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Liquid expanded-liquid condensed phase transition in Langmuir films of discotic molecules

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Résumé. — Nous avons mesuré les isothermes de pression superficielle pour des monocouches de benzène-hexa-*n*-alkanoates (BH-*n*) étalées à l'interface eau-air. Ces molécules en forme de disque se composent de six chaînes aliphatiques entourant un noyau benzénique auquel elles se trouvent attachées par des groupes esters. Ces groupes hydrophiles ancrent la molécule à l'interface et maintiennent le cycle aromatique à plat sur la surface de l'eau. Avec les homologues les plus bas, BH-5 à BH-7, nous avons observé une transition entre une phase liquide expansé et une phase liquide condensé en fonction du taux de compression latérale de la monocouche. La transition est probablement du 1^{er} ordre, avec une zone plateau bien définie et une seule discontinuité dans la compressibilité. La chaleur de transition associée, calculée à partir de l'équation de Clapeyron, décroît linéairement en fonction de la température et tombe à zéro à la température critique T_{crit} . Au-delà de T_{crit} , la transition disparaît et l'on n'observe plus que la phase liquide expansé. Contrairement au cas des phospholipides et des acides à chaîne grasse, T_{crit} est une fonction décroissante de la longueur des chaînes hydrocarbonées. Nous avons interprété la transition de phase comme une transition ordre-désordre des chaînes entre une conformation gauche et une conformation toute trans. A partir des données d'aire moyenne par molécule dans les phases liquide expansé et liquide condensé, on peut aussi admettre que les chaînes passent d'une orientation parallèle au plan de l'interface à une orientation verticale.

Abstract. — We have measured the surface pressure isotherms of Langmuir monolayers of benzene-hexa-*n*-alkanoates (BH-*n*) spread at an air-water interface. These disc-like molecules are composed of six aliphatic chains attached to the central benzene nucleus by six ester bonds. The hydrophilic ester groups act as pinning points and hold the benzene nucleus flat on the water surface. For the lower homologs BH-5 to BH-7, we observe that the so-called liquid expanded phase obtained at high areas per molecule transforms into the liquid condensed phase upon lateral compression. The transition is approximately first-order, with a plateau region of finite slope and a single discontinuity in the monolayer compressibility. The associated heat of transition, as calculated from the Clapeyron equation, decreases linearly with temperature and extrapolates to zero at the critical temperature T_{crit} . Above T_{crit} , the transition disappears and the liquid expanded phase is observed at all areas per molecule. Contrary to the phospholipid and single chain fatty acid cases, T_{crit} is found to decrease when the chain length increases. We interpret the phase change as an order-disorder transition of the aliphatic chains from a gauche to an all-trans conformation. Based on the areas per molecule occupied in each monolayer state, we can also infer that the chains get lifted up from an orientation parallel to an orientation vertical, relative to the interface.

1. Introduction.

In a recent paper, it was demonstrated for the first time that disc-like molecules which possess columnar liquid-crystalline phases in the bulk can be spread as

monolayers at the air-water interface [1]. For benzene-hexa-*n*-alkanoates, the necessary amphiphilic character is fulfilled by the combination of six hydrophilic groups surrounding a benzene nucleus with six hydrophobic long-chain hydrocarbons. As the monolayer is gradually compressed to lower and lower areas per molecule, surface pressure measurements have shown evidence for a liquid expanded-

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liquid condensed phase transition, at least for the lower homologs and in certain temperature ranges. The transition manifests itself as a plateau region in surface pressure, with a large, although not strictly infinite, monolayer compressibility. Such an observation is particularly interesting in view of the long-lasting dispute in the literature on the very nature of this phase transition in monolayers of fatty acids and phospholipids [2]. Indeed, the imperfect flatness of the surface pressure plateau in the transition region has been taken by some authors as an argument to postulate that the transition could be second-order instead of first-order for this class of materials. As a rationale, it was suggested that the projection of the long hydrocarbon chains could align preferentially in the plane of the interface and form a two-dimensional liquid-crystalline phase with long-range orientational ordering [3]. Such an interpretation however cannot hold in the case of disc-like molecules possessing six-fold symmetry and for which a preferential orientation of the chains would be hard to imagine. This led us to support the more common view that the liquid expanded-liquid condensed phase is indeed first-order and that the imperfect flatness of the plateau region in surface pressure measurements is due to additional effects which are not taken into account in the classical model: limitations in the size of the cooperatively transforming units [4], presence of impurities [5, 6], electrostatic effects [7-9].

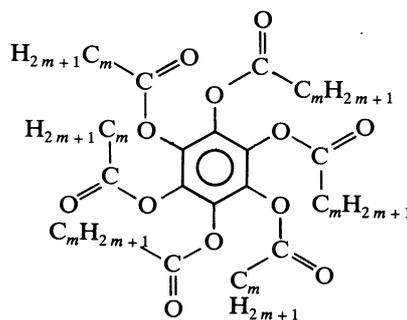
Here we present a detailed study of the surface pressure isotherms for different homologs of benzene hexa-*n*-alkanoates, namely BH-5 to BH-8. A simple physical interpretation of the phase transition between the liquid expanded and the liquid condensed states is suggested. It is based on the variation with chain length of the molecular areas measured in the liquid condensed phase and at the onset of the liquid expanded phase. We also correct our previous statement that the phase transition can be observed for all homologs [1]. In the temperature range 0-30 °C accessible to our experiments, benzene-hexa-*n*-octanoate displays only the liquid expanded phase.

