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Association probabilities between the single chain amphiphiles into a binary mixture in planar monolayers

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In this work, we have calculated the probabilities of selfassociation of single chain amphiphile molecules for 36 binary mixtures of molecules having an even number of carbon atoms (from 8 to 24 carbon atoms). The association probabilities depend on the dipole moment of head groups, the length of chains and the mole fraction of the mixture of both types of amphiphile. These calculations are useful for the quantitative and qualitative explanation of the cluster formation on the surface of the mono- or bilayers.

Introduction

Owing to the fact that in natural membranes there are different types of lipids, useful information can be obtained studying supermolecular aggregates made up of mixtures of two or more species of lipid molecules. Because the lipids in mixtures do not chemically react, the supermolecular aggregates may be considered as athermal solutions. The distribution of the components into the structure of the supermolecular aggregate is not done at random, but it is due to a selective association process among lipid molecules in the mixture. Jain [1] wrote about the existence of the microclusters separated by the microinterfaces in the mixtures of synthetic lipids. In this work we have calculated the selfassociation probabilities between single chain amphiphiles into binary mixtures organized as a planar monolayer.

Association probabilities

If we want to obtain the expressions of the association probabilities, we assume an athermal solution of the single hydrocarbon chain molecules having different radii, r, and dipole moments, $\vec{p}$, and also the chains length, mixed up in the mole fractions x_1 and x_2 and organized in a planar monolayer or bilayer. It is clear that the selectivity of association of a molecule to another molecule of the same type, or of different type is determinated by the difference between the coupling energies, which are determinated by the interaction forces between the associating molecules. Evidently, the molecules belonging to a couple interact through the electric dipoles of the polar head groups and through the van der Waals-London dispersion forces between the hydrocarbon chains. The interaction energies between two molecules of the same type, U_{11} and U_{22} or different type, U_{12}, have unequal values, and determine a selective association whose result is the formation of the clusters on the surface of the aggregate. We introduce the probabilities of formation of some couples P_{11}, P_{12}, P_{22} between which there are the following relations:

$$P_{11}/P_{12} = (x_1/x_2)\cdot\exp(-(U_{12} - U_{11})/RT) \tag{1}$$

$$P_{22}/P_{12} = (x_1/x_2)\cdot\exp(-(U_{12} - U_{22})/RT) \tag{2}$$

$$P_{11} + P_{12} + P_{22} = 1 \tag{3}$$

Solving this system, we have obtained the relations out of which the association probabilities are calculated:

$$P_{11} = x_1^2 e_1/(x_1^2 e_1 + x_2^2 e_2 + x_1 x_2) \tag{4}$$

$$P_{12} = x_1 x_2/(x_1^2 e_1 + x_2^2 e_2 + x_1 x_2) \tag{5}$$

$$P_{22} = x_2^2 e_2/(x_2^2 e_1 + x_2^2 e_2 + x_1 x_2) \tag{6}$$

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with following notations:

$$e_1 = \exp(-(U_{12} - U_{11})/RT); \quad e_2 = \exp(-(U_{12} - U_{22})/RT) \tag{7}$$

$$U_{11} = -\left(p_1^2 N_A/(4\pi\varepsilon(2r_1)^3) + W_{11} \right) \tag{8}$$

$$U_{12} = -(p_1 p_2 N_A/(4\pi\varepsilon(r_1 + r_2)^3 + W_{12}) \tag{9}$$

$$U_{22} = -\left(p_2^2 N_A/(4\pi\varepsilon(2r_2)^3) + W_{22} \right) \tag{10}$$

where, $\vec{p}_1$, r_1 and $\vec{p}_2$, r_2 are the electric dipole moment and the radius of the polar head group of a molecule in the first, respectively, in the second species of mixture. W_{11}, W_{12}, W_{22} are the molal energies of interaction through van der Waals-London dispersion forces between the chains of two molecules of the same type (W_{11}, W_{22}) or of a different type (W_{12}).

In the calculation of the dispersion energy we consider that in the saturated paraffin chains the electronic charge distribution is localized in bonds and atoms. Also the electronic correlation is negligible between distant points in one molecule and the covalent bonds of each carbon atom have a such spatial arrangement so that we can suppose that a CH_2 group is an attractive center. Under these conditions, within the limits of second-order perturbation theory it is acceptable to assume that dispersion forces are locally additive. So, the attraction force between two hydrophobic chains is obtained by adding all the forces between pairs of attractive centers one in each molecule [2].

The distance between the nearest attractive centers is about 7.14 Å, equal to the distance between the axes of two neighbours molecules with short chains. This is large compared with the dimensions of the attraction units (atoms, bonds), such as the interactions between them, verify London's invers-sixth power distance law ($W = -A/d^6$), where A is equal to $5.6 \cdot 10^3$ $Å^6 \cdot J \cdot kmol^{-1}$ [2].

Because the distance between the most shorter than 1000 Å, the retardation effects are not taken into account [3]. Owing to the fact that in the calculation of the selfassociation probabilities appears the difference between interaction energies, we think that the non-additivity of the dispersion forces does not modify our results and conclusions.

Selfassociation probabilities of the amphiphile molecules in a binary mixture depend on seven parameters:

(i) the lengths of the hydrocarbonic chains, identified with their number of carbon atoms N_1 and N_2;

(ii) the electric dipole moments of polar head groups $\vec{p}_1$ and $\vec{p}_2$;

(iii) the area per amphiphile occupied by the head group of each of the two components a_1 and a_2;

(iv) the molal fraction of one of the two components x_1 ($x_2 = 1 - x_1$)

We have imagened 36 binary systems in order to study the dependence of association probabilities of the two components on their chains length. These binary systems were arranged in eight series (sets) of mixtures (Table I). The head of series has the hydrocarbon chain with an even number of carbon atoms N_1 over the range 8–22. The second component has the hydrocarbonic chain with an even number of carbon atoms N_2 ranging between N_1 and 24. The first component has the surface area and the electric dipole moment of the polar head group equal to 40 $Å^2$ [4] and 5 D, respectively, and the second component has the are equal to 60 $Å^2$. These three parameters (a_1, a_2 and p_1) were considered fixed and available for all the samples.

The last two parameters (p_2 and x_1) were modified as follows: for each sample the dipole moment of the second component is equal to 5, 10, 15, 20, 25, 30, 35, 40, 45 D and for each value of the dipole moment (p_2), the molal fraction (x_1) of the first component is equal to 0.1; 0.2;...0.9. Therefore an enormous number of data for association probabilities was calculated. This paper will described only as much as necessary in order to see the influence of each of the variable parameters on the association probabilities.

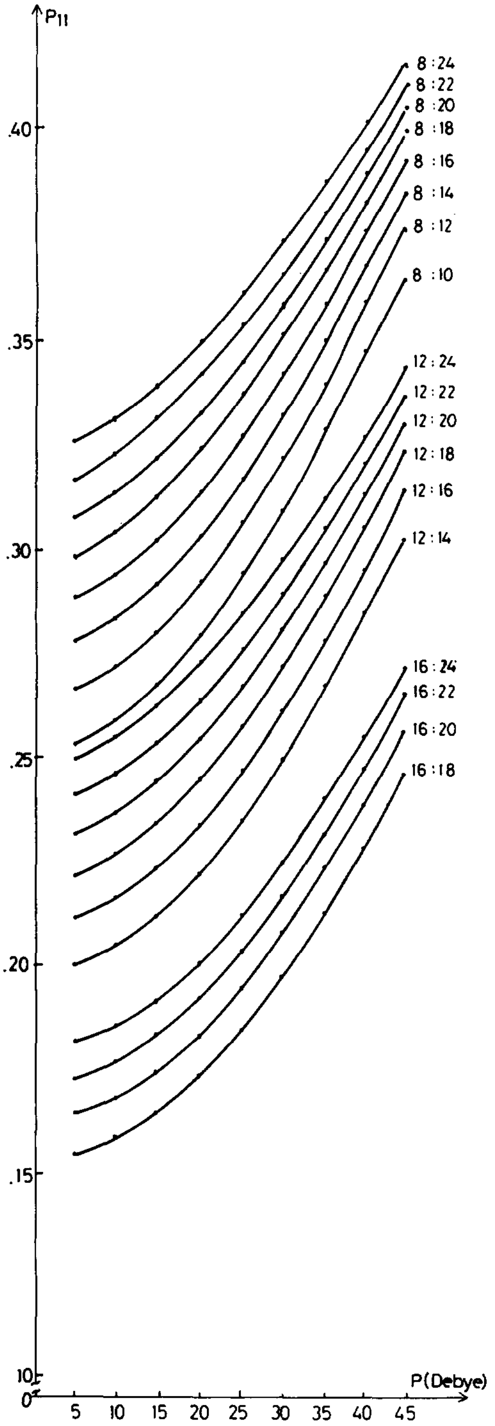
For an easy rendering the following notations will be used for the association probabilities: $P_{11}(a,a/a,b)$, $P_{12}(a,a/a,b)$, $P_{22}(b,b/a,b)$ in which the number and letters have the meaning presented in Table I. The index 1 refers to the component with the shorter chain (also named in the text 'the head of the series' or 'the first

