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A mono- and bilayer study of homologous branched-chain lecithins

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Electron spin resonance (E.S.R.) studies of the bulk phase and film balance measurements of the monolayers at the air–water interface of some members of homologous rac-1-acyl-2-hexadecyl-glycerophosphocholines (1-($2C_m$-16:0)-2-H-PC with m = length of the side chain and PC = phospholipid) are reported.

The results of the E.S.R. measurements using fatty acid spin labelled near the terminal methyl group suggest that in the lamellar gel phase of the short-chain branched phospholipids ($m < 9$) the hydrocarbon chains are interdigitated. In the monobranched phospholipid with $m = 14$ a gel phase with non-interdigitated chains is assumed.

The F/A isotherms (F = film pressure and A = molecular area) of four branched-chain lecithins were measured over a wide range of temperatures. A comparison of the isotherms at similar reduced temperatures indicates that both condensed and liquid-expanded states occupy increasing molecular areas with increasing m. The phospholipid with $m = 8$ does not form condensed films.

The temperature interval of the transition region between the liquid-expanded and the condensed films which is confined by T_0 (lowest temperature at which the liquid-expanded film occurs) and the critical temperature T_c decreases with increasing m and passes through a minimum at $m \approx 9$. Although the T_0-values are very similar, the T_c-values are strongly dependent on m.

The values of T_c for the monolayer transition and T_m for the main transition in bulk are identical for $m = 0$ (unbranched) and for $m = 14$, whereas for the phospholipids with $m = 3$, 4 and 8 the values of T_c are very much lower than values of T_m. This is discussed in terms of the interdigitation of the lecithins in the gel phase.

1. Introduction

Branched fatty acids occur widely as components of the lipids of microorganisms, plants and animals [1]. Despite their wide distribution and experimental usefulness, relatively little is known about the physical properties of branched-chain fatty acid-containing phospholipids (PCs) [2–12].

Previous studies on monobranched PCs, i.e. synthetic PCs containing one branched fatty acid in the 1-position and an unchanged hexadecyl residue in the 2-position, have shown that the thermotropic phase behaviour depends on the length of the branches [9]. The introduction and stepwise increase of the side chain cause a characteristic change of the main transition temperature T_m. First, the T_m-values decrease with increasing side-chain length, whereas for the compounds with $m = 12$ and 14 an increase of the T_m-values is observed. It seems that the T_m-values pass through a minimum at $m = 9$.

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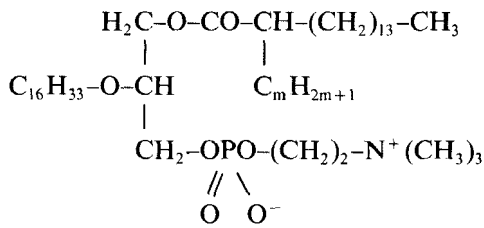
For the dibranched PCs it was found that the systematic change of the T_m-values is connected with a modified structural polymorphism [8]. In comparison with these results and on the basis of the molecule shape concept [13] it seems to be possible that the monobranched PCs exhibit a similar polymorphism.

It was shown [14] that the spin label (1-palmitoyl-2-(14-(4′,4′-dimethyloxazolidinyl-*N*-oxy)-stearoyl)-sn-glycero-3-phosphocholin) (14-PCSL) may be useful in detecting interdigitation of lipid bilayers. For this reason we initiated E.S.R. measurements of model membranes composed of synthetic monobranched PCs.

A second point of interest was concerned with the polymorphism of the monolayers of branched PCs. Some authors [5, 10–12] have investigated the monolayer properties of methyl-iso- and methyl-anteiso-branched PCs. However, no monolayer studies of monobranched PCs have been reported. Such monolayers are of interest because they resemble half of the bilayer of the lipid membranes. The shift of the monolayer phase transition temperature (critical temperature, T_c, of the transition between the liquid-expanded and the condensed films) when increasing the chain length is almost identical to the shift in the T_m-values observed for the bilayer system of the same unbranched PC [15–17]. The question arises of whether this is also valid for the monobranched PCs.

2. Materials and methods

The synthesis of 1-(2C_m-16 : 0)-2-H-PC (Scheme 1) is described in detail in [9]. The monohydrate of the lipids was obtained by drying in vacuum ($1{\cdot}33 \times 10^{-2}$ Pa) at 351 K for 2 h over phosphorus pentoxide [18]. All lipids were chromatographically pure.



Scheme 1.

The fatty acid spin label 5-SASL (5-(4′,4′-dimethyloxazolidinyl-*N*-oxy)-stearic acid) was obtained from Fa. Aldrich Chemical Company, U.S.A., and the phospholipid spin label 14-PCSL was from Syra, Palo Alto, California, U.S.A.

2.1. *Electron spin resonance measurements*

The lipid and the spin label were dissolved together at a 150 : 1 mole ratio in chloroform : methanol (1 : 1, v/v). The solvent was evaporated and the multilamellar dispersions were obtained by suspending the mixtures in water (50 wt %) above the main transition temperature of the lipid and vortexing for 1 min. The material obtained was loaded into Hilgenberg (F.R.G.) micropipettes, sealed with a flame and centrifuged at 2000 r.p.m.

