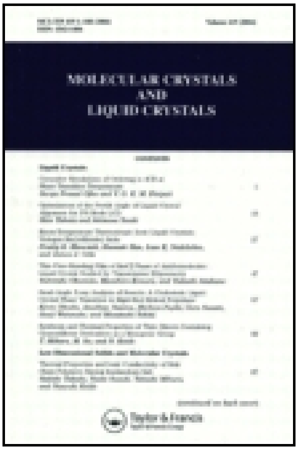

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Comparison of Bulk and Monolayer Behaviour of Selected Methyl-Branched Lecithins

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COMPARISON OF BULK AND MONOLAYER BEHAVIOUR OF SELECTED METHYL-BRANCHED LECITHINS

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Abstract The bulk properties of isomeric 1-(x-methylpalmitoyl)-2-hexadecyl-PCs with methyl groups at various locations x are reported. DSC measurements show that the main-transition parameters strongly depend on the position of the methyl branching. X-ray and electron spin resonance studies suggest that in the lamellar gel phase of the PCs investigated the hydrocarbon chains are interdigitated. The F/A-isotherms of three selected homologues methyl-branched in 3-position of the fatty acid residue were measured over a wide range of temperature. The critical temperatures of the monolayer were estimated and compared with the T_m-values. The disagreement between T_c and T_m is discussed in terms of interdigitation of chains in the gel phase.

INTRODUCTION

The self-organization of phospholipids as double-chain amphiphiles in water leads to the formation of mono- and multilayers, which can be considered as simple model systems for biological membranes [1]. More recently, phospholipids were especially used to understand the phase transitions in monolayers [2].

The investigations of the influence of the head group structure and the chain length of unbranched phospholipids on the phase behaviour have shown that

T_m (main-transition temperature of the bulk phase) and T_c (critical temperature of the monolayer) agree [3]. Previous studies on monobranched phosphatidylcholines (PCs) have revealed that the length of the side chain in 2-position has a remarkable influence on the phase behaviour [4]. The results show that T_m and T_c only agree if the chains of the PCs investigated in the bilayer are in opposite arrangement. However, if a gel phase with interdigitated chains exists, the T_c-values are much lower than the T_m-values. The question arises whether this is also valid for methyl-monobranched PCs with different locations of the methyl side group. Therefore, we have investigated the bulk properties of homologous 1-(x-methylpalmitoyl)-2-hexadecyl-PCs. For three selected homologues with the methyl group in 3-position of different fatty-acid residues the bulk and monolayer behaviour were investigated and compared.

EXPERIMENTAL

The calorimetric studies were done by means of a DSC-2 (Perkin-Elmer, Conn., U.S.A.). X-ray diffraction measurements were carried out with a powder diffractometer HZG 4 (VEB Präzisionsmechanik Freiberg, G.D.R.) using a transmission technique [5]. The ESR spectra were recorded with a JEOL (Japan) JES-PE 1X spectrometer using 100 kHz modulation [4]. The F/A-isotherms were taken on a home made Langmuir balance (Wilhelmy-type) equipped with continuous measuring system. For detailed description see reference 6. The synthesis of the PCs with one methyl branched fatty acid in 1-position and an unchanged hexadecyl residue in 2-position will be published elsewhere. The abbreviation 1-(xC_m-n:0)-2-H-PC (x = position of branches in the main chain, n = total length of the fatty acid, m = number of C-atoms of the branches) is used.

RESULTS and DISCUSSION

The main-transition temperatures and enthalpies of 1-(xC_1-16:0)-2-H-PC/water dispersions show a strong dependence on the position x of the methyl side-chain (Figure 1). The heat of transition decrease linearly while the transition temperatures show a weak alternation. Obviously, the introduction and the stepwise shifting of the methyl side-chain into the hydrophobic region cause an increasing fluidization of the bilayer. The same tendency has been observed for the homologous di(xC_1-16:0)PCs [5].

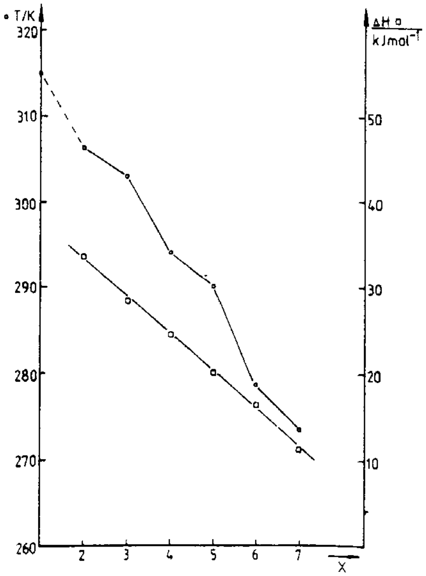

FIGURE 1 Main-transition temperatures (○) and enthalpies (□) of 1-(xC_1-16:0)-2-H-PC/ 50 % (w/w) water dispersions as a function of the position x of the methyl branching.