TABLE I

The composition of the single chain lipid mixtures for which the association probabilities in planar bilayers has been calculated

The serie	The first component: *a*	The second component: *b*
I	C_8	C_{10};C_{12};C_{14};C_{16};C_{18};C_{20};C_{22};C_{24} P_{11} (8,8/8,b) P_{22} (b,b/8,b) P_{12}(8,b/8,b)
II	C_{10}	C_{12};C_{14};C_{16};C_{18};C_{20};C_{22};C_{24} P_{11} (10,10/10,b) P_{22} (b,b/10,b) P_{12} (10,b/10,b)
III	C_{12}	C_{14};C_{16};C_{18};C_{20};C_{22};C_{24} P_{11} (12,12/12,b) P_{22} (b,b/12,b) P_{12} (12,b/12,b)
IV	C_{14}	C_{16};C_{18};C_{20};C_{22};C_{24} P_{11} (14,14/14,b) P_{22} (b,b/14,b) P_{12} (14,b/14,b)
V	C_{16}	C_{18};C_{20};C_{22};C_{24} P_{11} (16,16/16,b) P_{22} (b,b/16,b) P_{12} (16,b/16,b)
VI	C_{18}	C_{20};C_{22};C_{24} P_{11} (18,18/18,b) P_{22} (b,b/18,b) P_{12} (18,b/18,b)
VII	C_{20}	C_{22};C_{24} P_{11} (20,20/20,b) P_{22} (b,b/20,b) P_{12} (20,b/20,b)
VIII	C_{22}	C_{24} P_{11} (22,22/22,b) P_{22} (b,b/22,b) P_{12} (22,b/22,b)

component') and the index 2 refers to the component with the longer chain (also named in the text 'the second component'). Thus, P_{11} is the direct association probability of two molecules with the short chain, P_{22} is the direct association probability of two molecules with the long chain and P_{12} is the cross association probabil-



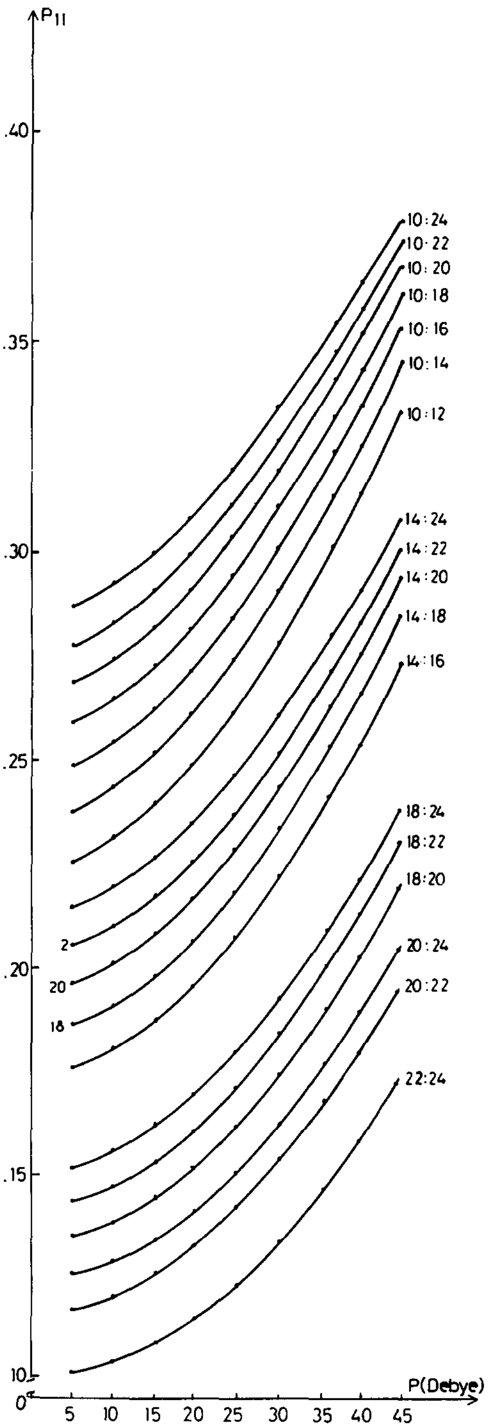
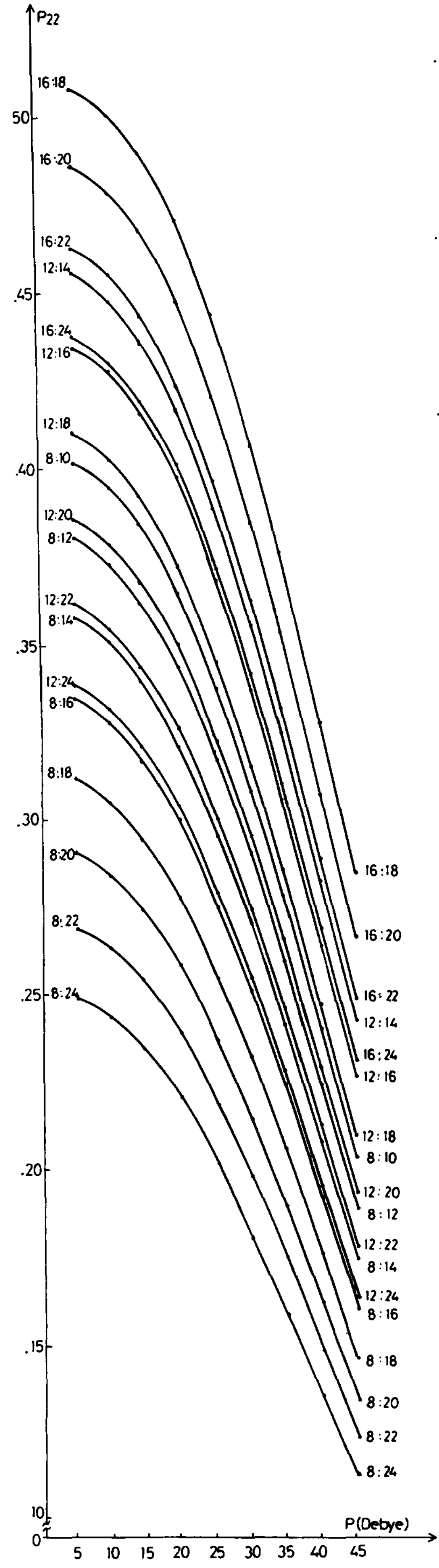
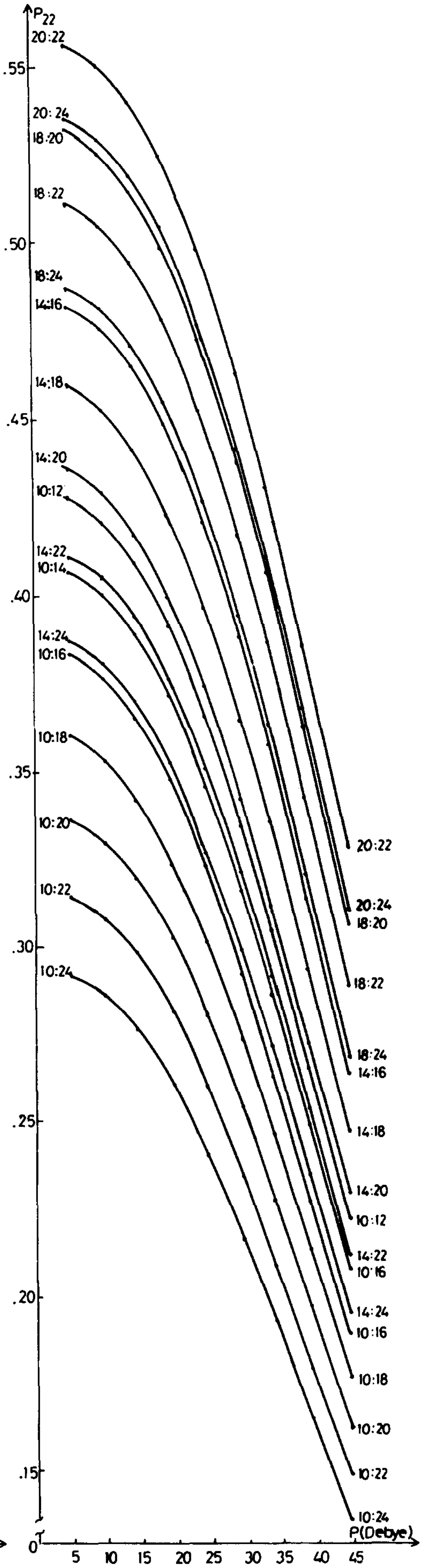


