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Selective association processes of single chain amphiphiles in monolayer films

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Abstract

The association processes in binary mixtures of amphiphilic molecules explains the existence of some structural inhomogeneities in supramolecular aggregates of lipid molecules. This paper presents the results of the selective association of a single-chain amphiphile in two series of binary mixtures organized in a flat monolayer. Starting from this study, some observations about the cluster formation and phase separation in binary mixtures can be made. The lyotropic liquid crystal defects may also have their origin in the association processes. The thermotropic behaviour of binary mixtures may be determined by the selective association of the mixture components.

Keywords: Binary mixtures; Association processes; Free end effect; Thermotropic behaviour

1. Introduction

The polar lipids have an interesting property: the hydrophobic and the hydrophilic parts are segregated from one another. Owing to this property, the polar lipids can organize themselves into supramolecular structures when they are dissolved in polar solvents [1]. On the other hand, both natural membranes and lipid supramolecular structures contain more than one phospholipid species, held in relationship to one another by intermolecular forces. Therefore, lipid mixtures seem worth much more attention.

Since lipids, in mixtures, do not chemically react, the lipid supramolecular aggregates may be considered as an athermal solution. The distribution of lipids over the lipid supramolecular structure is not made randomly, but it is determined by selective association of the mixed lipids [2,3]. Experimental results indicate the existence of microclusters separated by microinterfaces in mixtures of synthetic lipids [4]. In addition, collective lipid motions in lipid bilayer membranes has been demonstrated by transverse deuteron spin relaxation [5]. These are only some results in favour of the usefulness of theoretical studies on the self-association processes between single-chain amphiphiles in binary mixtures into a plain monolayer.

2. Association probabilities

Let us consider a planar monolayer obtained from a binary mixture of single chain hydrocarbon amphiphiles (for example, lysophospholipids). The two mixture components are different by their cross sections a_1 and a_2, their dipole moments p_1 and p_2, their chains length N_1 and N_2, and their molar fractions in the mixture ($x_1 + x_2 = 1$). The hydrophobic chain length is given by the number of carbon atoms in the chain.

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In a lipid supramolecular aggregate, two types of interactions between its amphiphiles are considered: (a) dipole–dipole interaction between the polar head groups localized on the aggregate surface, and (b) van der Waals–London dispersion interaction between hydrophobic chains inside the aggregate's hydrophobic core. It is clear that the selectivity of the association of a molecule to another molecule of the same type, or of different type is determined by the difference in the pair-interaction energies, which are determined by the interaction forces between the associating molecules.

The pair-interaction energies between two neighbouring molecules of the same species, U_{11} and U_{22}, or of different species, U_{12}, have unequal values, depending on the cross section, the dipole moment and chain length of both amphiphilic molecules. These determine a selective association between the mixture components, whose result is the formation of some structural inhomogeneities built into the lipid aggregate. The probabilities of formation of the three possible couples P_{11}, P_{12}, and P_{22} are now introduced, which are related by the following relations:

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

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

$$P_{11}+P_{12}+P_{22}=1. \quad (3)$$

Solving this system, we obtain the following relations from which the association probabilities are calculated:

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

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

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

where

$$e_1 = \exp(-(U_{12}-U_{11})/RT),$$

$$e_2 = \exp(-(U_{12}-U_{22})/RT), \quad (7)$$

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

$$U_{12} = -\left(p_1 p_2 N_A/\left(4\pi\epsilon(r_1+r_2)^3\right) + W_{12}\right), \quad (9)$$

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

In eqs. (8)–(10), p_1, r_1 and p_2, r_2 refer to the electric dipole moment components and to the cross-sectional radius of the polar head group of a molecule from the first, or the second type, respectively. W_{11}, W_{12}, W_{22} are the molar energies of interaction through van der Waals–London dispersion forces between the chains of two neighbouring molecules of the same species (W_{11}, W_{22}) or of different species (W_{12}).

For the calculation of the dispersion energy, we consider that in the saturated paraffin chains, the electronic charge distribution is localized in bonds and atoms. The electronic correlation is also negligible between distant points in one molecule and the covalent bonds of each carbon atom have such a spatial arrangement that we can suppose that a CH_2-group is an attractive center. Under these conditions, within the limits of the second-order perturbation theory, it is acceptable to assume that dispersion forces are locally additive. So the attraction force between two hydrophobic chains was obtained by adding all the forces between pairs of attractive centres one in each molecule [6].

The distance between the nearest attractive centres is of about 7.14 Å, equal to the distance between the axes of two neighbouring molecules which have smaller head group (here, the molecules with short hydrophobic chain). This distance is large compared with the sizes of the attraction units (atoms, bonds), such as are the interactions between them, and follow London's inverse-sixth power distance law ($W = -A/d^6$), where A is equal to 5.6×10^3 Å^6 J mol^{-1} [6].

Because the distance between the two most remote carbon atoms (the methylene group near the polar head and the methyl end on the longer chain) is shorter than 1000 Å, the retardation effects are not taken into account [7]. Using the more accurate formula of Langbein [7], instead of Salem's formula [6], in the calculation of van der Waals' dispersion energy an increased numerical value by about 4% was obtained [8]. Since in the calculation of the self-association probabilities the difference between interaction energies appears, we think that the non-additivity of the dispersion forces does not modify the results and conclusions presented in this paper.

3. Results and discussion

A number of 12 binary mixtures of single-chain amphiphiles were selected. For the understanding of the following text some conventions must be defined. So, one of the components of a binary system has a cross-sectional area of 40 Å^2. Throughout the remainder of this paper, it will be mentioned always as the first component of the mixture. It is the component which has the shorter acyl chain of the mixed species and will be identified by the index "1". The second component has a cross-sectional area of 60 Å^2 and its chain is longer and bears the index "2". In order to see the hydrophobic chain effect of on the association process, the binary mixtures considered in this work were divided in two series according to the first component. In other words, the first component is kept the same for all binary mixtures belonging to a series. More exact, the shorter chain component from all binary mixtures of the first group has $N_1 = 8$ carbon atoms, and from the second group it has $N_1 = 16$ carbon atoms. The longer chain component has an even number of carbon atoms, from $N_1 + 2$ to 24.