2. Experimental.

The trough containing the water subphase was of the constant-perimeter type [10]. In this design, the monolayer is contained within boundaries defined by an impregnated glass-fiber ribbon covered with teflon and forming a rectangular closed loop. A set of pulleys allows the area to be decreased while keeping the total perimeter constant. The net result is a gradual compression of the monolayer with no risk of leakage. Maximum and minimum areas were $36.5 \times 20 \text{ cm}^2$ and $3 \times 20 \text{ cm}^2$ respectively. The linear velocity was $1 \text{ cm} \cdot \text{min}^{-1}$, corresponding to a reduction of the average area per molecule within the monolayer of $10 \text{ \AA}^2 \cdot \text{min}^{-1}$. The temperature of

the subphase could be varied between 0 and 30 °C with an accuracy of 0.05 °C by circulating water from a thermostated bath into a serpent milled directly in the bottom of the trough. In order to limit the condensation on the different parts of the set-up, the atmosphere above the monolayer was independently regulated by a slight air flow. The trough was also equipped with an automatic water dispenser. The water level was thus kept constant, despite the inevitable water evaporation which was especially severe at the higher temperatures.

The benzene-hexa-*n*-alkanoates (BH-*n* for short) have the following chemical structure [11]



with $m = n - 1$ and $n = 5$ to 8. Four successive homologs were studied, namely from pentanoate (BH-5) to octanoate (BH-8). They were obtained from B. K. Sadashiva at the Raman Research Institute, Bangalore, India and used as received, without further purification. Solutions in methylene dichloride were prepared by weighing small quantities of benzene-hexa-*n*-alkanoates with an electronic micro-balance and dissolving them in known volumes of solvent. The final concentrations were between 0.188 and $0.250 \times 10^{-3} \text{ g} \cdot \text{ml}^{-1}$ depending on the compound. For each experiment and at each temperature, $100 \mu\text{l}$ of these stock solutions were spread on the water surface at maximum area, using a precision Hamilton syringe.

Methylene dichloride is a good spreading solvent, being highly volatile and immiscible with water. It has also been shown previously to contain minimum amounts of surface-active impurities [1]. Prior to spreading, residual surfactants were always removed by contacting the pure solvent with large specific areas adsorbants. A 1 : 1 : 1 mixed bed of molecular sieve (Siliporite K30), activated carbon coal (Acticarbone NC/35/8/16) and porous glass beads (Clarsil) was used. As a result, no surface pressure increases due to impurities contained in the solvent could be detected, even when quantities as large as ten times the ones used in the real experiments were spread on the water surface. The water itself was purified by triple distillation.

Surface pressures were measured by the Wilhelmy hanging plate technique [12]. A platinum blade was used as the detector. The output of the force

transducer was connected to a sensitive amplifier and continuously monitored as a function of the total area available to the monolayer. The accuracy was $0.01 \text{ dyne.cm}^{-1}$. For a given molecular density, the surface pressure was observed to stay constant over long period of times, once sufficient time had been given after the initial spreading of the monolayer to allow evaporation of the solvent. This was taken as a proof that the benzene-hexa-*n*-alkanoates were indeed insoluble in the aqueous subphase and that true thermodynamic equilibrium states could be reached within the monolayer.

3. Results.

For all compounds, the surface pressure measurements were performed at several temperatures. The corresponding surface pressure isotherms are shown in figure 1 for BH-5, 2 and 3 for BH-6, 4 for BH-7, 5 for BH-8. A rapid examination of the various figures shows that two types of curves can be observed :

3.1 SURFACE PRESSURE ISOTHERMS WITH A WELL-DEFINED PLATEAU REGION. — In figures 1 to 4, and for the lowest temperatures, the pressure π first increases regularly as the area available per molecule, A , decreases. Then, when π reaches a certain level, there is a transition to a regime of high compressibility in which the pressure becomes practically independent of A . At $T = 0.6^\circ\text{C}$ and for BH-5 for example, π changes by less than 0.3 dyne.cm^{-1} , when A is varied from 240 to 130 \AA^2 . The transition to this new regime is extremely sharp and manifests itself by a discontinuous change of slope in the isotherms. The pressure measured at the kink, π_t , is observed to be an increasing function of temperature for all BH's. On the other hand, the corresponding area per molecule A_t , decreases when the temperature increases. In the case of BH-5 and BH-6, the experimental data are numerous enough to show that the π_t and A_t variations are linear with temperature almost up to the temperature at which

the transition altogether disappears (see Figs. 6 and 7). It can also be noted that the absolute values for A_t at the various temperatures are always larger for BH-6 than for BH-5.

The observed plateau region does not extend up to the lowest areas per molecule experimentally accessible. Below a certain value, the pressure increases again sharply. For example, for BH-5 at 0.6°C , π more than doubles from 7 to 15 dyne.cm^{-1} when A varies by only 6% between 106 and 100 \AA^2 . The monolayer has now reached a condensed state where it is almost incompressible. Contrary to the high area case, this change of behaviour is not associated with a discontinuous change in the slope of the isotherm. It is nevertheless possible to define a limiting area per molecule, A_{lim} , by extrapolating to zero pressure the almost vertical part of the isotherm. The data obtained for the various homologs have been listed in table I. For a given compound, A_{lim} is independent of temperature, within experimental accuracy.