Fig. 1. The variation of selfassociation probability of two short hydrophobic chain molecules, P_{11}, in a binary mixture depending on the electric dipole moment of the second component. The two components do not chemically react and $x_1 = x_2 = 0.5$.

Fig. 2. The variation of selfassociation probability of two long hydrophobic chain molecules, P_{22}, in a binary mixture depending on the electric dipole moment of the second component. $x_1 = x_2 = 0.5$.


P22
16:18
16:20
16:22
12:14
16:24
12:16
12:18
8:10
12:20
8:12
12:22
8:14
12:24
8:16
8:18
8:20
8:22
8:24
50
.45
.40
.35
.30
.25
.20
.15
10
0
5
10
15
20
25
30
35
40
45
P(Debye)
16 : 18
16 : 20
16 : 22
12 : 14
16 : 24
12 : 16
12 : 18
8 : 10
12 : 20
8 : 12
12 : 22
8 : 14
12 : 24
8 : 16
8 : 18
8 : 20
8 : 22
8 : 24


P22
20:22
20:24
18:20
18:22
18:24
14:16
14:18
14:20
10:12
14:22
10:14
14:24
10:16
10:18
10:20
10:22
10:24
.55
.50
.45
.40
.35
.30
.25
.20
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0
5
10
15
20
25
30
35
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P(Debye)
20:22
20:24
18:20
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18:24
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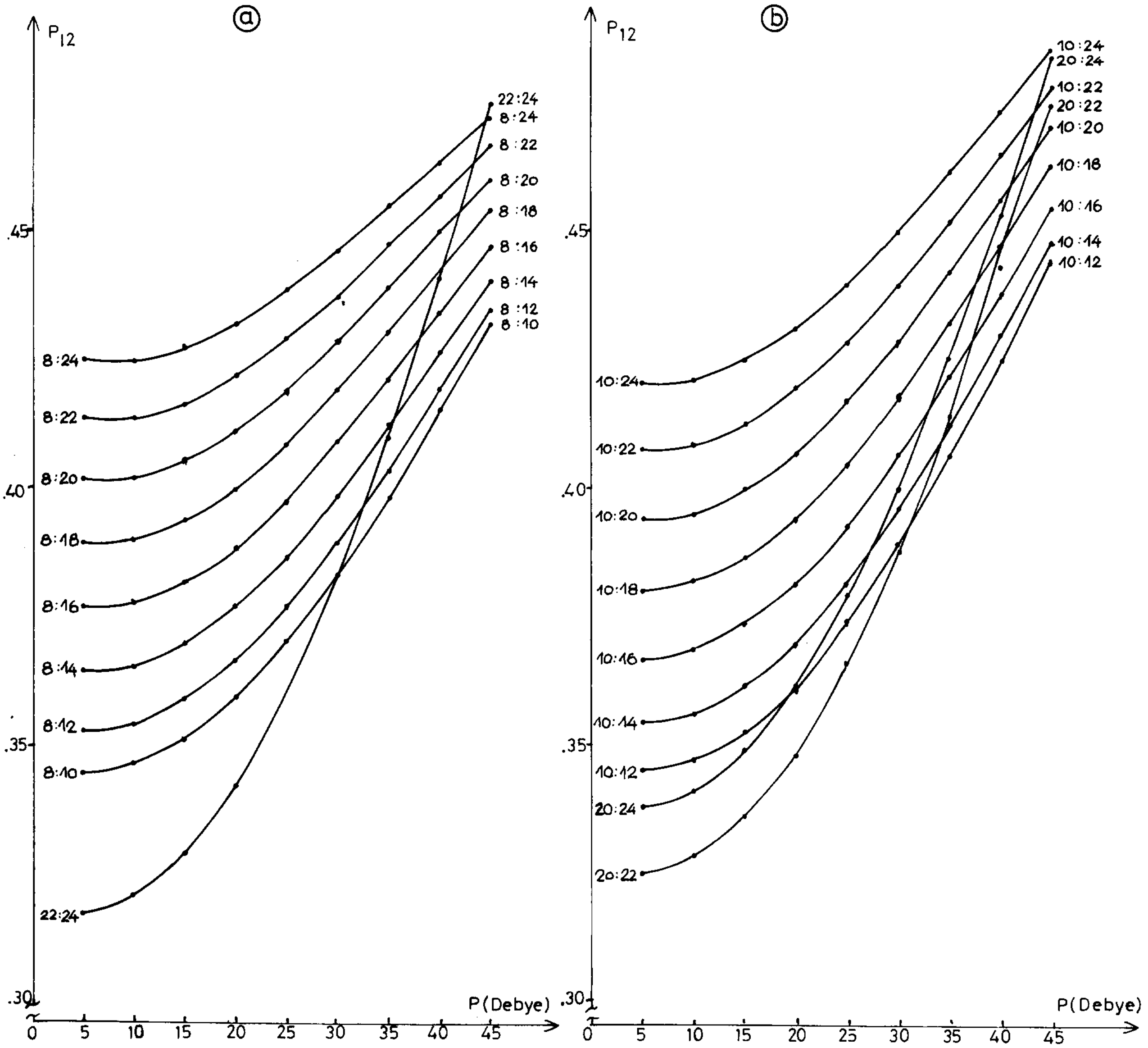


Fig. 3. The variation of cross association probability P_{12} depending on the electric dipole moment of the second component in a binary mixture in which the components do not chemically react. The series in which the first component with constant dipole moment (5 D) has 8 and 22 carbon atoms (a); 10 and 20 carbon atoms (b); 12 and 18 carbon atoms (c); 14 and 16 carbon atoms (d). In the Figs. 1–3 at the ends of each curve the mixture for which it was drawn was marked. The two numbers represent the chains length (the number of carbon atoms) of the two components in the mixture. The first number identifies the head of the series, the second regards the species with a variable dipole moment. Also, $x_1 = x_2 = 0.5$.

ity of two molecules with unequal chains, into a binary mixture. The letters to the left of the line (/) represent the chain length (the number of carbon atoms) of the association molecules and those to the right represent the chain length, N_1 and N_2, of molecules the mixture was made up of.