It is possible to regard all these binary systems as one single system. In this case the chain length of the two components must be regarded as variables.

The association probabilities depend on seven parameters which characterize the mixture components: the hydrophobic chain lengths N_1 and N_2, the dipole moments p_1 and p_2 of their polar head groups, and the cross-sectional areas a_1 and a_2. The molar fraction of one component must be added to these parameters. In this report we considered equimolar binary mixtures ($x_1 = x_2 = 0.5$) and we have studied only the effect of four parameters (N_1, N_2, p_1, p_2) on the association probabilities.

3.1. *The dipole moment effect*

The association probabilities calculated for each series of binary mixtures were drawn on separated plots. The plots denoted by "a" correspond to mixtures in which the shorter chain component has 8 carbon atoms. Those denoted by "b" were drawn for the binary mixtures which have the shorter chain component length equal to 16 carbon atoms. (The hydrophobic chain lengths of the binary components appear on the right of each curve for clarity.) The association probabilities P_{11}, P_{12}, P_{22} were calculated for increasing values of the dipole moment of one component while the dipole moment of the other component was kept constant.

In order to easier see the dipole moment influence on the molecules' association, two values were selected very different from one another for the dipole moment kept constant, namely 5 D and 45 D.

In Figs. 1a and b all three association probabilities are plotted with respect to the dipole moment p_2 at $p_1 = 5$ D. The association probabilities P_{11} and P_{12} increase while the probability P_{22} decreases with the increase of p_2. Apparently, the pair association of longer chain molecules is inhibited by the increase of the own dipole moment p_2 if the short chain component has a small dipole moment. On the other hand, the association probabilities were also calculated for the same binary mixtures taking $p_2 = 5$ D. The increase of the dipole moment p_1 of the short chain component has an opposite effect on the direct association probabilities P_{11} and P_{22}.

In other words, P_{11} decreases and P_{22} increases if the dipole moment p_1 increases (Figs. 2a and b). The above results may be resumed in the following scheme:

$p_1 = 5$ D and p_2 increases
$\Rightarrow P_{11}$ increases;
P_{12} increases; P_{22} decreases.
$p_2 = 5$ D and p_1 increases
$\Rightarrow P_{11}$ decreases;
P_{12} increases; P_{22} increases.

(Scheme I)

We have to remark a common effect of the dipole moments on the direct association probabilities, really existent for all binary mixtures of single-chain amphiphiles, i.e. when the dipole moment of one component takes a low value, then the direct self-association of the other single chain molecules having higher a dipole moment is inhibited, while the association of the molecules with low dipole moment is favoured. This statement results from Scheme I or from comparison of the patterns on Figs. 1a and 2a (or Figs. 1b and 2b):

$$P_{11}(5, p_2 > 5) \geqslant P_{11}(5, 5) \geqslant P_{11}(p_1 > 5, 5).$$

$$P_{22}(5, p_2 > 5) \leqslant P_{22}(5, 5) \leqslant P_{22}(p_1 > 5, 5).$$

What happens if one component has a high dipole moment? The association probabilities for the same binary mixtures have also been calculated when one of the two components has a high dipole moment (p_1, $p_2 = 45$ D).

If the dipole moment of the short chain molecule is high ($p_1 = 45$ D), the association probabilities P_{12} and P_{22} point to some new features. Only the association probability P_{11}