If one tries to decrease A below A_{lim} , a regime is eventually reached where the pressure, instead of increasing continuously, passes through a maximum and then decreases sharply. This corresponds to the collapse of the monolayer. The initial surface pressure cannot be recovered by re-expanding the monolayer to larger areas per molecule and the behaviour has become irreversible. The collapse pressure, π_{coll} , is of the order of 15 dyne.cm^{-1} for BH-5, 12 dyne.cm^{-1} for BH-6, 7 dyne.cm^{-1} for BH-7.

To summarize, this first type of surface pressure isotherm is characterized by a gradual increase in pressure upon compression, followed by a quasi plateau and then by a sharp increase. BH-5 at temperatures below 24.9°C , BH-6 below 22°C , BH-7 below 14°C are clear examples of such a behaviour.

3.2 SURFACE PRESSURE ISOTHERM WITH NO DISCERNABLE PLATEAU REGION. — A second type of

Table I. — *Physical characteristics of monolayers of benzene hexa-*n*-alkanoates spread at an air-water interface. A_{lim} is the limiting area per molecule in the fully condensed state. π_{crit} is the monolayer surface pressure at the critical point (the critical temperature is indicated in parentheses). A_{crit} is the available area per molecule at the critical point. d is the corresponding molecular diameter, as deduced from $d = 1.24 A_{\text{crit}}^{1/2}$ (see text). $d_{\text{X-ray}}$ is the value derived from the X-ray measurements in the bulk columnar liquid-crystalline phase (see Ref. [11]). d_m is calculated from molecular models assuming fully extended (all-trans) chains extending radially outwards from the benzene nucleus.*

Compound Name	$A_{\text{lim}} (\text{\AA}^2)$	$\pi_{\text{crit}} (\text{dyne.cm}^{-1})$	$A_{\text{crit}} (\text{\AA}^2)$	$d (\text{\AA})$	$d_{\text{X-ray}} (\text{\AA})$ from Ref. [11]	$d_m (\text{\AA})$ from Ref. [1]
BH-5	106	11 ($T_{\text{crit}} = 28^\circ\text{C}$)	145	15	—	21
BH-6	120	8.8 ($T_{\text{crit}} = 25^\circ\text{C}$)	200	17.5	—	23
BH-7	120	6 ($T_{\text{crit}} 15\text{-}20^\circ\text{C}$)	250	19.6	17.4	25.4

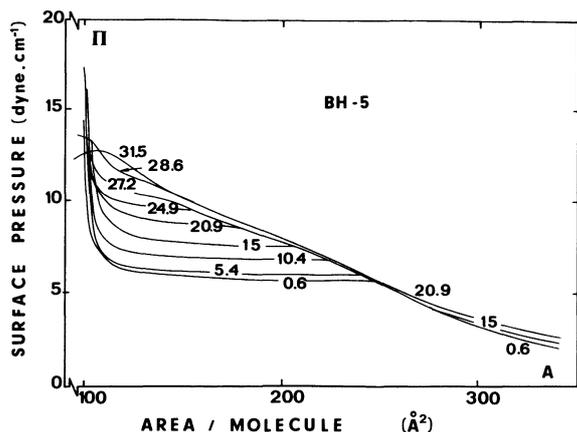


Fig. 1. — Surface pressure isotherms for monolayers of benzene hexa-*n*-pentanoate (BH-5) spread at the air/water interface. The temperatures, in degrees centigrade, are indicated on each curve. The onset of the liquid expanded-liquid condensed phase transition corresponds to the abrupt change of slope in the high area region. The kink ceases to be discernable for temperatures higher than 27.2 °C.

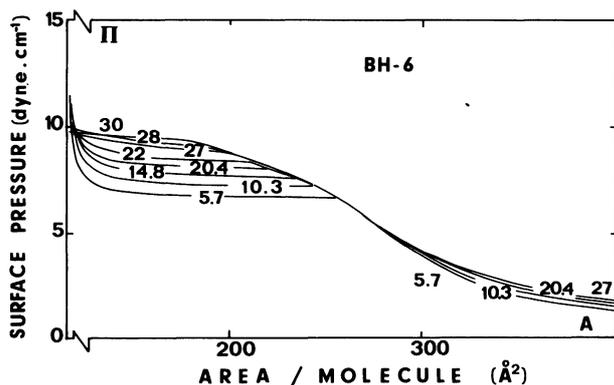


Fig. 2. — Same as figure 1, but for benzene hexa-*n*-hexanoate (BH-6).

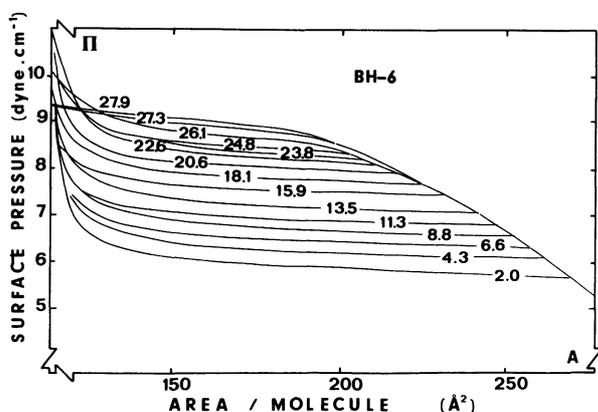


Fig. 3. — Same as figure 2 but with expanded abscissa scales to show the quasi-flatness of the plateau zone. The kink ceases to be discernable above 23.8 °C.