Results and Discussions

Looking at Figs. 1–3, we can easily see that regardless of the difference between the lengths of the chains of the two components, P_{11} and P_{12} increases and P_{22} decreases as the dipole moment of the long chain molecules increases. In Fig. 1, some groups of curves may be noticed, each group corresponding to a series of binary mixtures, in which the first component is the same. As one can easily see, the curves from each group move towards the top of the picture as the second number increases.

On the other hand the curves corresponding to those binary mixtures (comprised in a vertical row of Fig. 9) in which the second component has a certain chain length, move towards the top of the picture as the first number decreases.

In other words, for each value of the electric dipole moment p_2, the association probability of the shorter

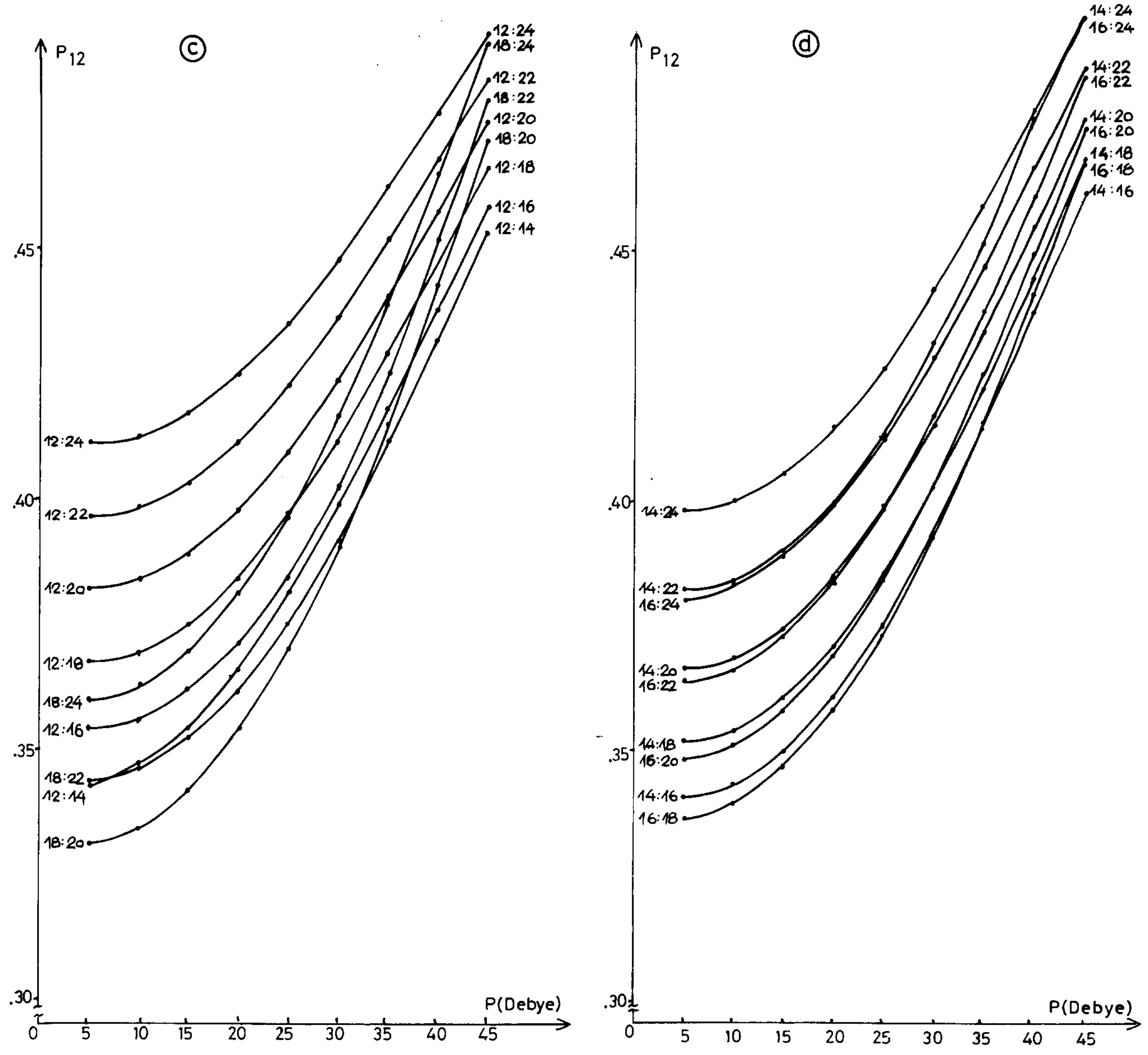


Fig. 3 (continued).

chain molecules P_{11} increases when the chain length, N_2, of the second component increases and N_1 is assumed constant, but decreases when the chain length of the first component, N_1, increases and N_2 is maintained constant (Fig. 1). So, we can write the following table of inequalities for the selfassociation probability P_{11}:

Analysing Fig. 2 in the same manner as Fig. 1, we can say that in binary mixtures the association probability of the longer chain molecules, P_{22}, decreases as the chain length of the second component increases and N_1 is constant. A similar table to P_{11} may be written for P_{22}, but with the reversed sens of inequalities:

$$\begin{array}{ccccc}
P_{11}(8,8/8,10) < & P_{11}(8,8/8,12) < & P_{11}(8,8/8,14) < & \ldots\ldots & < P_{11}(8,8/8,24) \\
 & \vee & \vee & & \vee \\
 & P_{11}(10,10/10,12) < & P_{11}(10,10/10,14) < & \ldots\ldots & < P_{11}(10,10/10,24) \\
 & & \vee & & \vee \\
 & & P_{11}(12,12/12,14) < & \ldots\ldots & < P_{11}(12,12/12,24) \\
 & & & & \vee \\
 & & \ldots\ldots & \ldots\ldots & \ldots\ldots \\
 & & & & \vee \\
 & & & & P_{11}(22,22/22,24)
\end{array}$$

$$\begin{array}{rrrrr}
P_{22}(8,8/8,10) > & P_{22}(8,8/8,12) > & P_{22}(8,8/8,14) > & \ldots\ldots\ldots\ldots > & P_{22}(8,8/8,24) \\
 & \wedge & \wedge & & \wedge \\
 & P_{22}(10,10/10,12) > & P_{22}(10,10/10,14) > & \ldots\ldots\ldots\ldots > & P_{22}(10,10/10,24) \\
 & & \wedge & & \wedge \\
 & & P_{22}(12,12/12,14) > & \ldots\ldots\ldots\ldots > & P_{22}(12,12/12,24) \\
 & & & & \wedge \\
 & & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots \\
 & & & & \wedge \\
 & & & & (P_{22}(22,22/22,24)
\end{array}$$