E.S.R. spectra were recorded with a Jeol (Japan) JES-PE-1X spectrometer using 100 kHz modulation. The micropipette containing the sample was inserted into the variable-temperature unit and thermostated by blowing heated nitrogen into the

sample compartment. The overall reproducibility of the temperature dependent measurements was better than $\pm 0{\cdot}5$ K. The spectra were recorded at least three times. The maximum hyperfine splitting A_{max} and the motional parameter τ were measured as described in [19–21]. A_{max} was used as a measure of the order parameter of the nitrogen 2p π-orbital.

2.2. *Film balance measurements*

The film balance used for measuring the surface pressure F as a function of the molecular area is described in detail in [22]. The monolayers were spread from an $8{\cdot}5 : 1{\cdot}5$ (v/v) mixture of freshly distilled chloroform and absolute methanol. The lipid concentration was about $0{\cdot}5\,mg\,ml^{-1}$.

Compression was started 8 min after spreading, always from the same value of area ($500\,cm^2$). The films were compressed continuously with a velocity of $0{\cdot}008\,nm^2\,molecule^{-1}\,min^{-1}$. All isotherms were run at least twice. Each compression was performed with a freshly spread film. This minimized the lipid oxidation during the measurement [17]. The temperature during an experiment was kept constant within 0·2 K. The whole trough was enclosed in a thermostated box.

The equilibrium spreading pressures were obtained by putting some small crystals on the aqueous substrate and monitoring the rise in surface pressure until a steady value was achieved.

3. Results and discussion of the E.S.R. experiments

The maximum hyperfine splitting A_{max} exhibits drastic changes as the system undergoes a phase transition. By means of spin probes with a nitroxide group attached at various depths of the hydrophobic region, the flexibility profile along the hydrocarbon chain of the lipid can be investigated. However, it must be noted that the spin label flexibility profiles can be considered as only approximate, due to the disturbing influence of the bulky nitroxide group. In non-interdigitated gel phases and liquid-crystalline phases of phospholipids a fluidity gradient exists along the fatty-acid chains, normally found by spin labels and by N.M.R. [23, 24]. The order parameter of 14-PCSL is normally much less than that of 5-SASL, even in the gel phase of phospholipids.

The line slope of the spectra of 14-PCSL in the short-branched PCs ($m < 9$) indicates that it still has anisotropic motion below T_m, like 5-SASL, and is not immobilized. A comparison of figures 1 and 2 shows that A_{max} of the spectrum of a fatty acid spin labelled near the terminal methyl, 14-PCSL, is increased to a similar value to that of a fatty acid spin labelled closer to the aqueous interface, 5-SASL. Thus, the order parameter of 14-PCSL has been increased to the degree experienced further up on the chain. 5-SASL is affected much less, therefore the fluidity gradient is almost abolished. The large increase of A_{max} is maintained up to close to the phase transition temperature, where the highly oriented anisotropic motion is transformed over a temperature interval of 8 K into an isotropic type of motion characteristic of 14-PCSL in the liquid-crystalline phase. The transition region monitored by the spin label is much broader than that monitored by differential scanning calorimetry measurements. Two component spectra were obtained in the transition range.

For the lipid with the longest side chain ($m = 14$) a temperature dependence of A_{max} of the spin label 14-PCSL similar to the behaviour of 14-PCSL in the non-interdigitated gel phase of di(16 : 0)PC could be observed. A_{max} of 14-PCSL (see figure 2)

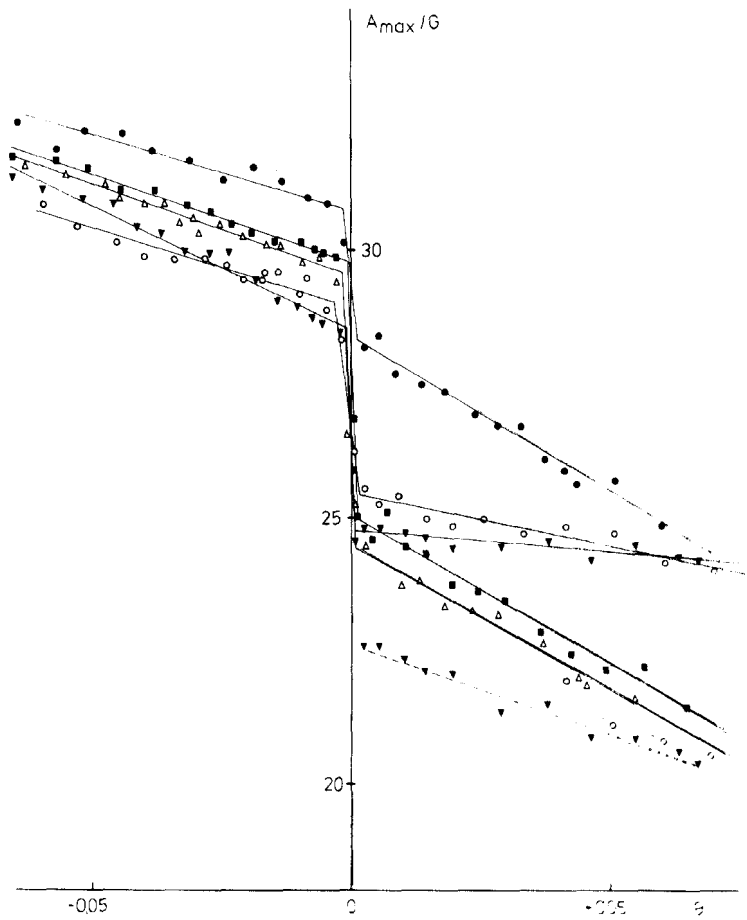


Figure 1. Dependence of the maximum hyperfine splitting A_{max} of 5-SASL on the reduced temperature $\theta = (T - T_m)/T_m$. ▼, 1-(2C$_3$-16:0)-2-H-PC; ○, 1-(2C$_4$-16:0)-2-H-PC; ■, 1-(2C$_6$-16:0)-2-H-PC; ●, 1-(2C$_8$-16:0)-2-H-PC; △, 1-(2C$_{14}$-16:0)-2-H-PC.