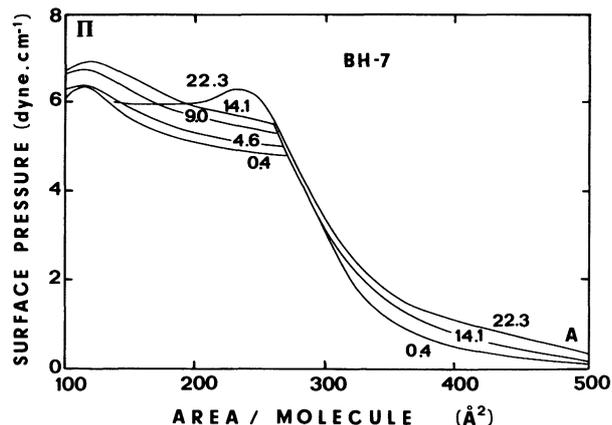


Fig. 4. — Same as figure 1 but for benzene hexa-heptanoate (BH-7). The kink ceases to be discernable for temperatures higher than 14.1 °C.

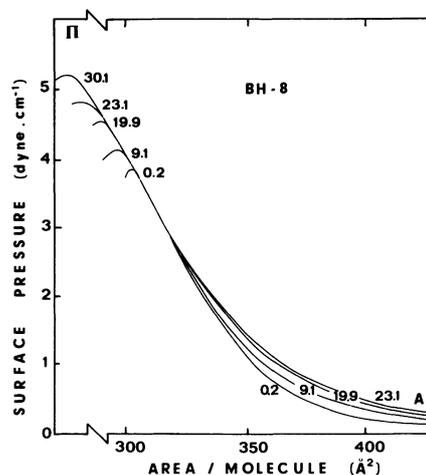


Fig. 5. — Same as figure 1, but for benzene hexa-*n*-octanoate (BH-8). No kink is observable in the temperature range of 0.2-30.1 °C.

surface-pressure isotherm is observed with BH-5, BH-6 and BH-7 at high temperatures and with BH-8 at all temperatures (see Figs. 1, 5). In such cases, the surface pressure π increases monotonically upon decrease in the average area per molecule, until a saturation is reached at the lowest areas accessible. This saturation pressure increases slightly with temperature. A further decrease in area per molecule does not induce a dramatic variation in the surface pressure. The presence of a collapse point is hardly evidenced. Rather, it seems as if the monolayer could be compressed indefinitely without inducing detectable changes in the pressure (see for instance Fig. 2 at 28 and 30 °C).

4. Discussion.

The surface pressure isotherms measured in the present experiments on discotics are qualitatively

similar to the ones displayed by fatty acids and phospholipids in the case of a liquid expanded-liquid condensed (LE/LC) phase transition. Such isotherms have been discussed by several authors [2, 4, 13].

The sharp pressure increase at the lowest areas per molecule corresponds to the onset of the closed-packed state where the area A available per molecule becomes comparable to the molecular cross-section. The most probable molecular orientation is then with the benzene nucleus flat on the interface and the six chains standing vertically in an all-trans conformation. This explains why the molecular cross-section, A_{lim} , obtained by extrapolating to zero pressure the nearly vertical portion of the pressure isotherms is practically independent of chain length. Molecular models indicate that the lowest molecular area for a fully closed-in structure should be of the order of 95 \AA^2 , quite in the same range as the values of 106 to 120 \AA^2 measured here for BH-5 to BH-7. At this stage, we should emphasize that the present A_{lim} data should not be compared without much precautions to the limiting areas quoted as A_e values in reference [1]. Indeed the A_e measurements were performed at the equilibrium spreading pressure π_e without specifying the exact nature of the monolayer state at this pressure. The isotherms shown in figures 1 to 5 indicate that, depending on temperature, the monolayer can be either in the liquid expanded or the liquid condensed states. For example, π_e at 21°C corresponds to the liquid condensed state for BH-5 and BH-6 but to the liquid expanded state for BH-7 and BH-8. Examination of the results given in reference [1] allows to say that this latter condition probably holds also for BH-9 and BH-10 at 21°C . Therefore, since they correspond to different states of the monolayer, it is not difficult to understand why the A_e values quoted in table II of reference [1] (or equivalently the A_c values derived from the collapse pressure) are identical for BH-5 and BH-6 but increases widely between BH-7 and BH-10. It is satisfying to see that the A_e values of $120 \pm 10 \text{ \AA}^2$ previously measured for

BH-5 and BH-6 at 21°C compare well with the A_{lim} values of $106\text{--}120 \text{ \AA}^2$ obtained in the present experiments. On the other hand, it is understandable that the A_e value of 193 \AA^2 measured at 21°C for BH-7 is much larger than A_{lim} since it actually belongs to the liquid expanded state (the critical temperature for BH-7 is lower than 21°C). Similar arguments should hold also for BH-8 to BH-10, unfortunately we have not been able to measure A_{lim} for these compounds in our experimental temperature range of 0 to 30°C .

At intermediate areas per molecule, the plateau region, when observed, corresponds to the cooperative transformation of the all-trans chains in the liquid condensed state into disordered aliphatic chains in the liquid expanded state. Even at low temperatures, the plateau is never completely horizontal and its most conspicuous feature is the existence of a sharp break on the high area side, indicating a sudden change in the monolayer compressibility. Despite the imperfect flatness of the plateau, most authors consider the transition to be first-order. Several interesting explanations have been proposed recently to explain this anomaly but a definite consensus has not yet been reached. It is quite possible that, depending upon the particular system under study, one has to privilege one argument over the others.