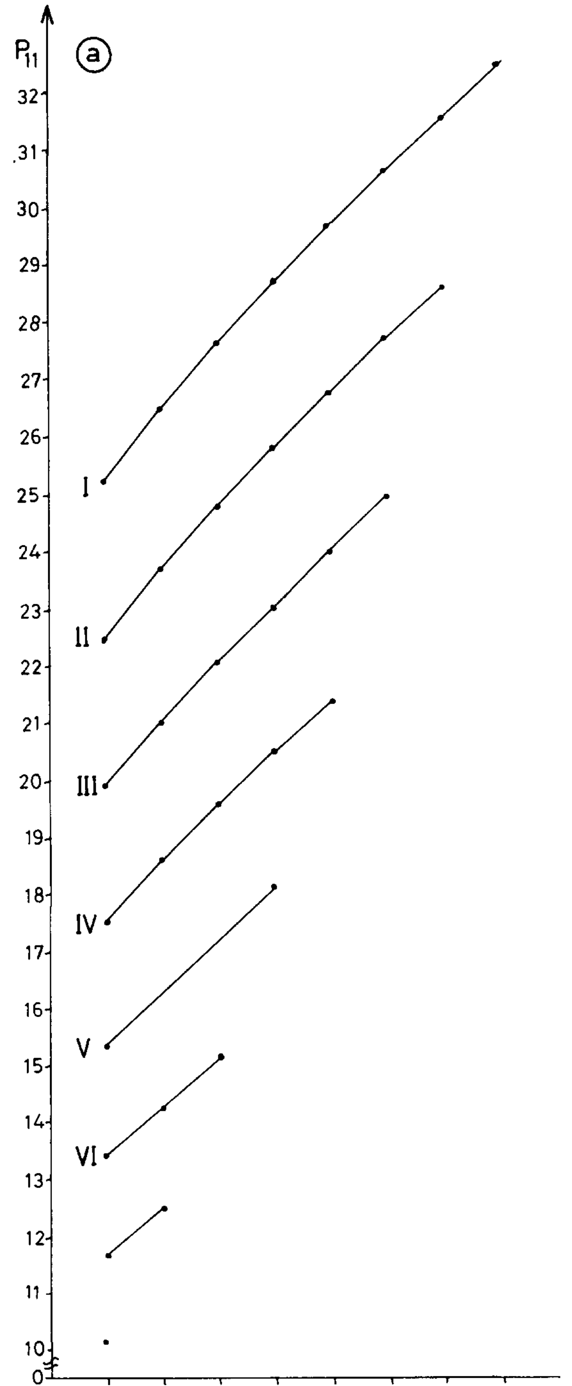
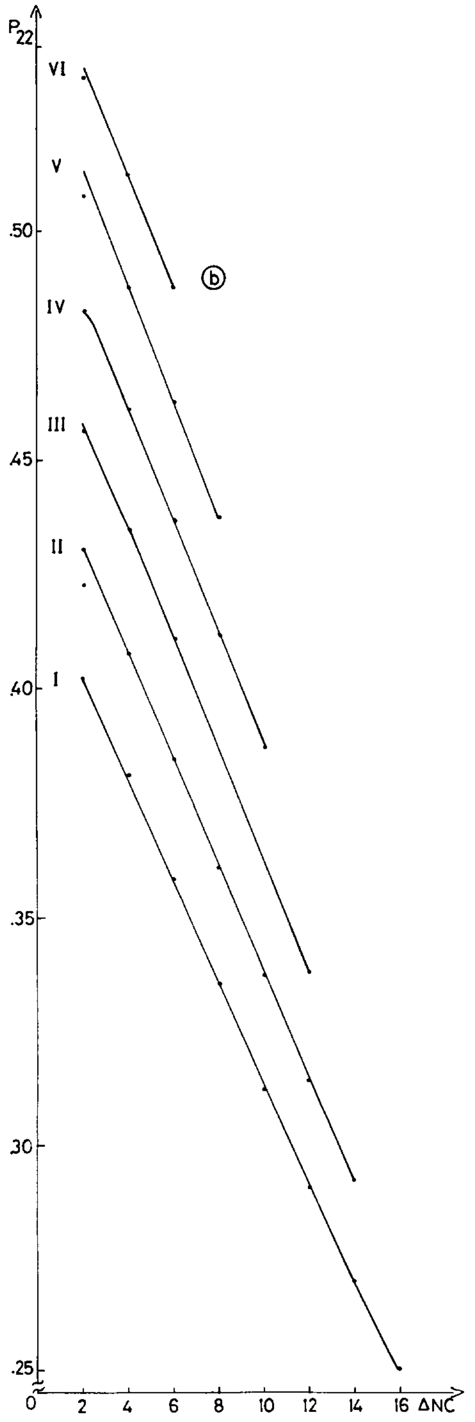


Fig. 4. The association probabilities variation P_{11} (a), P_{22} (b) and P_{12} (c) versus the difference between the lengths of the two mixed molecules species, $\Delta N_C = N_2 - N_1$, corresponding to each series. In (c) the curves for the other series which are situated (in increasig order according to the rank of the series) between the straight lines represented in the diagram. All curves have been drawn for $x_1 = x_2 = 0.5$ and $p_1 = p_2 = 5$ D.



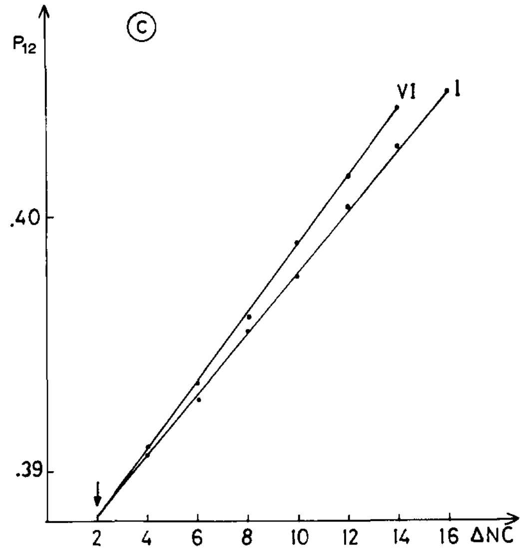


Fig. 4 (continued).

For both tables the sequences of inequalities are available for all values of the dipole moment of the second component of the mixture.

The cross association probability P_{12} between two amphiphiles with different chains increases as the chain length of the second increases (N_1 = constant) and decreases when the chain length of the first component increases (N_2 = constant) for each value of the dipole moment p_2.

All curves are nearly parallel in the Figs. 1 and 2. But, unlike the curves in Figs. 1 and 2, the slope of curves $P_{12} = f(p_2)$ increases as the chain length of the head of series increases and the higher the dipole moment p_2, the higher the slope is. For this reason the curves corresponding to binary mixtures in which the second component is the same, get near one to another, when the dipole moment p_2 increases. A symmetry is noticed to the mixtures in which the head of the series would have a chain with 15 carbon atoms. This is more clear for a high electric dipole moment ($p_2 = 45$ D) when there the following approximate equalities:

$$P_{12}(8,24/8,24) \cong P_{12}(22,24/22,24) \qquad \text{(Fig. 3a)}$$

$$\begin{aligned} &P_{12}(10,10/10,24) \cong P_{12}(20,20/20,24) \\ &P_{12}(10,22/10,22) \cong P_{12}(20,22/20,22) \end{aligned} \qquad \text{(Fig. 3b)}$$

$$\begin{aligned} &P_{12}(12,24/12,24) \cong P_{12}(18,24/18,24) \\ &P_{12}(12,22/12,22) \cong P_{12}(18,22/18,22) \\ &P_{12}(12,20/12,20) \cong P_{12}(18,20/18,20) \end{aligned} \qquad \text{(Fig. 3c)}$$

$$\begin{aligned} &P_{12}(14,24/14,24) \cong P_{12}(16,24/16,24) \\ &P_{12}(14,22/14,22) \cong P_{12}(16,22/16,22) \\ &P_{12}(14,20/14,20) \cong P_{12}(16,20/16,20) \\ &P_{12}(14,18/14,18) \cong P_{12}(16,18/16,18) \end{aligned} \qquad \text{(Fig. 3d)}$$