has much lower values for 1-(2C$_{14}$-16:0)-2-H-PC compared with the short-chain branched PCs and decreases drastically with increasing temperature.

The results suggest that in the lamellar gel phase of the short-chain branched PCs ($m < 9$) the hydrocarbon chains are interdigitated. The disappearance of the fluidity gradient is to be expected since the terminal ends of the fatty-acid chains of lipids in one monolayer would be located in the region of the methylene segments much closer to the glycerol backbone of lipids in the opposite monolayer of the interdigitated bilayer. In the homologue 1-(2C$_{14}$-16:0)-2-H-PC a gel phase with non-interdigitated chains is assumed. For 1-(2C$_{14}$-16:0)-2-H-PC a repeat distance of about 6·90 nm was found by X-ray measurements [25]. Similar behaviour was observed for the dibranched PCs [8]. In the homologues with short-chain branches the repeat distance d_L of about 5·05 nm measured by X-ray investigations was of the same order of magnitude as in other interdigitated PC phases [26, 27]. Therefore, in dibranched PCs with short-chain branches a gel phase with interdigitated chains was assumed; however, in the homologue 1,2-di(2C$_{14}$-16:0)PC the chains in the bilayer are in the opposite arrangement (d_L = 6·39 nm).

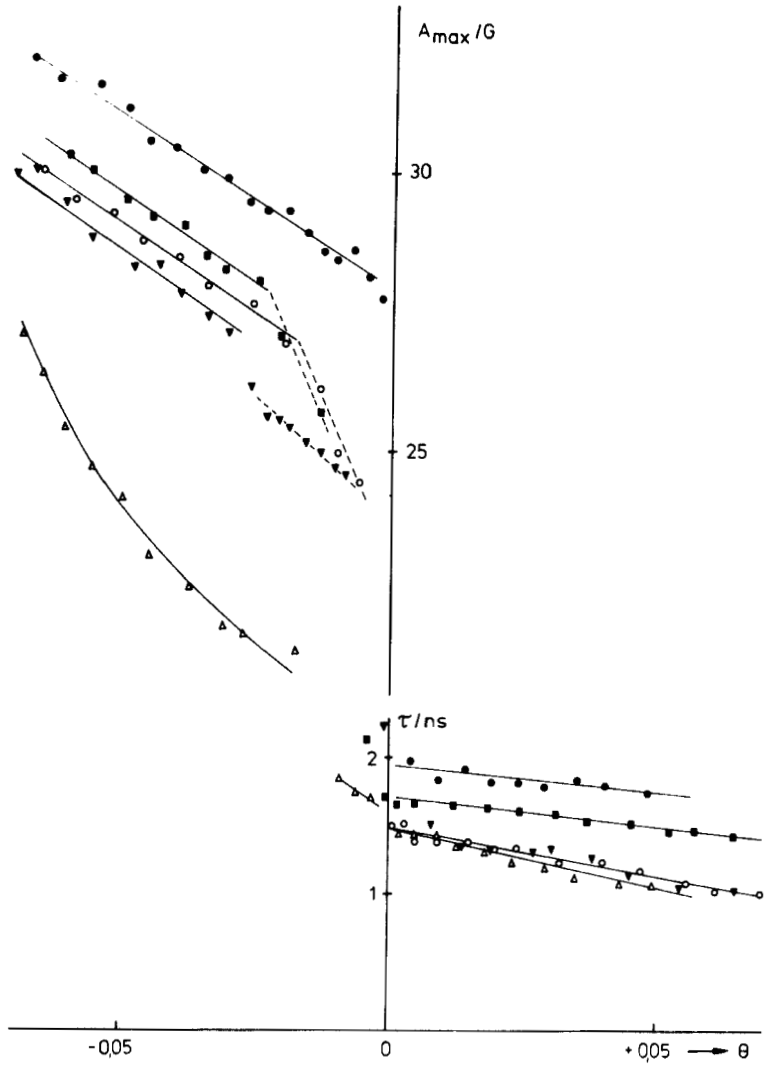


Figure 2. Dependence of the maximum hyperfine splitting A_{max} of 14-PCSL on the reduced temperature $\theta = (T - T_m)/T_m$. ▼, 1-(2C_3-16 : 0)-2-H-PC; ○, 1-(2C_4-16 : 0)-2-H-PC; ■, 1-(2C_6-16 : 0)-2-H-PC; ●, 1-(2C_8-16 : 0)-2-H-PC; △, 1-(2C_{14}-16 : 0)-2-H-PC.