Albrecht *et al.* [4] have proposed that the size of the cooperatively transforming units could stay finite even though the transition is first-order. This assumption is of course difficult to prove unambiguously. However a rough calculation seems to show that transforming units incorporating a few hundred molecules will suffice to explain the experimental data.

Pethica *et al.* [5] have considered in great details the effect on the surface pressure isotherms of residual impurities contained in the fatty acids. By extensive recrystallization and purification of their starting material, they were able to show that the plateau could be made horizontal in the case of n -

Table II. — *Thermodynamic data for the liquid expanded - liquid condensed phase transition of monolayers of benzene hexa- n -alkanoates (BH- n with $n = 5\text{--}7$). T_{crit} is the temperature at which the first-order phase transition vanishes; its value has been derived either from the observation of the disappearance of the slope discontinuity in the surface pressure isotherms (column 2) or by extrapolating the heat of transition versus temperature curves to the point where ΔH_t vanishes (columns 3 and 4). Two different estimates of ΔA have been used (see text), leading to two different ΔH_t values ($\Delta H_{t,1}$ and $\Delta H_{t,2}$). The last column gives the $\Delta H_{t,2}$ value calculated at a temperature of 10°C , for the six-chain discotic molecule.*

Compound Name	T_{crit} ($^\circ\text{C}$) from isotherms	T_{crit} ($^\circ\text{C}$) from $\Delta H_{t,1} \rightarrow 0$	T_{crit} ($^\circ\text{C}$) from $\Delta H_{t,2} \rightarrow 0$	$\Delta H_{t,2}$ (kcal mol^{-1}) $T = 10^\circ\text{C}$
BH-5	$28.6 > T_{\text{crit}} > 27.2$	39.0	28.2	51
BH-6	$24.8 > T_{\text{crit}} > 23.8$	52.8	25.7	45
BH-7	$22.3 > T_{\text{crit}} > 14.1$	—	—	—

pentadecanoic and *n*-hexadecanoic acids spread from hexane solutions. Apparently a mere 0.1 % decrease in the absolute purity of the fatty acids (from 99.95 % to 99.85 %) is sufficient to create a pressure increase of 1-2 dyne.cm⁻¹ across the plateau region. Very recently, Bois *et al.* [14] have investigated the influence of the spreading solvents on the final properties of pentadecanoic monolayers. Spreading from hexane at high surface dilution, followed by either stepwise or continuous mechanical compression yields surface pressure isotherms with a flat plateau region while spreading from chloroform does not. The contention of the authors is that solvent retention by the monolayer, postulated long ago by Robbins and La Mer [15] is more severe with hexane than with chloroform and makes the transition first-order. On the other hand, they observe little change in the isotherms when adding 7 % of myristic acid as an impurity to the pentadecanoic monolayer.

To be totally convinced of the influence of impurities, it is important to perform experiments where known amounts of foreign molecules (higher homologs for instance) are deliberately added to the monolayer in a systematic manner. Lösche and Möhwald [6] have used a fluorescent dye as the impurity in monolayers of L- α -dimyristoyl phosphatidic acid. At fixed molecular density, they observed a linear increase of the transition pressure π_t with impurity concentration. However, the amplitude of the variation was one order of magnitude smaller than the one which could be deduced from Pallas and Pethica results in pentadecanoic acid. As pointed out by the German group, this supports the view that still other effects have to be taken into account, especially at very low impurity levels. Two groups working independently [7, 8] have proved, from direct optical observation of the monolayer by epifluorescence microscopy, the existence of long range repulsive forces in the plateau region. As the monolayer is compressed through the transition region, droplets of the liquid condensed phase grow into the continuous liquid expanded phase till the transformation is complete. Mc Connell *et al.* have published striking photographs in which a periodic arrangement of the liquid condensed domains is clearly seen. It is almost certain that the quasi-hexagonal patterns observed are stabilized by electrostatic forces. However the detailed mechanism is still unraveled. Möhwald *et al.* [7] have suggested that the electrostatic repulsion could originate from the differences in surface potential, or in surface charge between the liquid expanded and liquid condensed phases. Andelman *et al.* [9] prefer to think in terms of dipoles. This latter approach has the advantage to make clear why electrostatic interactions can modify the phase diagrams, and lead to finite slope of the plateau in the transition region,

even with non-ionizable substances such as benzene hexa-*n*-alkanoates.

For the time being, the present experiments cannot differentiate between those three mechanisms to explain the non-zero flatness of the plateau region. However, they certainly help to disprove the possibility of a second-order phase transition in which the necessary break of symmetry [16] would be supplied by a cooperative uniaxial tilt of the aliphatic chains in a plane perpendicular to the interface. Indeed, such a two-dimensional nematic monolayer, as proposed by Firpo *et al.* [17] for single-chain hydrocarbons, cannot exist with discotic molecules which possess a six-fold symmetry.

If we accept that the liquid expanded to liquid condensed transition in monolayers of benzene hexa-*n*-alkanoates is first-order, the heat of transition ΔH_t can then be easily calculated from the well-known Clapeyron equation.

$$\frac{d\pi_t}{dt} = \frac{\Delta S_t}{\Delta A} = \frac{\Delta H_t}{T \Delta A}$$

where ΔS_t and ΔH_t are the entropy and enthalpy changes respectively and ΔA is the change in the available area per molecule within the plateau region.