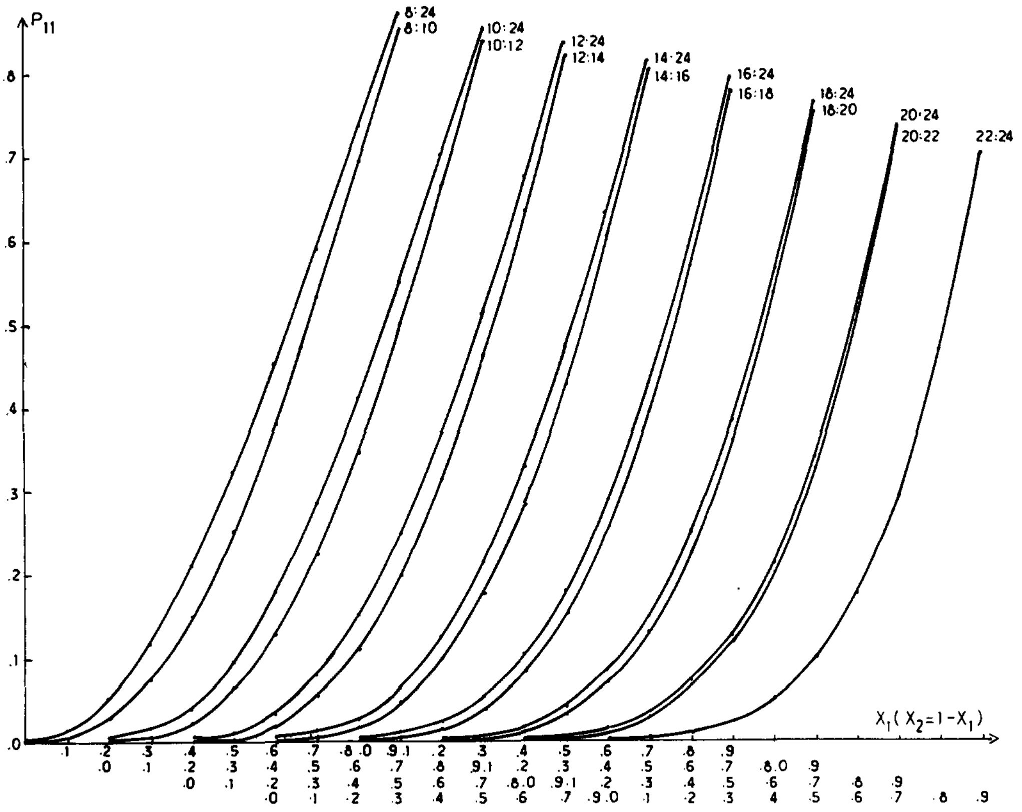


Fig. 5. The association probability variation P_{11} of the shorter chain molecules in a binary mixture organized in a planar bilayer depending on the molal fraction of the first component. $p_1 = p_2 = 5$ D.

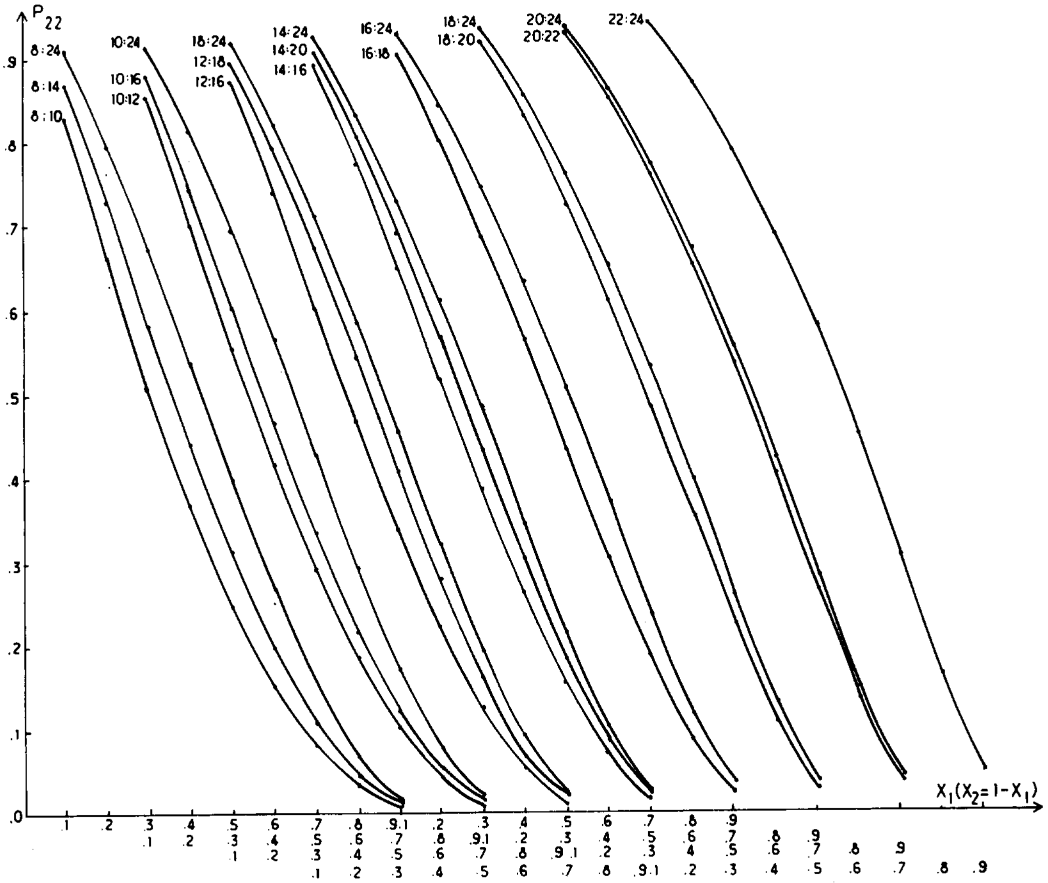


Fig. 6. The association probability variation P_{22} of the longer chain molecules in a binary mixture depending on the molal fraction of the first component. In Figs. 5 and 6 in every group of curves the order from bottom to top corresponds to the increase in the length of the second component. The order from the left to the right of the sets of curves corresponds to the increase in the hydrocarbon chain length of the head of series. The omited curves are placed between the curves which was drawn.

One can write a table of inequalities for P_{12}, but the vertical sequences of inequalities will not be real for all values of the dipole moment p_2. We can sum up the conclusions resultated from Figs. 1–3 in a scheme valid for each value of the dipole moment p_2 (Scheme I).

N_2 = constant and N_1 increases ⇒ P_{11} decreases; P_{12} decreases; P_{22} increases

N_1 = constant and N_2 increases ⇒ P_{11} increases; P_{12} increases; P_{22} decreases

Scheme I

This scheme shows a most interesting aspect: the insertion of a CH_2 group into the shorter chain or into the longer chain has opposite effects on each of the three association probabilities, P_{11}, P_{12} and P_{22}. At the same time if all the curves from Fig. 2 would be drawn on a single rectangular axes then some groupings of probability curves P_{22} from different series would appear. For example, the curves marked with the number pairs 8 : 12, 10 : 16, 12 : 20, 14 : 24 would form a group in this order.

For the binary systems corresponding to these curves grouped together, the association probability P_{22} is approximately the same for each value of the dipole moment p_2. For each group of such curves the short chain of the first component increases with two carbon atoms and the long chain of the second component increases with four carbon atoms. Taking into account that P_{22} increases when N_1 increases and decreases when N_2 increases, we can say that a carbon atom added to the short chain is twice more effective on the association probability P_{22} than a carbon atom added to the long chain.

Making the same reasoning for the association probability P_{11} we find that a carbon atom inserted into the short chain is nearly four times more effective than a carbon atom inserted into the long chain. For example, the following curves 12 : 16 and 14 : 24 will be nearly overlapped.

In each series of mixtures association probabilities P_{11} and P_{12} have a linear increasing variations (Figs. 4a,c) and P_{22} has a linear decreasing variation (Fig. 4b) as the difference between the lengths of the chains of the two components of the mixture, ΔN_C ($\Delta N_c = N_1 - N_2$, N_1 is constant for each series), increases.

The monotony of the straight lines from Figs. 4a,b,c confirms the conclusion from the second row of Scheme I, but at the same time, the shifting of curves in Figs. 4a,b confirms the difference between the efficiency of a carbon atom on P_{11} and P_{22}, when it is added to a shorter or a longer chain. So, adding a carbon atom to the short chain the diminishing of P_{11} is greater than the increasing of P_{11} due to the adding of a carbon atom to the long chain, resulting, a shift of lines towards the bottom of Fig. 4a. Also, adding a carbon atom to the short chain, the increase of P_{22} is higher than the decrease of P_{22} due to the adding of a carbon atom to the long chain, resulting a shift of lines towards the top of Fig. 4b.