4. Results and discussion of the film balance experiments

In figures 3–5 the surface pressure versus molecular area (F/A isotherms) for the monobranched PCs with $m = 3$, 4 and 14, respectively, are shown as function of temperature. All of the isotherms may be classified according to the film types liquid-expanded (l.e.), liquid-condensed (l.c.) and solid-condensed (s.c.). Exceptionally, the PC with $m = 8$ (see figure 6) forms at all temperatures measured only l.e. films. Therefore the branched PCs under investigation show the same polymorphism as the unbranched PCs [28].

The true collapse pressure of the films were not measured because the film pushed over the edge of the Langmuir trough before collapse occurred. Therefore, the vertical extrapolated area A_v of the dense packing of the film is given instead of the collapse

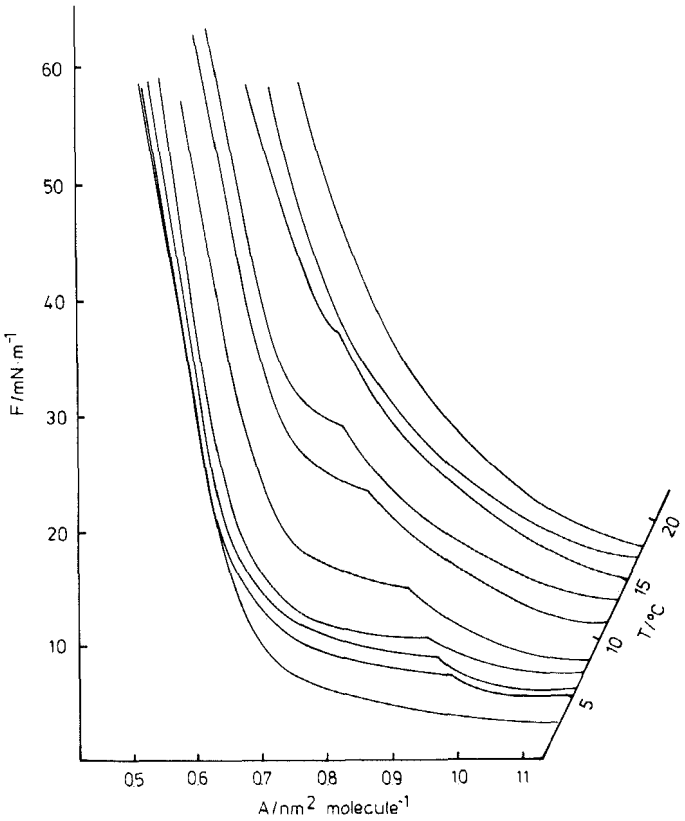


Figure 3. F/A isotherms of 1-($2C_3$-16:0)-2-H-PC monolayers as a function of temperature. The temperatures, from the lowest to the highest curve, are 3·2, 5·0, 5·8, 7·2, 8·0, 11·6, 13·2, 15·3, 17·0 and 18·0°C.

area A^K. The value may be nearly identical, due to the high incompressibility of the condensed films. From measurements of the equilibrium spreading pressure F^e it is known [29] that, studying the phospholipids, the maximum value occurs at the temperature of the main transition T_m. At lower temperatures overcompression of the continuously compressed films may occur, and therefore the collapse pressure is thermodynamically not well established [22].

As an example we consider the isotherms for the PC with $m = 4$ in more detail. The F/A isotherms are presented in figure 4 for the temperature range 3·4–12·6°C. The compression curves with exception of that of 12·6°C show the transition between the l.e. and the l.c. film. The transition is characterized by the (equilibrium) transition film pressure F_1 [30] which represents the onset of the l.e.–l.c. transition. The transition film pressure F_1 depends linearly on the temperature (see figure 7). From the representation in figure 7 the lowest temperature, T_0, at which the isotherms exhibit this transition can be obtained by extrapolation of the linear F_1–T function to $F_1 = 0$ [10]. T_0 is 275 K. On the other hand, the highest temperature of the transition is the critical point T_c, which can be estimated from the temperature dependence of the transition enthalpies ΔH_1 [17, 22]. The ΔH_1-values are available from these isotherms by application of the Clausius–Clapeyron-type