$\frac{d\pi_t}{dT}$ can be estimated experimentally from the slope of the π_t versus T curves shown in figures 6 and 7. For BH-5, we obtain

$$\frac{d\pi_t}{dT} = 0.170 \pm 0.05 \text{ dyne.cm}^{-1} \cdot \text{K}^{-1}$$

while for BH-6

$$\frac{d\pi_t}{dT} = 0.115 \pm 0.05 \text{ dyne.cm}^{-1} \cdot \text{K}^{-1}.$$

On the other hand, ΔA cannot be measured in an unequivocal manner because of the absence of a sharp slope discontinuity on the low area side. Some authors take ΔA as the difference between the area A_t measured at π_t and the limiting value A_{lim} obtained by extrapolation of the sharp pressure rise. Others prefer to take ΔA as the difference in area between A_t and the value at which the residual π variation in the plateau region starts to deviate from linearity. For the time being, we will use both definitions for ΔA but we will see in the following that only the second one leads to plausible results for ΔH_t . The ΔH_t values calculated from the Clapeyron equation are shown as a function of temperature, in figure 8 for BH-5 and in figure 9 for BH-6. In both cases, we observe that the variation is approximately linear except close to the critical temperature T_{crit} where the liquid expanded-liquid condensed phase transition no longer exists. The extrapolation of the linear region to the point where ΔH_t tends to

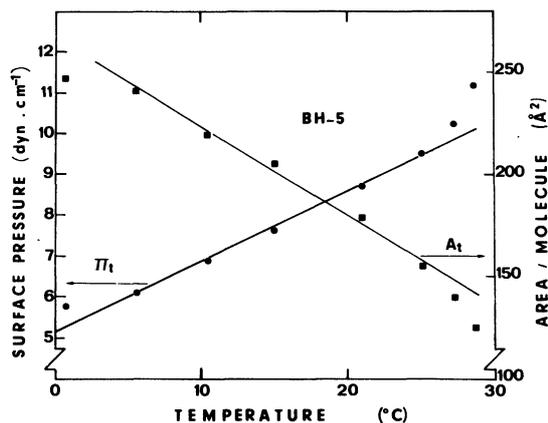


Fig. 6. — Surface pressure π_t (left scale) and area per molecule A_t (right scale) at the onset of the liquid expanded-liquid condensed phase transition as a function of temperature for benzene-hexa-*n*-pentanoate. The variations are linear over most of the temperature range.

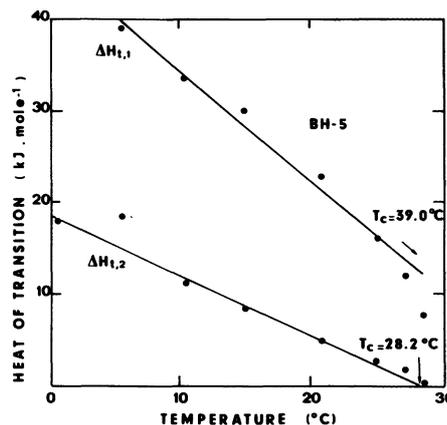


Fig. 8. — Heat of transition *versus* temperature for benzene-hexa-*n*-pentanoate. $\Delta H_{t,1}$ is calculated from the liquid expanded-liquid condensed transition plateau taking the largest possible change in area per molecule ΔA . $\Delta H_{t,2}$ is calculated by taking ΔA from the strictly linear portion of the transition plateau.

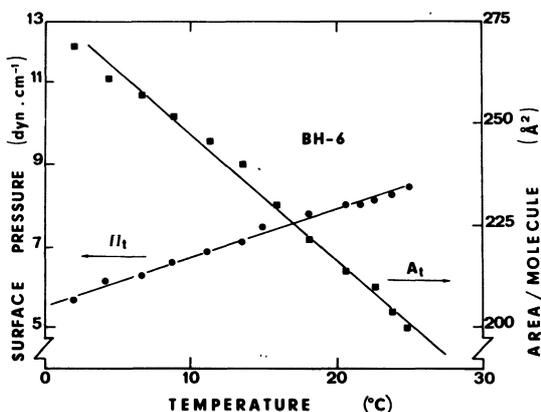


Fig. 7. — Same as figure 6 but for benzene-hexa-*n*-hexanoate. The variations are again linear over most of the temperature range.

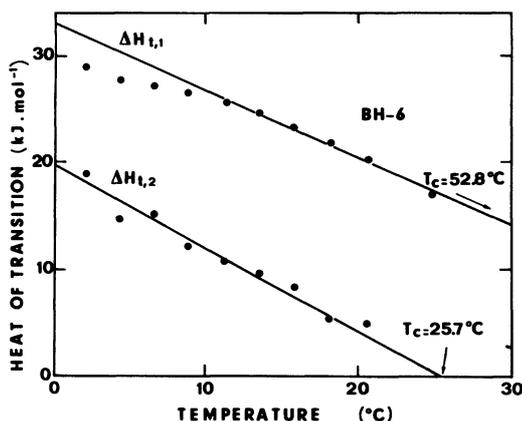


Fig. 9. — Same as figure 10 but for benzene-hexa-*n*-hexanoate.

zero yields absolute measurements for T_{crit} . Using the $\Delta H_{t,1}$ curve (i.e. the largest ΔA determination), we obtain $T_{crit} = 39.0^\circ\text{C}$ for BH-5 and 52.8°C for BH-6. Using the $\Delta H_{t,2}$ curve (i.e. the lowest ΔA determination), we obtain $T_{crit} = 28.2^\circ\text{C}$ and 25.7°C respectively. It is quite clear that only in the latter case do these extrapolations have a physical meaning. Direct observation of the temperature for which the slope discontinuity is replaced by a mere rounding-off in figures 1 and 2 puts T_{crit} between 28.6 and 27.2°C for BH-5 and between 24.8 and 23.8°C for BH-6. On the other hand no such calculations have been attempted for BH-7 because of the small variation in the isotherms over the restricted temperature range investigated. Visual observation of figure 4 suggests that for BH-7, T_{crit} is located between 14.1 and 22.3°C . Finally, for BH-8, it has been possible to detect only the liquid expanded phase in the investigated temperature range of 0.2 - 30.1°C ⁽¹⁾.