If we introduce the notion of the ratio of efficiency, k, as the ratio between the number of carbon atoms added to the short chain and the number of carbon atoms added to the longer chain that modifies the association probability with the same quantity (absolute value) we can sum up that:

$$k = \begin{cases} 1/2 \text{ for the association probability } P_{11} \\ 1/4 \text{ for the association probability } P_{12} \\ 1/4 \text{ for the association probability } P_{22} \end{cases} \qquad (11)$$

The latter value results from the fact that the lines which represent the P_{12} versus ΔN_C do not move, but

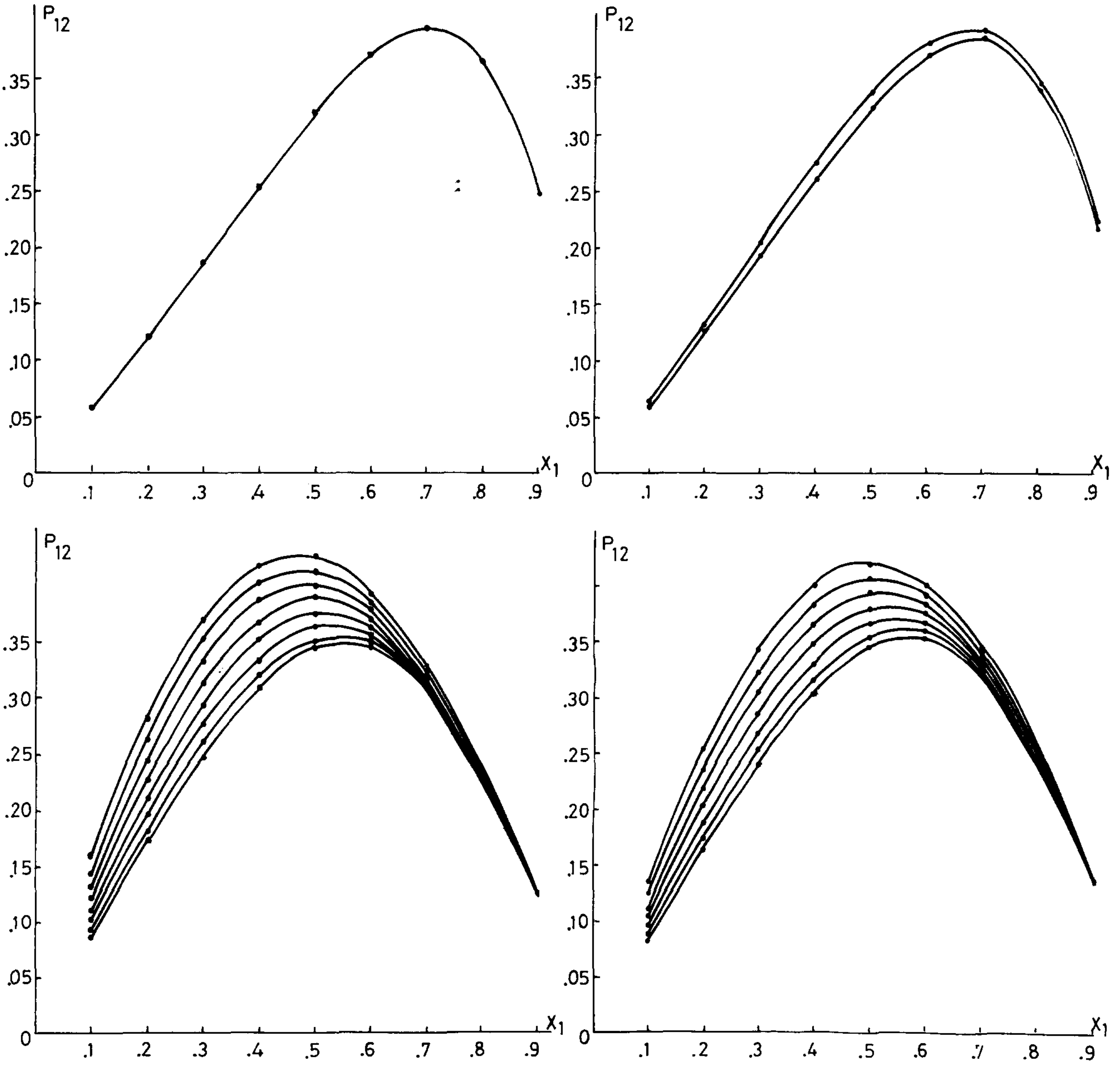


Fig. 7. The cross association probability variation P_{12} depending on the molal fraction of the first component. The series VIII, VII, I, II.

make a slight rotation (Fig. 4c). From this rotation and owing to the straight lines in Figs. 4a,b there are aproximately parallel results that the ratio of efficiency depends slowly on the difference of chain lengths.

Normally, if the shorter chain molecules concentration increases, then the association probability P_{11} increases (Fig. 5), the association probability P_{22} decreases (Fig. 6) and P_{12} has a parabolic variation whose maximum increases and moves towards the small concentrations of the first component when the chain length of the second component increases (Figs. 7 and 8).

It is useful not only to know how the association probabilities P_{11}, P_{12}, P_{22} depend on each of the parameters (N_1, N_2, p_2, x_1) but also their absolute values and their succesion for some combination of values of these parameters. Fig. 9 gives all the binary mixtures that have been studied. The numerator is the shorter chain and the denominator is the longer chain of the molecules in the binary mixture. The solid brooken line devides all the binary mixtures in three classes, each of them being characterised by a certain succesion of the three association probabilities, available when $p_1 = p_2 = 5$ D, and $x_1 = x_2 = 0.5$. Each class contains all binary mixtures for which one of the following succesion of inequalities is valid: $P_{22} < P_{11} < P_{12}$ (class A); $P_{11} < P_{22} < P_{12}$ (class B) and $P_{11} < P_{12} < P_{22}$ (class C).