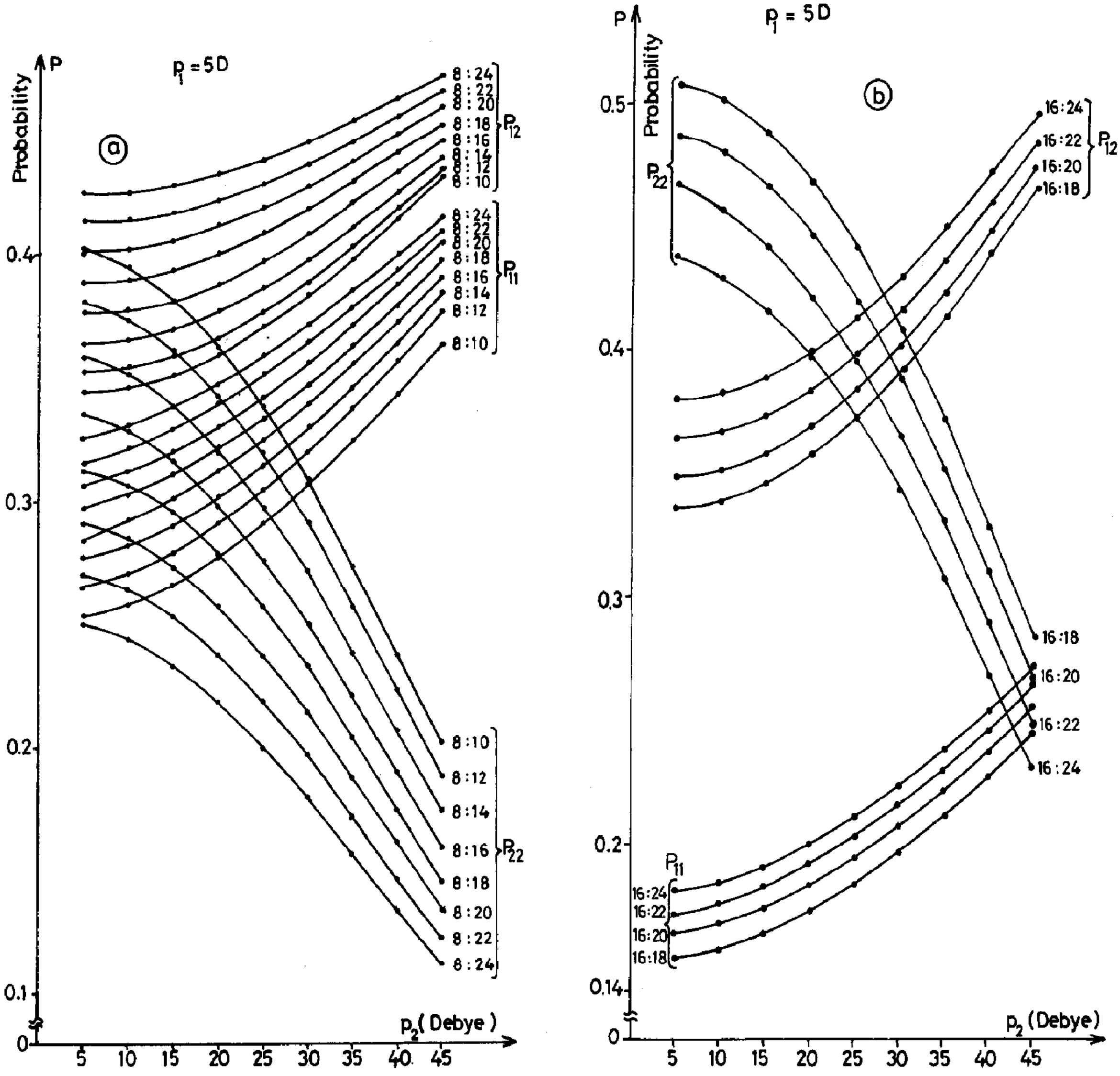

Fig. 1. The association probabilities P_{11}, P_{12}, P_{22} versus the dipole moment, p_2, of the longer chain component from equimolar binary mixture in the case when the dipole moment of the shorter chain component has a fixed value ($p_1 = 5$ D). $N_1 = 8$ (a), and $N_1 = 16$ (b).

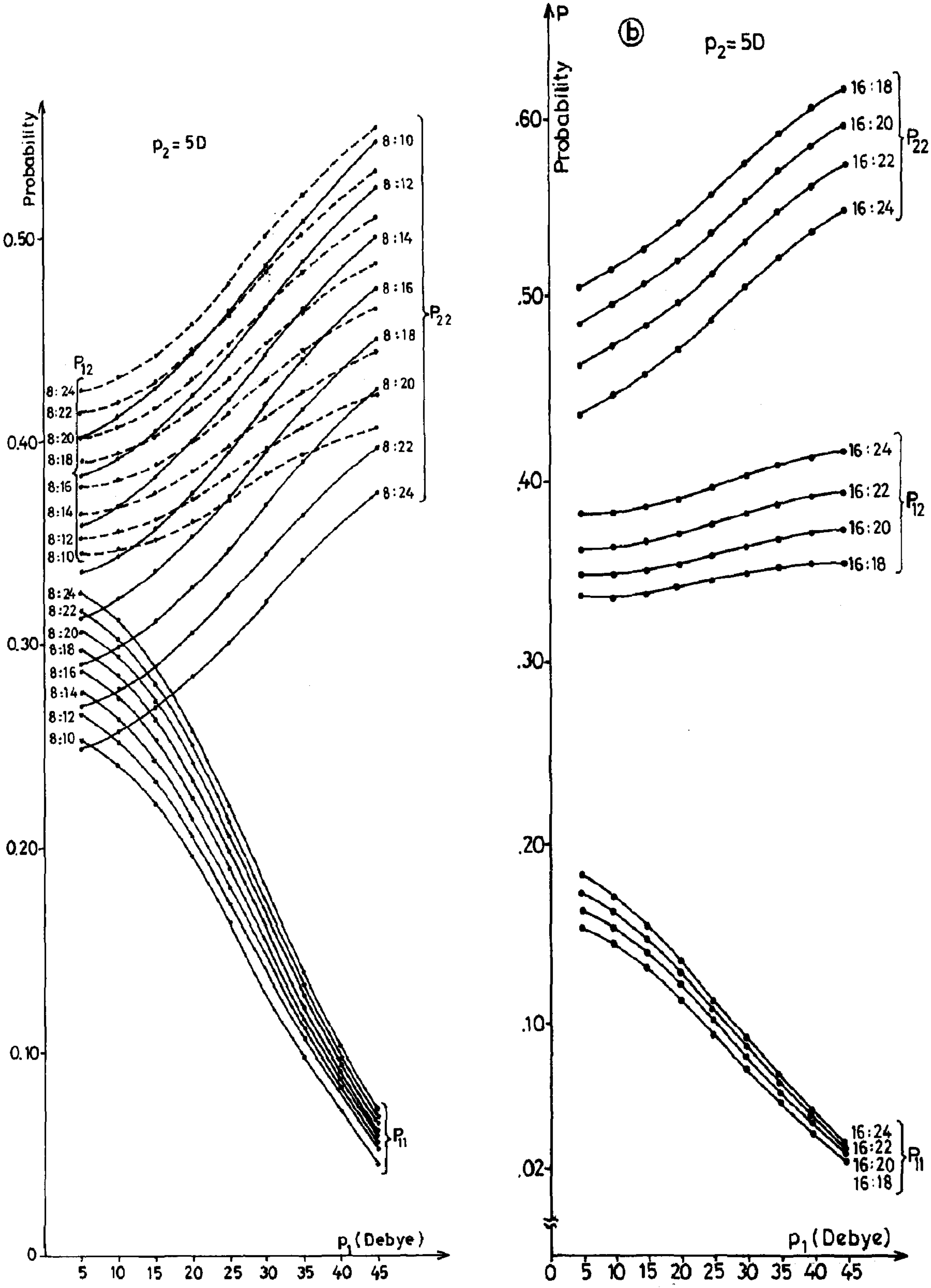

Fig. 2. The association probabilities P_{11}, P_{12}, P_{22} versus the dipole moment, p_1, of the shorter chain component from equimolar binary mixture, in the case when the dipole moment of the longer chain component has a fixed value ($p_2 = 5$ D). $N_1 = 8$ (a), and $N_1 = 16$ (b).

keeps its monotony as a function of p_2 but its values are very diminished. For example, for the binary mixture C8 : C10, the association probability P_{11} covers the range (0.25–0.34) for $p_1 = 5$ D (Fig. 1a) and the range (0.048–0.14) for $p_1 = 45$ D (Fig. 3a). The above statement is also valid for all the other binary mixtures. As concerns the association probability P_{22}, as a function of p_2, presents a maximum if short chain dipole moment p_1 is greater than a certain "critical" value. From our calculations, this critical value is approximatively 20 D.