(1) In our previous work [1], preliminary data seemed to show the existence of a liquid expanded-liquid condensed transition for BH-8 at 40°C . Although not strictly incompatible with the present data, we now believe that this observation was erroneous. Indeed the transition was reported at that time to occur at a surface concentration of the order of $0.2 \times 10^{-3} \text{ g} \cdot \text{m}^{-2}$, corresponding to an area per molecule A_t of 900 \AA^2 . This value is certainly much too large by comparison with the present experiments on BH-8 at 19.9°C . As shown in figure 5 of this paper, the transition is not yet observed at areas per molecule as low as 300 \AA^2 . Moreover, we know from the experiments on BH-5, BH-6 and BH-7, that A_t is a decreasing function of temperature. Therefore one would expect A_t for BH-8 to be even lower at 40°C than at 19.9°C . Our earlier report is clearly not compatible with that upper boundary. Similarly we believe that the observation of a kink at 40 and 60°C for BH-9 and at 40°C for BH-10 was probably erroneous. This stresses the difficulty of obtaining meaningful pressure isotherm data at elevated temperatures.

The T_{crit} values can also be estimated from the surface pressure behavior around the collapse region. If T is larger than T_{crit} , the monolayer is liquid at all areas per molecule. In that case, as discussed by Gaines [12], the monolayer pressure cannot exceed the equilibrium spreading pressure π_e and no hump should be observed in the isotherm at the collapse. On the contrary, if T is lower than T_{crit} , the monolayer becomes solid-like at the lowest areas per molecule. Mechanical relaxation processes within the monolayer are then very slow and non-equilibrium states can be reached in which the surface pressures will exceed the equilibrium spreading pressure π_e . Eventually the surface pressure will drop sharply as small three-dimensional crystals start to be formed [18]. At this stage, the monolayer is no longer truly two-dimensional. The observation of such overshoots, even at moderate compression rates, provide clear evidence that the temperature of the experiment is smaller than T_{crit} . Application of this criterion to our data points yield T_{crit} values in good agreement with the other determinations. We find that T_{crit} is included between 27.2 and 28.6 °C for BH-5, between 22 and 25 °C for BH-6 and between 14.1 and 22.3 °C for BH-7. These values have been reported in table II. It is striking to observe that T_{crit} decreases as the aliphatic chain length increases. This is opposite to what is known for long-chain phospholipids [4] and fatty acids [12]. For instance, it is a common rule to say that T_c increases by 10 °C for each additional methylene group in a fatty acid chain. Our observation also contradicts the classical results of the lattice-gas model in which T_{crit} is proportional to the energy of interaction between neighbouring molecules and therefore increases with the number of methylene units in the hydrocarbon chains [19]. The fact that this simple rule is not obeyed with benzene-hexa-*n*-alkanoates suggest that the intermolecular forces responsible for the phase change are more subtle than plain chain-chain van der Waals attraction. For instance, the bulky benzenic head group may impose steric constraints on the first few carbon atoms of the alkanolate chain. Also chains with 5 to 10 carbon atoms show stronger internal correlations and rigidity effects than chains such as palmitic or stearic acids [20]. Therefore, the detailed mechanism of the transition need not be the same for phospholipids or fatty acids and for disc-like materials. This point deserves to be confirmed with other discotics.

Once T_{crit} is known, we can in principle derive the critical surface pressure π_{crit} and the critical area per molecule A_{crit} from a simple observation of the surface pressure isotherms. However, the most objective determination is obtained by using the linear dependence of π_t and A_t with temperature: the values of π_t and A_t for $T = T_{\text{crit}}$ will yield π_{crit} and A_{crit} . From figures 6 and 7 for BH-5 and BH-6, and

from the visual observation of the isotherm for BH-7, we obtain π_{crit} values which decrease steadily from 11 dyne.cm⁻¹ for BH-5 to 6 dyne.cm⁻¹ for BH-7. As shown in figure 10, π_{crit} decreases roughly linearly with the number of carbon atoms in the aliphatic chains of the discotic molecules. Using similar procedures, we obtain A_{crit} values which increase markedly from 145 Å² for BH-5 to 250 Å² for BH-7. All results are summarized in table I.

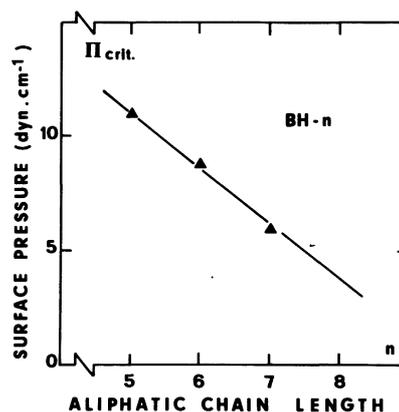


Fig. 10. — Surface pressure at the critical point π_{crit} as a function of the aliphatic chain length of the benzene-hexa-*n*-alkanoates. The solid line has no physical meaning but helps to show that a linear variation is observed.