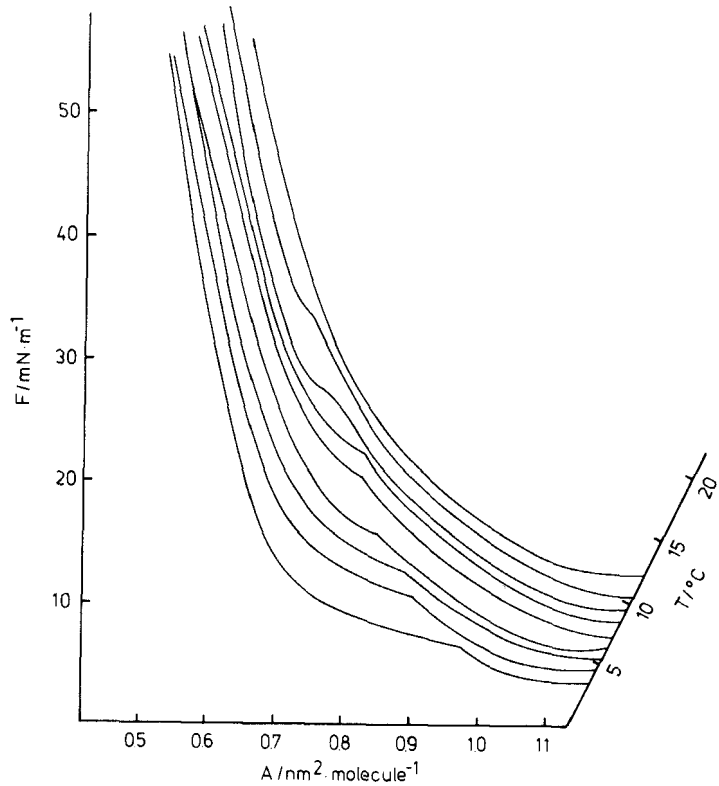


Figure 4. *F/A* isotherms of 1-($2C_4$-16 : 0)-2-H-PC monolayers as a function of temperature. The temperatures, from the lowest to the highest curve, are 3·4, 4·6, 5·2, 6·3, 7·3, 8·5, 9·5, 10·2 and 12·6°C.

equation

$$\frac{dF_1}{dT} = \frac{\Delta H_1}{T(A_1 - A_{1.c.})} \tag{1}$$

The indices 1 and l.c. denote the liquid-expanded and the liquid-condensed phases. The area A_1 is the area of the onset of the l.e.–l.c. transition and the area $A_{l.c.}$ is defined by the elongation of the tangent at the l.c. part of the isotherm to the pressure F_1 [22]. The least-squares fit of the values of ΔA $(= A_1 - A_{l.c.})$ result in a linear function which was used to calculate the ΔH_1-values according to equation (1). The slope of the F_1–T curve in figure 6 is 2·07 mN m^{-1} K^{-1}. As can be seen from figure 8, ΔH_1 decreases linearly with the temperature and becomes zero at T_c, which occurs at $T = 10{\cdot}4$°C. This result can clearly be seen from figure 4, too. At temperatures above 10·4°C the film exhibits only the l.e. phase. Thus, the temperature range over which the transition region is detectable is only 8·2 K (see also figure 7).

The films in the temperature range 3·4–9·5°C form condensed films at higher film pressures and have an A_v-value between 0·505 and 0·530 nm^2 molecule^{-1}. The isotherm at $T = 12{\cdot}6$°C appears to be fully expanded and above T_c. The A_v-value is 0·55 nm^2 molecule^{-1} and is therefore only slightly greater than those for the condensed films.

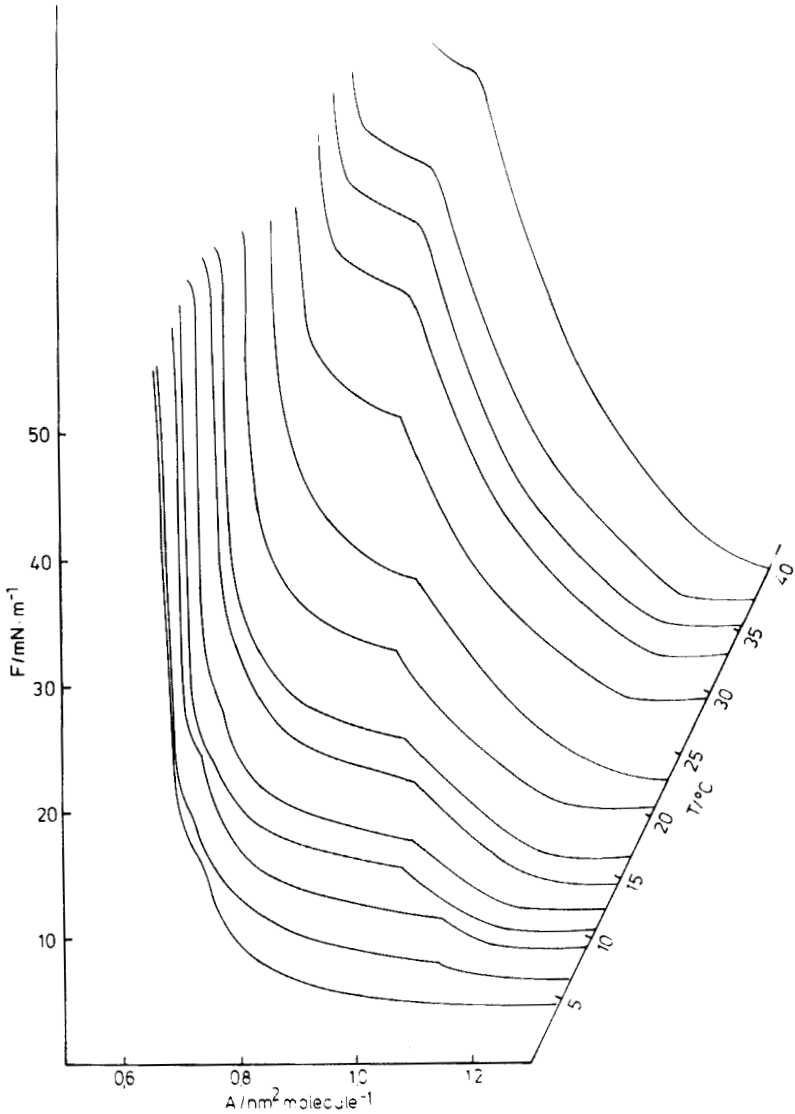


Figure 5. F/A isotherms of 1-($2C_{14}$-16 : 0)-2-H-PC monolayers as a function of temperature. The temperatures, from the lowest to the highest curve, are 4·8, 6·8, 9·2, 10·6, 12·5, 14·6, 16·9, 20·8, 22·0, 29·5, 33·0, 35·3, 37·4 and 40·0°C.