Let us consider the binary mixture C8 : C10. For this mixture the probability of self-association P_{22} has a maximum value of 0.46 for $p_2 = 10$ D if $p_1 = 25$ D (unpublished result) and a value equal to 0.58 for $p_2 = 25$ D if $p_1 = 45$ D (Fig. 3a). Therefore, the larger the dipole moment p_1, the larger the maximum value of P_{22} and the larger value of p_2 for which its maximum value is obtained. It is interesting that in all binary mixtures studied here, the association probability P_{22} takes its maximum value for the same pair-values of the dipole moments p_1 and p_2. As for example when $p_1 = 45$ D, the P_{22} curves show their maximum values at $p_2 = 25$ D (Figs. 3a,b) for all binary mixtures. It seems that between the dipole moment values (p_1, p_2) for which the P_{22} has a maximum value there is an independent relation of the lengths of the hydrophobic chains of the mixture components.

When looking at the pattern of the curves corresponding to P_{11} and P_{22} from Fig. 1a, Fig. 3a (or Figs. 1b, 3b) in this order, we can see that if the dipole moment p_1 increases from 5 D to 45 D then the P_{11} association probability curves move towards the bottom and the P_{22} ones move towards the top of the picture. It results that:

$$p_1 \text{ increases} \Rightarrow P_{11} \text{ decreases and } P_{22} \text{ increases,}$$

whatever the value of the dipole moment of the long chain component. For the high dipole moment of the shorter chain component, it is possible for the cross association probability to have a minimum value. The minimum of P_{12} depends on all four parameters (p_1, p_2, N_1, N_2) analysed in the report. About the values of N_1, N_2, p_1, p_2 for which the cross association probability P_{12} takes its minimum value, we can make the following two remarks:

(1) For a given binary mixture the higher value of the dipole moment p_1, the higher dipole moment p_2 for which P_{12} has its minimum value. Let us consider the binary system C8 : C10. The cross association probability P_{12} has its minimum for $p_2 = 25$ D if $p_1 = 25$ D (unpublished result) and for $p_2 = 35$ D if $p_1 = 45$ D (Fig. 3a).

(2) The chains' length also influence the existence and the position of the P_{12} minimum, such that the decrease of the longer chain length as well as the increase of the shorter chain length "stimulate" the appearance of the minimum value of the cross association probability. For instance, we can analyse the mixtures C8 : C10, C8 : C24 and C16 : C24 for the case when $p_1 = 45$ D (Figs. 3a,b). The cross association probability P_{12} is a monotonically decreasing function of the dipole moment p_2, for the mixture C8 : C24, (therefore P_{12} has no minimum value). However, it has a minimum at $p_2 = 35$ D in the case of the mixtures C8 : C10 and C16 : C24. In conclusion, the increasing of the hydrophobic chain of first component and of the second component has an opposite effect on the minimum position of P_{12}. The analysis of the association probabilities for a binary mixture in which the longer chain component has large dipole moments, may be made from two points of view: (a) as an increase of p_2 from 5 D to 45 D, and (b) as an interchange of the dipole moments between the mixture components. For the first type of analysis, a comparison of Fig. 2a with Fig. 4a (or Fig. 2b with Fig. 4b) should be made.

Generally, the effect of the dipole moment p_1 on the association probabilities P_{11} and P_{22} observed at low values of p_2 are confirmed (see Scheme I, the first row). If we had drawn the curves from Fig. 4a and Fig. 2a (or Fig. 4b and Fig. 2b) on the same plot, we would observe that the probability curves drawn for $p_2 = 45$ D (Fig. 4a) support a change in position with respect to the corresponding curves drawn for $p_2 = 5$ D (Fig. 2a) as follows:

(1) The association probabilities P_{11} curves are translated to the top of the plot keeping their decreasing slope. This confirms the stimulating

effect of the dipole moment p_1 and the inhibition effect of the dipole moment p_2 on the selfassociation of the short chain molecules. If the longer chain component has a large dipole moment, then there is a value of the dipole moment p_1 for which the association probability P_{11} takes a maximum value. But, in the case of a given binary mixture, the larger the dipole moment p_2 the larger the dipole moment p_1, for which the direct association P_{11} has a maximum value. For example, if the second component of the binary mixture C8:C10 has its dipole moment p_2 equal to 35 D, the probability P_{11} takes a maximum value for $p_1 = 5$ D (unpublished result), but if $p_2 = 45$ D, the association probability P_{11} has the maximum value for $p_1 = 10$ D (Fig. 4a). The chain length of mixture components affects little the appearance of the maximum. So, the increase of the longer chain length moves the maximum position of P_{11} towards higher values of p_1, while the increase of the shorter chain length moves the maximum position of P_{11} towards lower values of p_1. For instance, P_{11} has its maximum value for $p_1 = 10$ D in the case of binary mixtures C8:C10 (Fig. 4a) and C16:C24 (Fig. 4b) for $p_1 = 12.5$ D in the case of binary mixture C8:C24 (Fig. 4a).