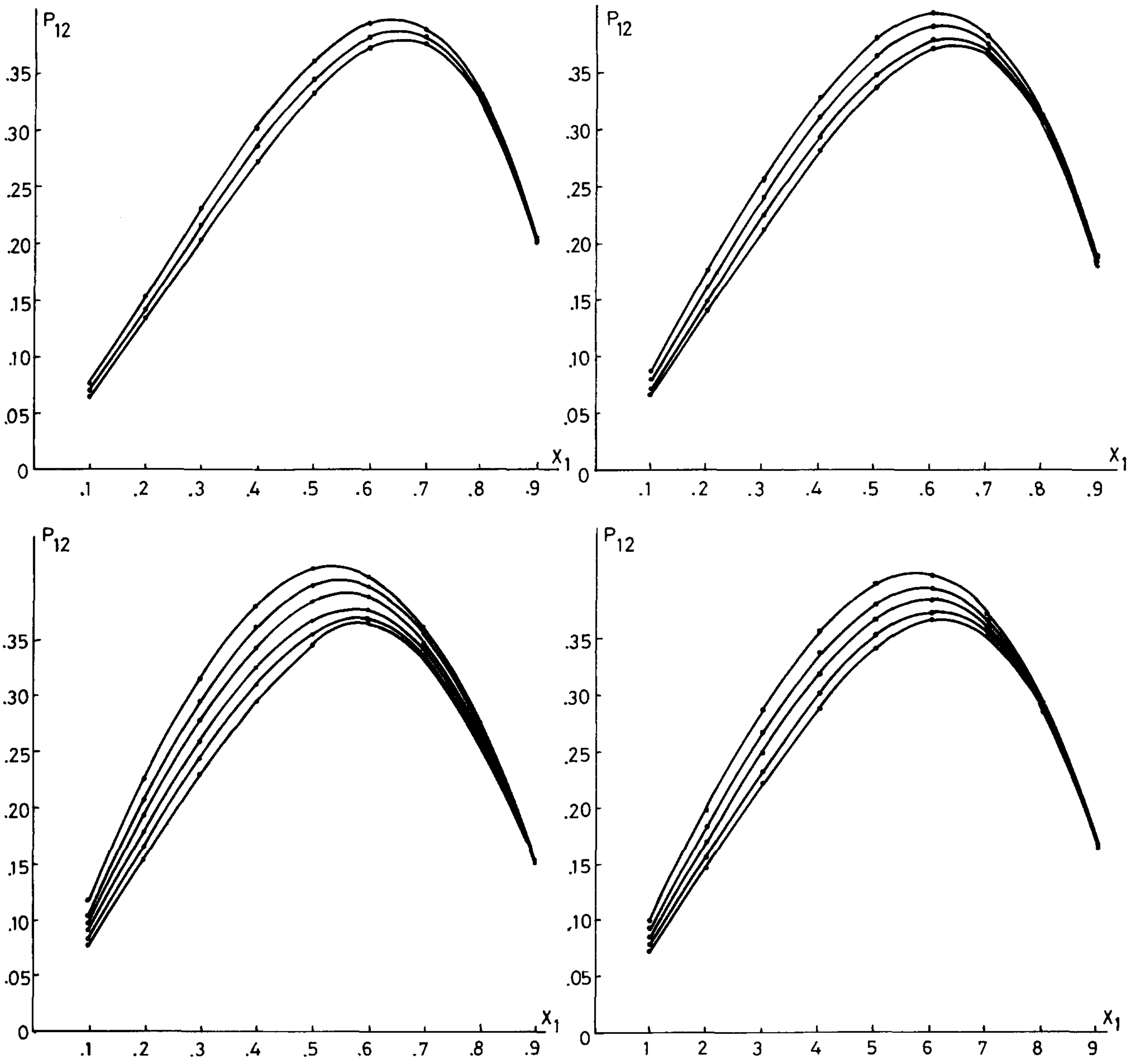


Fig. 8. The cross association probability variation P_{12} depending on the molal fraction of the first component. The series VI, V, III, IV. In Figs. 7 and 8 the reading of the series one make from left to right, beginning at the top of the picture. In each group of curves the order from bottom to top corresponds to the increase in the length of the second component. $x_1 = x_2 = 0.5$ and $p_1 = p_2 = 5$ D.

With the increase of the electric dipole moment p_2 some binary mixtures pass from a class into another. In Fig. 9 the circled number to the left of each fraction represents the value of the dipole moment for which this binary mixture passes from class A into class B, and the circled number to the right of each fraction is the value of the dipole moment for which this binary mixture passes from class B into class C. For example the dashed broken line points the division of all binary mixtures into the three classes when $p_1 = 5$ D and $p_2 = 35$ D. Finally (when $p_1 = 5$ D and $p_2 = 45$ D) there are only two classes, B and C, separated by the line marked with A_2 in Fig. 9. So, the cross association of single chain molecules is favoured for higher electric dipole moment.

It is well known that the hydrophobic chains of natural phospholipids are unequal, having 14–22 carbon atoms [5] and the dipole moment $p \geqslant 35$ D [6]. It is a very interesting coincidence the fact that for the binary systems formed of single chain amphiphile molecules that have the chain length of 14 to 22 carbon atoms, $p_1 = 5$ D, $p_2 \geqslant 35$ D and $x_1 = x_2 = 0.5$, the cross association probability P_{12} is much higher than the other two ($P_{12} > p_{22} > P_{11}$). On the other hand, even both chains of a phospholipid molecule have equal lengths the molecules adopt such a conformation that their chains appear to be unequal. This has been observed in crystalline state of the phospholipid bilayers using X-rays diffraction [7]. Therefore, the selective association of single chain molecules in a binary mixture could explain some problems regarding the aggregation of the lipid molecules into supermolecular structures: either micelles or plane and spherical bilayers.

We think that the stability of such supermolecular structures increases if P_{12} increases, because these aggregates whould have an ordered structure of 'cells' (like crystal) each 'cell' being formed of a cross pair of unequal chain molecules. Accordingly, a bilayer can be more stable because of the possible interdiggit of the hydrophobic unequal chains from the two monolayers of a bilayer. The micelles formed of mixture of single unequal molecules should be more stable, too.

A lot of binary mixtures studied here have the cross association probability P_{12} larger than P_{11} or P_{22}. As the electric dipole moment p_2 increases the number of binary systems for which P_{12} is larger than P_{11} and P_{22} increases and P_{12} increases too.

On the other hand, the selective association between molecules can be the cause of phase separations in binary or ternary mixtures making up separate clusters through microinterfaces [1]. These preferential association give birth to structural nonhomogeneities with different degree of stability and are the first cause of thickness fluctuations of the bilayers. The separation of lipids has been detected in binary lipid mixtures in the gel phase using differential calorimetry with scanning

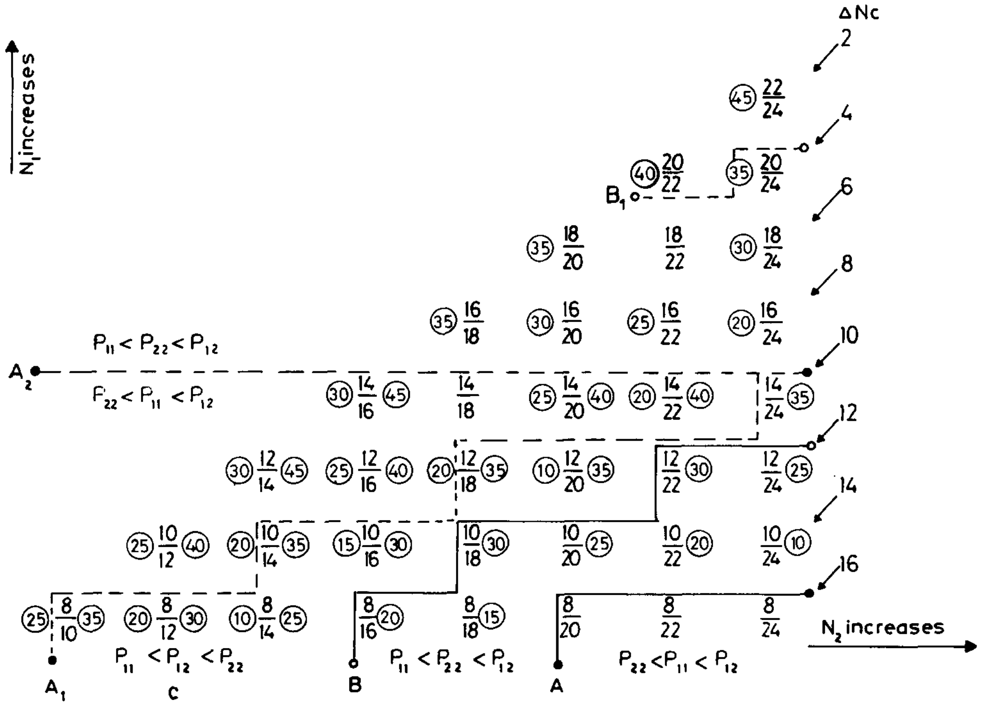


Fig. 9. The diagram of the all binary mixtures studied in this work. Under the diagram there are the inequalities between the association probabilities valid for each class. This diagram is useful to know the composition of each class for different values of the electric dipole moment p_2.

[8]. There are experimental attempts of studying liquid crystals made up of such biological lipid mixtures [9,10].

When one of the association probabilities is much smaller than the other two, these clusters are like little defects in the aggregate structure.

The values of a_1 and a_2 influence both dipole-dipole interactions and disperse forces, but detailed effects on the association probabilities will be given in a future paper.

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