A_0, the area of the lift-off of the F/A isotherms (first detectable film pressure greater than 0·2 mN m^{-1}), increases with increasing temperature (1·06 nm^2 at 3·8°C and 1·12 nm^2 at 12·6°C).

The equilibrium spreading pressure reaches the maximum value at T = 29·6°C. The corresponding F^e-value is 46·0 mN m^{-1}. A detailed analysis will be given in a later paper [31].

It can be stated that the isotherms of 1-($2C_4$-16 : 0)-2-H-PC show the feature which is also characteristic for the other lipids. However, there are two exceptions.

(*a*) 1-($2C_8$-16 : 0)-2-H-PC forms, at all temperatures measured above T = 3·0°C, only l.e. films. It is very likely that the critical point T_c is much lower than 0°C.

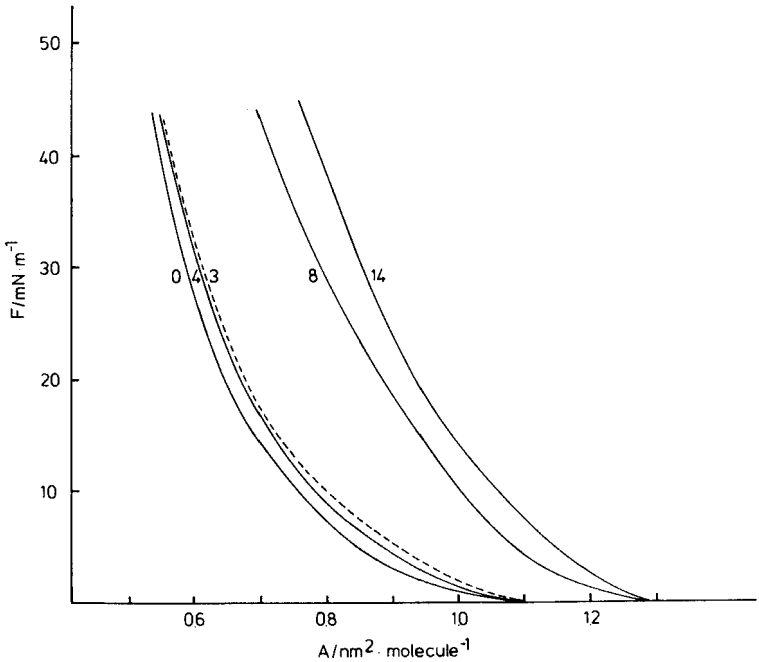


Figure 6. Comparison of the F/A isotherms of the monobranched PCs at T = 18·0°C (m = 3), T = 13·5°C (m = 4), T = 5·5°C (m = 8), T = 45·0°C (m = 14) and T = 44·0°C (m = 0). Dashed curve (m = 3) is used for clearness.

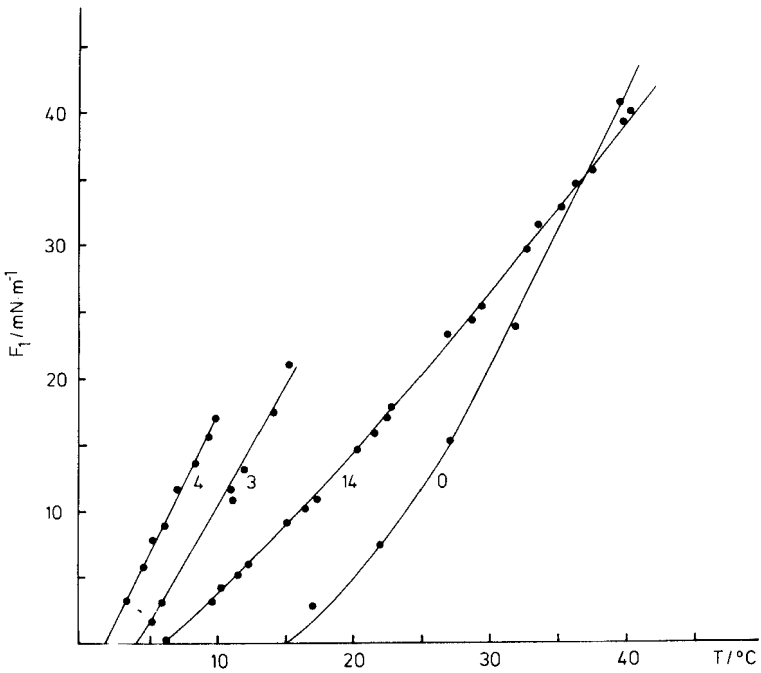


Figure 7. Transition film pressure F_1 of the l.e.–l.c. transition plotted as a function of temperature. The fully points represent the measured values. The solid lines constitute a least-squares fit of the data. The numbers refer to the length m of the side chain. m = 0 refers to di(16 : 0)PC.