(2) The change of p_2 from 5 D to 45 D diminishes the association probability P_{22}, but the effect of p_1 on the increase of P_{22} becomes more efficient. In this way, one explains the fact that for $p_2 = 45$ D and $p_1 = 45$ D (Fig. 4a and 4b) the association probability has approximatively the same value as for $p_2 = 5$ D and $p_1 = 45$ D (Figs. 2a and b), although in the first case the association probability P_{22} starts from lower values for $p_1 = 5$ D and $p_2 = 45$ D (Figs. 4a, b) than in the second case when $p_1 = p_2 = 5$ D (Figs. 2a, b) for each binary mixture. For example, for the binary mixture C8:C10 the association probability P_{22} covers the range (0.40–0.55) if $p_2 = 5$ D (Fig. 2a) and the range (0.20–0.55) if $p_2 = 45$ D (Fig. 4a).

The cross association probability has a particular dependence on the first component's dipole moment, strongly influenced by the dipole moment value of the longer chain molecules. In fact, this special behaviour of P_{12} as a function of p_1 is the result of cooperative effects of the chain length and dipole moment value of the second component. In this effect, from an increasing function at $p_2 = 5$ D (Fig. 2a) it becomes a function with decreasing trend at $p_2 = 45$ D (Fig. 4a), which can have both maximum and minimum (Fig. 4a, the curve C8:C20) or only a minimum value or none at all. The increase of each chain strengthens the decreasing feature of P_{12} as a function of p_1 (Figs. 4a, b).

3.2. *The hydrophobic chain effect*

The curves form groups and appear ordered according to the length of the second component as follows: the curves for association probabilities P_{11} and P_{12} are shifted towards the top and those of P_{22} towards the bottom of every plot in Figs. 1–4, when the second component length increases. This observation is equivalent to the statement that the association probabilities P_{11} and P_{12} increase, while P_{22} decreases with the increase of the hydrophobic chain of the longer chain component, irrespective of the value of the other parameters (N_1, p_1, p_2).

In other words, the increase of the longer chain favours the direct association of the shorter chain molecules and the cross association, but inhibits their own direct self-association.

In Fig. 5, the dependence of the association probabilities on second component length has been depicted for $N_1 = 8$ (long lines) and for those with $N_1 = 16$ (short lines), for the pairs of the extreme values of rank values selected for p_1 and p_2(p_1, p_2): (5, 5), (5, 45), (45, 5), and (45, 45). The graphic representations in Fig. 5 indicate monotony and the linear (or roughly linear) dependence of each association probability P_{11}, P_{12}, P_{22} on the chain length of the second component. This conclusion is also applicable to the other pair values of the dipole moments p_1 and p_2.

Let us compare the pairs of curves drawn for the binary mixtures which have common second component: (C8:C18 and C16:C18), (C8:C20 and C16:C20), (C8:C22 and C16:C22), (C8:C24 and C16:C24) from the plots denoted by "a" and "b" on each of Figs. 1–4. On all plots denoted by letter "b", the clusters of curves for association probabilities P_{11}, P_{12}, P_{22} are more separated between themselves, than in the corresponding