The bulk phase and monolayer properties of the homologues with x = 3 and a chain length of n = 14, 16 and 18 C-atoms have been investigated in more details. The comparison of the T_m-values with those of the corresponding unbranched PCs shows that the fluidization effect of the methyl side group decreases with increasing length of the main chain (see Table I). As an example let us discuss the structure behaviour of the 1-($3C_1$-16:0)-2-H-PC. The analysis of the X-ray diffraction patterns reveals that in the temperature range from 253 K to 323 K the phases have a lamellar structure. The repeat distance of the gel phase increases slightly with increasing temperature. The half-width of the short spacings increases with decreasing temperature indicating a tendency to a tilted arrangement of the chains in the gel phase. The d_L-value of about 5.5 nm, just below the main transition, is much lower than the d_L-values of gel phases with opposite arranged chains. An order parameter can be measured rather easily from the ESR spectra of nonoriented lipid dispersions using the extreme hyperfine splittings. The investigations indicate that the order parameter of a fatty acid spin labeled near the terminal methyl has been dramatically increased. The large increase is maintained up to the main-transition temperature, where the highly oriented anisotropic motion is transformed into an isotropic type of motion [4]. Therefore, a gel phase with interdigitated chains is assumed. Above the main transition a liquid-crystalline phase $L\alpha$ with a d_L-value of about 6.93 nm could be observed.

The spread monolayers of the three homologues were studied in the temperature range between 2 °C and 40 °C. As an example, the F/A-isotherms of 1-($3C_1$-

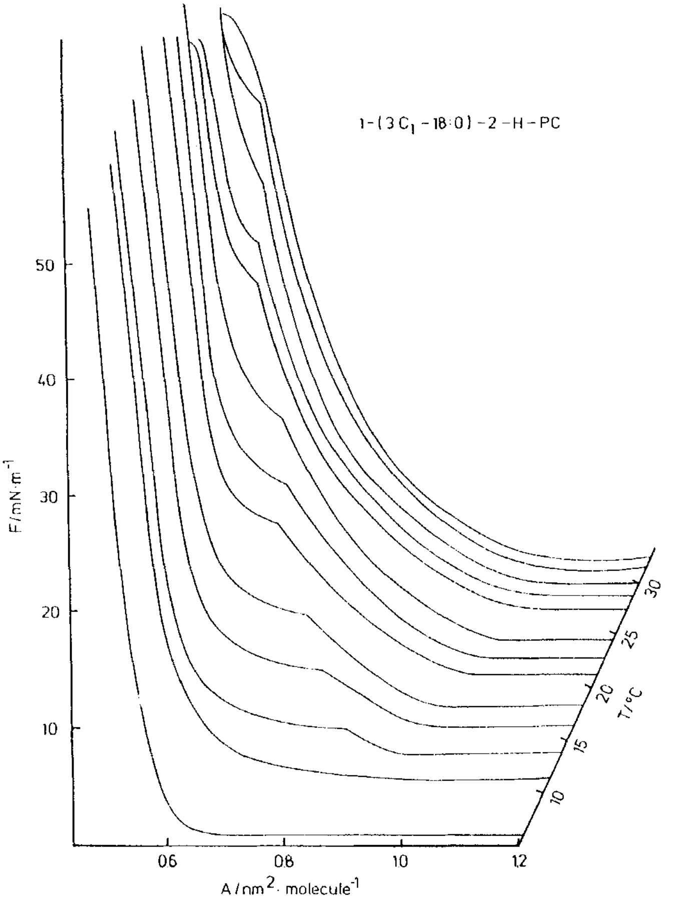

FIGURE 2 F/A-isotherms of 1-($3C_1$-18:0)-2-H-PC monolayers as a function of temperature. The temperatures, from the lowest to the highest curve, are: 6.0, 11.2, 13.7, 16.3, 18.4, 21.3, 22.7, 24.6, 27.3, 28.8, 30.0, 31.0 and 32.4 °C.

18:0)-2-H-PC measured at various temperatures are shown in Figure 2.

The isotherms below T = 11 °C show only the condensed state with a molecular area $A^{K'}$ (area where the film ruptures [1]) of 0.47 nm^2. A fully expanded state exists only at T = 32.4 °C. The lift-off area A_0, where the first observable film pressure occurs, is 1.0 nm^2.