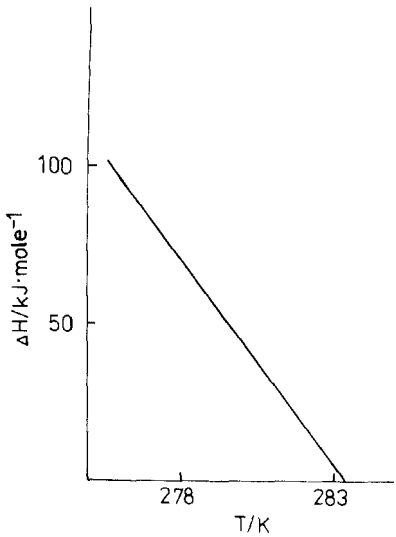


Figure 8. Transition enthalpies ΔH_1 of the l.e.–l.c. transition calculated according to equation (1) for monolayers of 1-($2C_4$-16:0)-2-H-PC.

(*b*) The isotherms of 1-($2C_{14}$-16:0)-2-H-PC indicate an additional transition which appears between the l.c. and the s.c. film. The isotherm at $T = 14{\cdot}5°C$ show only a break (abrupt change in the slope of the isotherm) at lower areas. However, with decreasing temperature the transition region of the isotherm becomes broader, which is accompanied by a change in area during the transition. Similar behaviour could be observed studying *n*-docosyldimethylphosphine oxide [32].

The equilibrium spreading pressures of the PC with $m = 14$ are identical to the transition pressures F_1 [31]. Obviously this means that the second transition occurs within a metastable film with regard to the stable bulk phase.

5. Comparison of the film properties of branched and unbranched lecithins

It is particularly interesting to compare the behaviour of the branched PCs under investigation with the corresponding unbranched PC. Unfortunately, such data are not available. Therefore, we take into consideration the behaviour of dipalmitoylphosphatidyl lecithin (di(16:0)PC). The difference is that di(16:0)PC has two ester bonds. We know from the comparative study of Paltauf *et al.* [33] that the introduction of two ether bonds does not markedly influence the monolayer and bilayer properties. Therefore, we assume that one ether bond also does not affect the properties.

To discuss the influence of the elongation of the side chain on the condensed films in figure 7, F/A isotherms for the branched PCs with $m = 3$, 4 and 14 and the unbranched di(16:0)PC are compared at equal values of reduced temperature $(T - T_0)/T_0 = 0{\cdot}010 \pm 0{\cdot}003$. It is seen that the area A_v increases with increasing m (see also table). The A_v-value for the 1-(C_{14}-16:0)-2-H-PC with $A_v = 0{\cdot}587\,nm^2$ molecule^{-1} seems to be a limiting value for three alkyl chains and can be compared with the corresponding value of triglycerides [34]. There is also the same tendency as with the *n*-alkyl-stearic acids. Studying these substances, Weitzel *et al.* [35] found that the increase of the number of methylene groups within the side chain leads to an

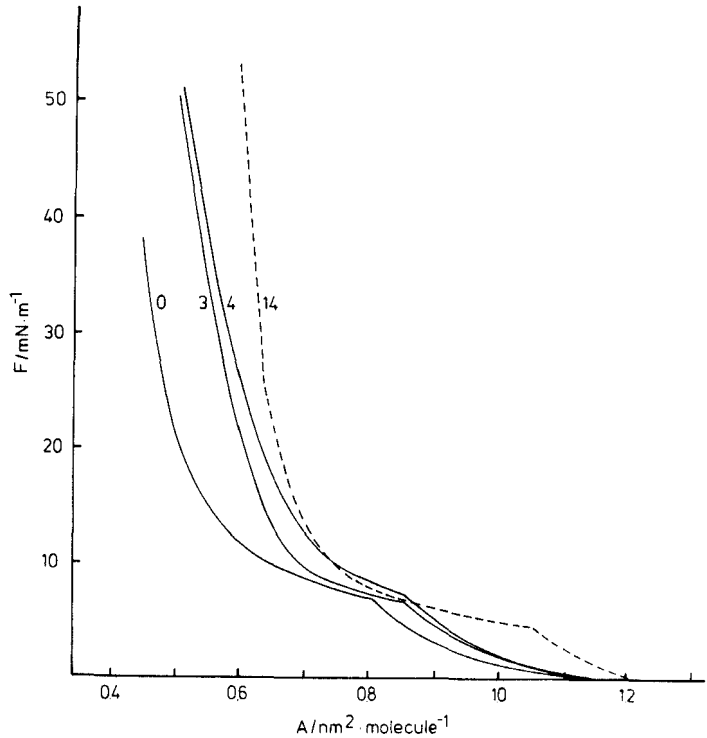


Figure 9. Comparison of the F/A isotherms of the monobranched PCs at $T = 7{\cdot}7°C$ ($m = 3$), $T = 4{\cdot}6°C$ ($m = 4$), $T = 10{\cdot}2°C$ ($m = 14$) and $T = 22{\cdot}8°C$ ($m = 0$). Dashed curve ($m = 14$) is used for clearness.

Influence of the length of the side chain of monobranched PCs on characteristic monolayer data.

Compound	T_0/°C	T_c/°C	A_v/nm² molecule^{-1} †	A_0/nm² molecule^{-1} ‡
di(16:0)PC	15·0	41·0	0·440	1·08
1-($2C_3$-16:0)-2-H-PC	4·1	15·9	0·502	1·10
1-($2C_4$-16:0)-2-H-PC	1·8	10·4	0·505	1·10
1-($2C_8$-16:0)-2-H-PC				1·27
1-($2C_{14}$-16:0)-2-H-PC	6·0	42·6	0·587	1·28

† At $T \approx T_0$. ‡ $T > T_c$.

increasing collapse area which becomes constant from more than eight methylene groups. The result is also consistent with the finding of Balthasar *et al.* [12] that the areas of condensed states of iso- and anteiso-branched lecithins are larger than the corresponding areas of the unbranched lecithins with the same length of hydrophobic chains.