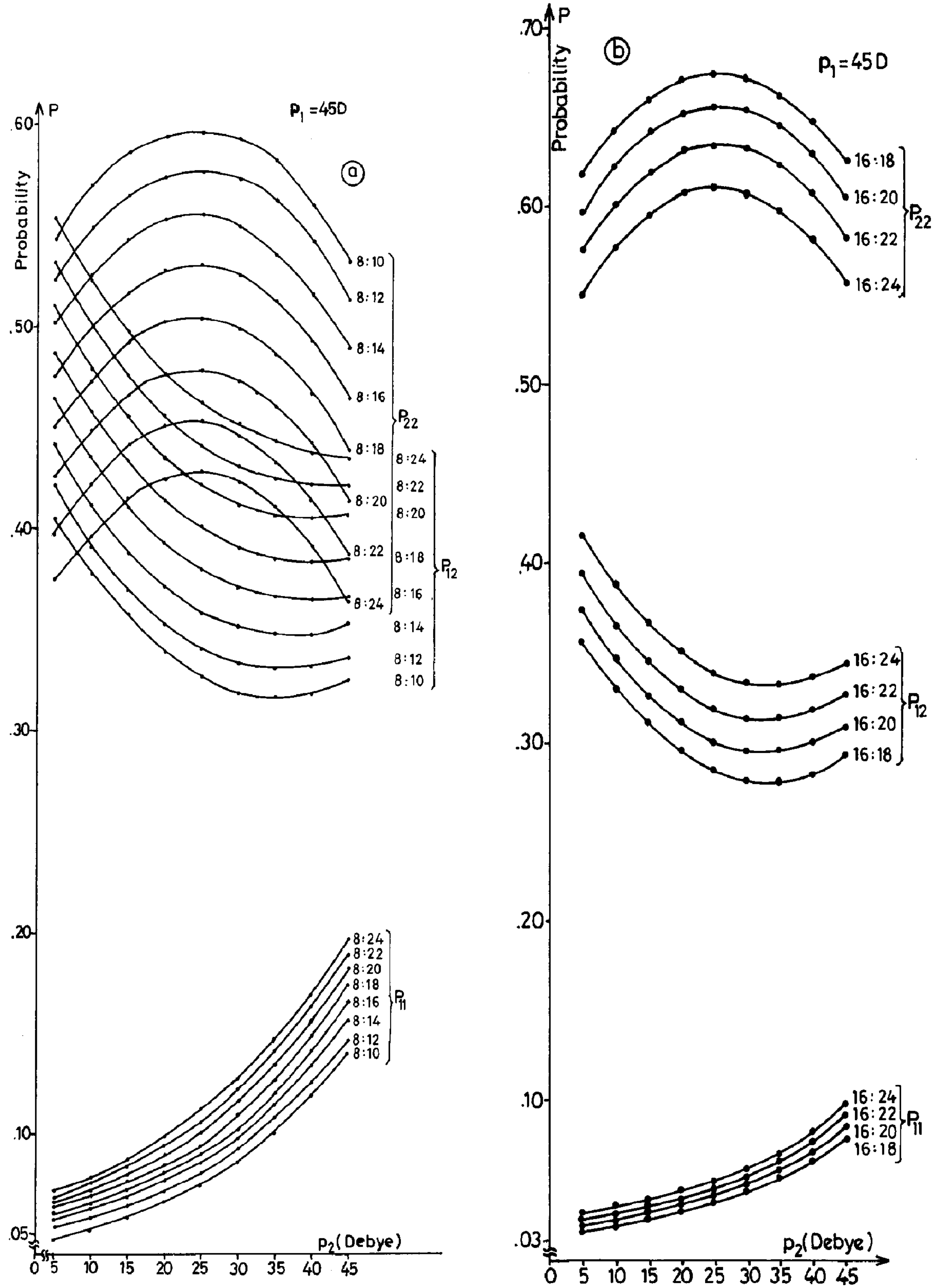

Fig. 3. The association probabilities P_{11}, P_{12}, P_{22} versus the dipole moment, p_2, of the longer chain component from equimolar binary mixture in the case when the dipole moment of the shorter chain component has a fixed value ($p_1 = 45$ D). $N_1 = 8$ (a); $N_1 = 16$ (b).

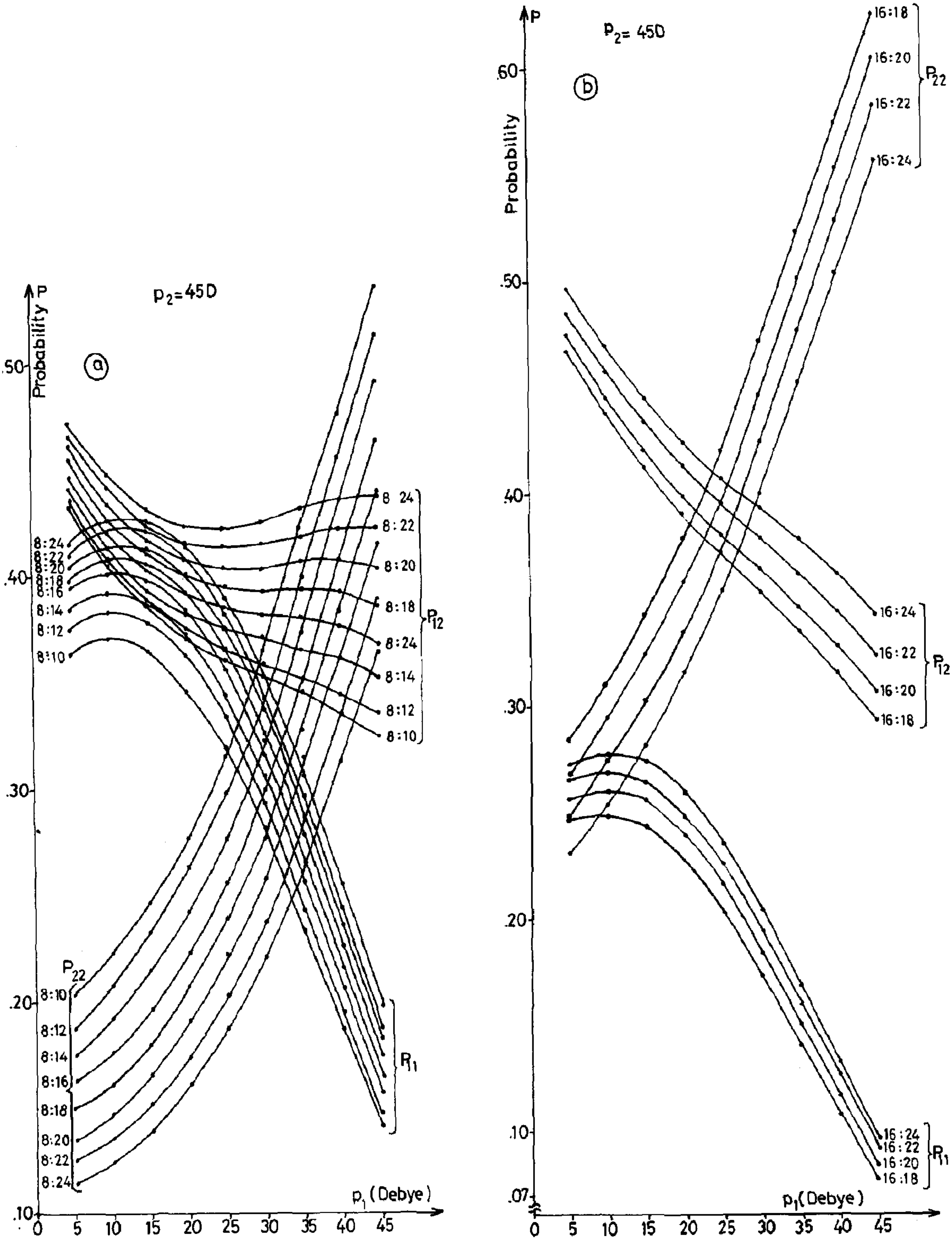

Fig. 4. The association probabilities P_{11}, P_{12}, P_{22} versus the dipole moment, p_1, of the shorter chain component from equimolar binary mixture, in the case when the dipole moment of the shorter chain component has a fixed value ($p_2 = 45$ D). $N_1 = 8$ (a); $N_1 = 16$ (b).

cases for the binary mixtures in which the short chain component has $N_1 = 8$ carbon atoms. The increase of the short chain from $N_1 = 8$ to $N_1 = 16$ carbon atoms results in the shifting of the whole group of curves of the association probability P_{22} towards the top (higher values of P_{22}) and those of association probability P_{11} towards the bottom of the plots (lower values of P_{11}). Therefore, P_{11} decreases and P_{22} increases with the increase of length of the shorter chain.