Between 11.0 °C (= T_o, see reference 4) and the critical temperature T_c = 32 °C (see below) the two monolayer phases coexist. The $A^{K'}$- and the A_o-values are rather independent of temperature and lie in the range of 0.47–0.50 nm^2 and 0.97–1.0 nm^2, respectively. The plots of the transition pressure F_1 as a function of temperature are given in Figure 3. In accordance with published data of di-iso- and di-anteiso-methyl-branched PCs [7,8] the F_1-T-curve is nonlinear at lower temperatures. Above transition pressures of 22 mN·m^{-1} the plots become linear. In this region the slope

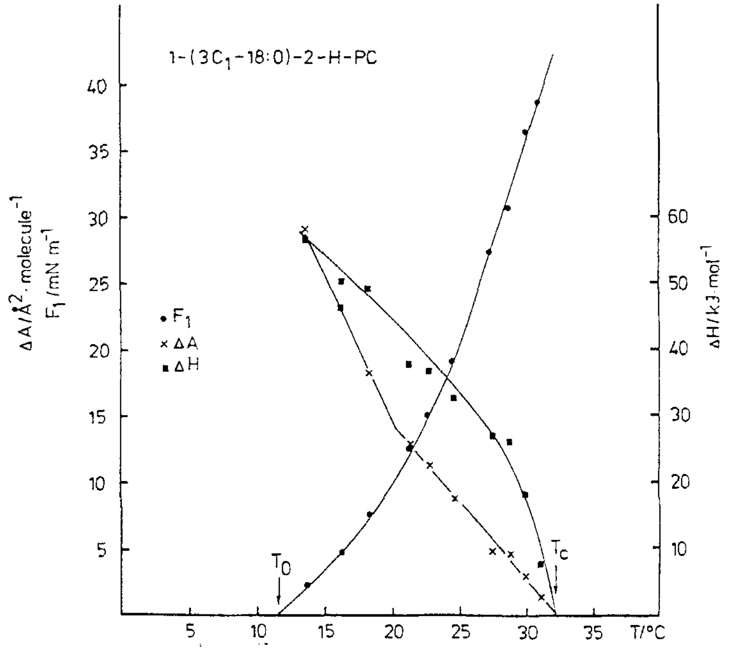

FIGURE 3 Transition pressure F_1, area of transition ΔA and transition enthalpy ΔH of 1-($3C_1$-18:0)-2-H-PC as a function of temperature. F_1 and ΔA are obtained from the curves in Figure 2. ΔH is calculated by means of Eq. (1).

has a value of 2.8 $mN \cdot m^{-1} \cdot K^{-1}$. This is considerably higher than that of unbranched PCs [4,8].

The area change at the transition $\Delta A = A_1 - A^C$ is plotted in Figure 3. A_1 is the molecular area at the transition pressure. A^C is the area of the condensed film linearly extrapolated to F_1. The procedure is described in detail in reference 4 and 6. There are nearly two linear parts of the curve, separated by a smooth break. The change of area becomes zero upon approaching the critical temperature T_c [4,9].

The enthalpy of transition ΔH can be obtained by application of the Clausius-Clapeyron-equation (1):

$$\frac{dF_1}{dT} = \frac{\Delta H}{T \cdot \Delta A} \qquad (1)$$

From the plots of ΔH vs. T it can be seen that ΔH converges also towards zero at T_c. Due to the strong temperature dependence of ΔH in the vicinity of T_c, the critical temperature can be estimated more precisely from the plots ΔA vs. T.

The behaviour of the two other homologues is very similar although equivalent states are found at different temperatures. This can be derived from the systematical shift of the temperatures T_c and T_o (Table I). The intermediate region ($T_c - T_o$), where the transition occurs, exists in all cases studied over nearly 20 K. By comparison, this region is more extended in the case of unbranched PCs ($T_c - T_o \sim 25$ K [4,8]). The reduced transition region seems to be typical for the branched systems [4,7,8].

The $A^{K'}$-values which are independent of the chain length indicate that the introduction of the methyl branch leads to more expanded condensed states as also found for other methyl-branched PCs [7,8,10].

TABLE I Comparison of the characteristic temperatures of the 1-($3C_1$-n:O)-2-H-PCs in bulk and monolayer.

n	T_m/°C	T_o/°C	T_c/°C	T_m-T_c/°C
14	21.7	<0	16.0	5.7
16	29.7	5.2	25.5	4.2
18	35.6	11.4	32.0	3.6

The A_o-values tend to decrease in the series n = 18,16, 14. This seems to be due to the fact that the compound with the longer chain exhibits the same physical state at higher temperatures. This involves that the area change of transition ΔA, plotted in a reduced temperature scale, is larger for the compounds with the longer chains.

Finally, the comparison between the bulk and monolayer properties yields some interesting conclusions.
(a) The introduction and stepwise shifting of a methyl side chain into the hydrophobic region lead to an increasing fluidization of the bulk phase and the monolayer systems.
(b) T_c of the monolayer agrees with T_m of the bulk phase only in the case of an opposite arrangement of the alkyl chains in the gel phase. In the case of an interdigitated gel phase T_c is always lower than T_m.
(c) The interdigitation of the chains leads to a certain stabilization of the gel phase of branched-chain PCs. Such an arrangement cannot be realized in the monolayer. Therefore, the fluidization effect of the methyl side chain is more effective in the monolayer than in the corresponding bilayer.
(d) Both in bulk phase and monolayer systems the shortening of the chain length of the methyl-branched fatty

acid enhances the fluidization effect in regard to the corresponding unbranched PC.

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