs. A2–A6 into eq. A1, we obtain:

$$\frac{G_{ex}}{2RT} = \{(b-\tfrac{1}{2})(U_E^h - U_C^h + [U_E^h(S) - U_C^h(S)])$$
$$+ (a-\tfrac{1}{2})(U_E^c - U_C^c + [U_E^c(S) - U_C^c(S)])\}$$
$$\times \frac{ZX_E X_C}{2RT} \qquad \text{(A7)}$$
$$= X_E X_C \left\{ \frac{Z(b-\tfrac{1}{2})(U_E^h - U_C^h)}{RT} \right.$$
$$\times \left[\frac{1}{2} - \frac{\left(\frac{4}{Z}L_E^* f_E - \frac{4}{Z}L_C^* f_C\right)}{2(U_E^h - U_C^h)} S \right]$$
$$+ \frac{2(a-\tfrac{1}{2})\Delta H_s |L_E - L_C|}{RT} \left[\frac{1}{2} - \frac{(L_C f_C - L_E f_E)}{\Delta H_s (L_E - L_C)} S \right]$$
$$\left. + \text{higher order terms in } S \right\} \qquad \text{(A8)}$$

where

$$f_i = -2W_i S_0 - 3Z_i S_0^2$$

and numerically:

$$f_C = R \times 971.8 \text{ [cal/mol]}, \qquad f_E = R \times 957.8 \text{ [cal/mol]}.$$

The chain length mismatch between the PE and PC molecules results in incomplete van der Waals bonds, independently of the sign of $L_E - L_C$. Therefore, $|L_E - L_C|$ is used in the second term of eq. A8.

Discarding the second- and third-order terms in S, one can make a comparison with the phenomenological excess free energy term (see the last term of eq. 2):

$$\frac{2(L_E^* f_E - L_C^* f_C)}{Z(U_E^h - U_C^h)} = 1 \qquad \text{(A9)}$$

$$Z(b-\tfrac{1}{2})(U_E^h - U_C^h) = \gamma. \qquad \text{(A10)}$$

$$2(a-\tfrac{1}{2})\Delta H_s = \sigma. \qquad \text{(A11)}$$

$$\frac{L_C f_C - L_E f_E}{\Delta H_s (L_E - L_C)} = \frac{(L_C - L_E) f_C + L_E (f_C - f_E)}{\Delta H_s (L_E - L_C)}$$
$$\approx -\frac{f_C}{\Delta H_s} = 1 \qquad \text{(A12)}$$

where the approximation in eq. A12 is valid, since

$|L_C - L_E| f_C$ is 10-times higher than $L_E(f_C - f_E)$ even in the worst case when $|L_C - L_E| = 2$. (At $|L_C - L_E| = 0$, the second term of eq. A8 vanishes completely.)

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