The effect of the short chain increase on the cross association probability P_{12} is more difficult to appreciate, because of the opposite effect that dipole moment (p) increase has on P_{12}. In order to cancel the dipole moment effect equal values for both dipole moments were adopted. For equal values of dipole moments ($p_1 = p_2$) the following inequalities (Fig. 6) can be written:

$$\begin{aligned}&P_{12}(8, 18) > P_{12}(16, 18),\\&P_{12}(8, 22) > P_{12}(16, 22),\\&P_{12}(8, 20) > P_{12}(16, 20),\\&P_{12}(8, 24) > P_{12}(16, 24).\end{aligned} \qquad (11)$$

For $p_1 = p_2 = 5$ D, these inequalities can be also deduced from our plots, when observing that the left end of each curve drawn for the cross association probability P_{12} on Fig. 1b (or Fig. 2b) is shifted downwards in comparison with the left end of the homologous curve from Fig. 1a (or Fig. 2a). Similarly, we may compare the right ends of the P_{12} homologous curves from Figs. 4a and 4b

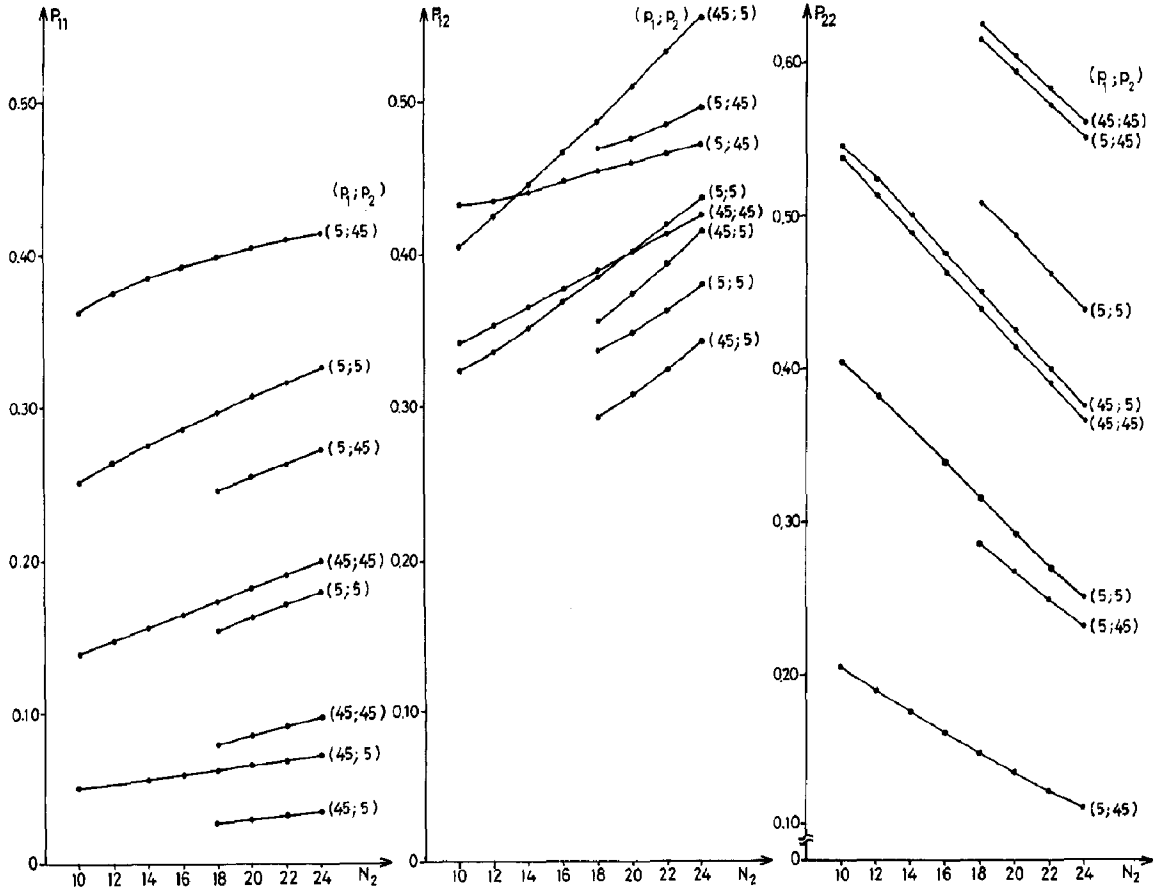

Fig. 5. The dependence of the association probabilities on the hydrophobic chain length of the longer chain component from the binary mixture in which the first component hydrophobic chain has $N_1 = 8$ (long lines) and $N_1 = 16$ (short lines).

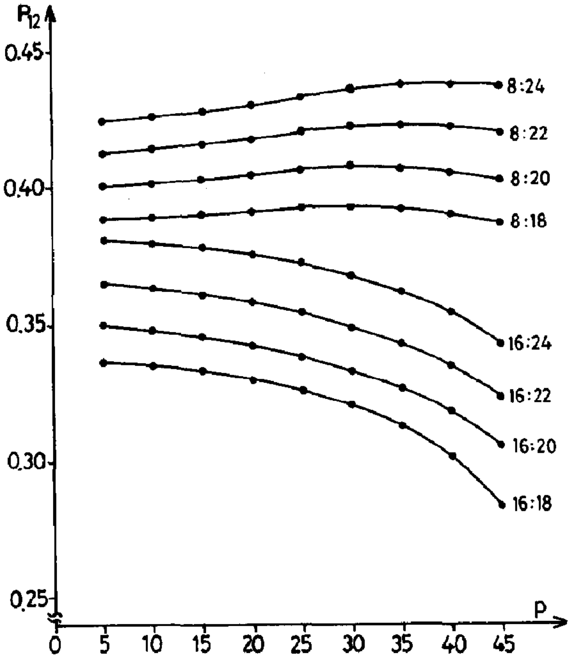

Fig. 6. The cross association probability P_{12} versus the equal dipole moments, in order to see the shorter chain effect.

(or Fig. 3a with Fig. 3b) in the case $p_1 = p_2 = 45$ D. From these observations one can conclude that the increase of the short chain determines the decrease of cross association probability P_{12}.