In figure 6 the isotherms of the l.e. films at temperatures a few degrees above T_c are compared. It can be seen that the number of methylene groups within the side chain also increases the areas. However, the introduction of three and four methylene groups does not have such a remarkable influence on the l.e. film compared with the condensed film. The elongation to $m = 8$ effects a remarkable shift of the l.e. film areas. A more detailed analysis shows that the isotherms only shifted to larger areas with regard to the unbranched di(16:0)PC. Considering the film properties of the

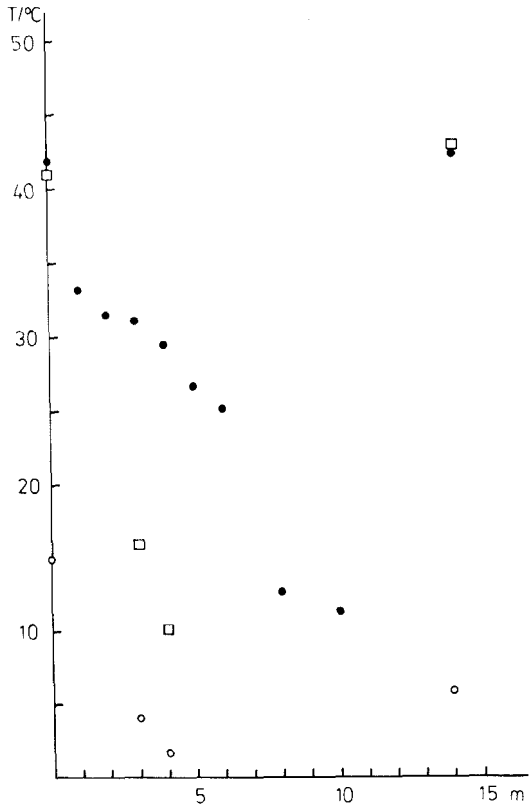


Figure 10. Transition temperatures T_m (●) (main transition of the bulk phase), T_c (□) (critical temperature of the film transition) and T_0 (○) (lower limit for the occurrence of the transition between l.e. and l.c. film) plotted against the length m of the side chain.

1-(C_{14}-16:0)-2-H-PC we see that there is, in contradiction to the behaviour of the lipids with shorter side chains, a relatively greater influence on the l.e. film than on the condensed film.

Examination of the temperature interval of the occurrence of the transition range ($T_0 - T_c$) shows that this region of the members with $m = 3$ and $m = 4$ is smaller than the unbranched lecithin and than the lecithin with $m = 14$. Comparing the broadness of the transition region ($A_{l.c.} - A_l$) of the isotherms of figure 9 it is immediately obvious that the intermediate state of the propyl- and butyl-branched PCs is also more restricted than of the other lipids. However, this does not result in a lower transition enthalpy according to equation (1).

We must bear in mind that the compression curves in figure 9 are compared at different temperatures. It seems from the analysis of figures 6, 8 and 9 that the elongation of the side chain leads to a destabilization of the condensed film (more than of the l.e. film) which is accompanied by the lowering of the critical temperature T_c. At eight methylene groups in the side chain no condensation of the film can occur and only the l.e. film can be observed. However, if the side chain contains 14 methylene groups a stabilization occurs and the film properties are very similar to those of the straight PC: large transition ($T_0 - T_c$), high critical temperature T_c and high film pressure at T_c.

6. Comparison between bulk and monolayer properties

In figure 10 the temperatures of the main transition T_m of the water-saturated bilayer system (bulk phase) are compared with the characteristic data of the monolayer investigations: T_c and T_0. There are some interesting conclusions.

(*a*) The T_m-values go through a minimum.

(*b*) The monolayer data T_0 and T_c seem to behave in the same way. Unfortunately there are insufficient data to check this completely. It is interesting that the critical temperatures depend more strongly on the number of methylene groups of the side chain than the T_0-values.

(*c*) Obviously this means that the observed restriction of the transition region between the l.e. and l.c. film is due to the strong dependence of the T_cs. The difference $(T_0 - T_c)$ also goes through a minimum. Therefore it may be concluded that the PCs with the middle number of methylene groups ($6 < m < 10$) of the side chain cannot form condensed films.

(*d*) The discussed agreement of the film properties of di(16 : 0)PC and 1-(C_{14}-16 : 0)-2-H-PC is confirmed by the interesting fact that T_m and T_c agree.

It is very interesting that this agreement is typical for unbranched lecithins [15]. The data of the branched PCs with $m = 3$, 4 and 8 presented exhibit deviations from this rule. Obviously this means that T_m and T_c agree if the chains of the PCs in the gel-phase bilayer are in opposite arrangement. In this case the monolayer can be considered as half of the bilayer. In the case of the PCs with $m = 3$, 4 and 8 the gel phase is stabilized by the interdigitation of the chains. Such an arrangement cannot be realized in the monolayer. The T_c-values are therefore much lower than the T_m-values.

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