3.3. *The hydrophobic chain free end effect*

The slopes of the straight lines in Fig. 5 represent the change produced on each association probability when adding a methylene group to the acyl chain of the second component. (The dipole moment values are written in Fig. 5 at the end of each line.) This will be called the hydrophobic chain free end effect. In order to understand our results, the following correspondence between the Figs. 1-4 and Fig. 5 should be clear: the lines marked with (5, 5) and (5, 45) correspond to Fig. 1, those with (5, 5) and (45, 5) to Fig. 2, those with (45, 5) and (45, 45) to Fig. 3 and those with (5, 45) and (45, 45) to Fig. 4.

After an attentive analysis of Fig. 5, especially with regard to the curves' linearity and parallelism, one can reach at some interesting conclusions concerning the longer chain free end effect on the association probabilities:

(1) This effect is different for each association probability and does not depend on the initial length of longer chain component;

(2) In some cases (especially when the first component has its chain greater than 14 carbon atoms) there is a weak dependence;

(3) Neither the chain length of the first component, nor the increase of one or both dipole moments from 5 D to 45 D modify the longer chain free end effect on the direct association probabilities (P_{11}, P_{22}). This is so because all curves corresponding to each of the direct association probabilities (both long or short lines) are parallel. There is an exception when p_2 increases from 5 D to 45 D. In this case, the free end effect is visibly modified for P_{11} (if $p_1 = 45$ D) and for P_{22} (if $p_1 = 5$ D). The free end effect regarding the cross association P_{12} is most sensible of the dipole moment change of each component as well as shorter chain length. This is the reason for which the left ends of curves for P_{12} are close and the right ends are spread (Figs. 2a and 4a). The slopes (fitted by a straight line) from Fig. 5 have been collected in the Table 1. From both Table 1 and Fig. 5 the influences on the longer chain free end effect as one dipole moment increases from 5

Table 1

The hydrophobic chain free end effect (the slopes of the right lines from Fig. 5) on the association probabilities of single chain amphiphiles in binary mixtures. The hydrophobic chain of the first component has 8 respectively 16 carbon atoms (at p_2 in 5 D or 45 D)

N_{11}	8		16	
	5 D	45 D	5 D	45 D
P_{11}				
5	1.0230	0.8596	0.9057	0.8612
45	0.3018	0.8173	0.1995	0.5799
P_{12}				
5	1.1779	0.6072	1.4649	0.9648
45	2.1588	1.6573	2.0261	1.6800
P_{22}				
5	−2.2017	−1.3178	−2.3706	−1.8260
45	−2.4755	−2.4746	−2.2335	−2.2600

D to 45 D (under the condition that the other dipole moment remains unmodified at 5 D or 45 D), as well as of the increase of shorter chain, may be seen.

Even though we did not give any result here, we certainly affirm that the initial length of the shorter chain influences the free end effect.

4. Concluding remarks

From the relations (1)–(3) it results that the association probabilities are symmetrical at the interchange of the dipole moments p_1 and p_2. In other words, the P_{11} and P_{22} in the case when p_1 is fixed correspond to P_{22} and P_{11}, respectively, when p_2 is fixed, both p_1 and p_2 having the same values. If we interchange the dipole moments of the two mixture components, the properties of the symmetrical probabilities are conserved, but there are some differences which are determined by the difference between the two components (chain lengths, head group sizes).

On the other hand, it was demonstrated that a mixture of lysophosphatidylcholine and fatty acid forms bilayers in an aqueous phase [9]. Therefore, starting from this experimental result, it is well possible for the mixed single chain amphiphiles to form bilayers when dispersed in aqueous phase.

Generally, the association probability, P_{11}, of the short chain component is smaller than both the other association probabilities, P_{12} and P_{22}, even in the case of equimolar mixtures. So, the short chain molecules most likely exist associated with the longer ones as well as single molecules dispersed among the other couples. In this way, the short chain molecules give birth to the thickness fluctuations or defects which can be the cause of the appearance of statistical pores in a bilayer type of organization [10–12]. In addition, this selective association process of amphiphiles molecules explains the formation of cluster in supramolecular structures [4].

Owing to the fact that, generally, the association probabilities P_{12} and P_{22} are much higher than P_{11} and the unpaired short chain molecules diffuse easier among the formed couples, it is possible that these separate themselves and a phase segregation to appear. The selective association process may be correlated with the thermotropic phase transition behaviour of single chain binary mixtures. Unfortunately, there is a lack of experimental data regarding the properties of binary mixtures of single chain lipids and for those for which they exist, the dipole moment of the mixed components were not specified. In fact, the effective electrical charges and the distance between them are dependent on external aqueous medium. Therefore, the dipole moment value of polar head group is difficult to determine, but surely it appears between those selected in this report. As an argument, the phosphatidylcholine dipole moment was found to be greater than 35 D [13].

The author beliefs that the differential scanning calorimetry (DSC) scans of a single chain binary mixture should contain four endothermic peaks (one of them due to the dipole–dipole interaction) their position being dependent on the nature of the mixture components. Each of the other three peaks is necessary to correspond to one of the three possible association ways of mixed single chain lipids. The increase of chain length of one component from a binary mixture involves the shifting of two peaks towards higher temperatures. These peaks correspond to the association complexes which contain the modifying component. The association probabilities must be proportional to the surface of the corresponding peaks. The DSC scans of equimolar binary mixtures of palmitoyl lysophosphatidylcholine (LPC) with two fatty acids (palmitic (PA) and stearic acid (SA)) [9] may be interpreted using the association processes. The first binary mixture (LPC + PA) displays two narrow peaks. The former at 315.3 K and the later (which is the greater of the two) at 320 K. The thermotropic behaviour of the second binary mixture point us also a twin peak. The first peak appears also at 315.3 K, while the second is moved to higher temperature (about 324 K) and is formed from two overlapping peaks. For some binary mixtures not all the peaks can be separated (for example, LPC : PA), depending on the resolution power of the differential scanning calorimeter.

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