The strong dependence of A_{crit} on aliphatic chain length for benzene-hexa-*n*-alkanoates is unusual and provides an important piece of information on the molecular conformation in the liquid expanded state. For single chain fatty acids for instance, A_{crit} increases by only 2 Å² for each additional methylene group when going from myristic [21] to pentadecanoic [22] and palmitic acid [22]. This is consistent with the fact that the chains in the liquid expanded state, although disordered, conserve on the average the same vertical orientation as in the liquid condensed state. Their molecular cross-section in the plane of the interface is therefore little dependent on chain length. Another proof of the same fact is that the extrapolated zero-pressure area for expanded films of fatty acids is at most two or three times the limiting molecular cross-section A_{lim} [12]. On the contrary, in the present experiments, A_{crit} increases by an hefty 50 Å² between BH-5 and BH-6 and by another 50 Å² between BH-6 and BH-7. By the same token, the extrapolated zero pressure area in the liquid expanded state can be as large as five to six times the A_{lim} value. There must therefore be a drastic change of conformation between the liquid expanded and liquid condensed states. From the A_{crit} values, it is possible to estimate the mean molecular diameter occupied by the benzene-hexa-*n*-alkanoates in the plane of the interface.

Molecular models show that there can be little interpenetration between the hydrocarbon chains attached to two neighbouring benzene nucleus. As a consequence, d is calculated to be $1.24 A_{\text{crit}}$ from simple geometric relations. The d values thus obtained for BH-5 to BH-7 have been listed in column 5 of table I. They range from 15 to 19.6 Å and are only slightly smaller than the d_m values obtained from molecular models assuming fully-extended, all-trans, aliphatic chains. These latter data are shown in column 7 for comparison.

We can therefore say that in the liquid expanded state the benzene-hexa- n -alkanoates chains extend radially outwards from the benzene nucleus in a conformation more or less parallel to the interface. The residual difference between the d and d_m values is quite understandable since chains in the fluid state are known to be disordered by a limited number of gauche conformation. Reference [20] for instance indicates that chains with sixteen carbon atoms (therefore slightly longer than the present chains) possesses about four gauche bonds in bilayers above the melting transition. It is also striking to compare the experimental d value obtained for BH-7 with an independent X-ray measurement of the lattice spacing, $d_{\text{X-ray}}$ in the three dimensional columnar phase of BH-7 [11]. In this bulk liquid crystalline phase, the disc molecules are stacked on top of each other in fluid columns forming an ordered hexagonal, two-dimensional array. On the other hand, the aliphatic chains are believed to extend radially from the column axis. As can be seen in table I, the values for d and $d_{\text{X-ray}}$ are extremely close to each other, indicating a strong similarity between the molecular conformations in the columnar phase and in the monolayer.

Combining the above result for A_{crit} with the fact that A_{lim} is independent of the chain length, we can now draw a coherent picture of the liquid expanded-liquid condensed phase transition for monolayers of discotic molecules. In the liquid expanded state the chains are disordered and lie more or less parallel to the water surface. In the liquid condensed state, the chains orient vertically and become ordered in an all-trans conformation. The whole phase change can then be described by an order-disorder transition. It is particularly interesting in this respect to mention the recent work of Alexander [23] on the adsorption of long chain molecules when the dominant surface attraction is due to a specific segment of the chain, e.g. a polar head. As the surface density is increased, this author predicts a first-order transition to a state where the chains are stretched vertically. The only condition is that the surface attraction experienced by the aliphatic chains should be significant but not too large. After the transition is completed, the chains find themselves confined to a narrow cylinder whose cross-section is the free area per polar head.

In his conclusion, Alexander stresses that the same model may also be valid for shorter chains, therefore more akin to those considered here. In that case however, the simple power laws relating the monolayer thickness to the number of statistical units per chain are no longer applicable.

5. Conclusion.

To conclude, we can say that monolayers of benzene-hexa- n -alkanoates exhibit a liquid expanded-liquid condensed phase transitions in the temperature range of 0-30 °C for the three lowest homologs (BH-5, BH-6 and BH-7). The surface pressure isotherms observed at low temperatures are typical of the quasi-first order transitions also encountered in monolayers of fatty acids and phospholipids. Their main features are :

- i) discontinuous jump to a state of high compressibility upon lateral compression
- ii) existence of a quasi-plateau over a wide range of areas per molecule
- iii) steep increase of the surface pressure in the fully condensed regime.

We note that the limiting molecular area in the region of nearly zero compressibility is independent of the alkanolate chain length. Therefore, the molecular conformation in the condensed phase is such that the aliphatic chains attached to the benzene nucleus are standing vertical relative to the interface. Upon compression from the liquid expanded state, the chains are transformed from disordered chains with a limited number of gauche conformations into stretched, all-trans, chains. There is a critical temperature, T_{crit} , at which the transition disappears. T_{crit} is observed to decrease with increasing chain length, contrary to what has been reported for phospholipids and single chain fatty acids. The area per molecule at $T = T_{\text{crit}}$ is a strong function of the chain length and probably evidences the fact that, in the liquid expanded state, the disordered chains extend radially outwards in the plane of the benzene ring. This orientation of the chains parallel to the interface may be due to the increased rigidity of the first few methylene units closest to the benzene nucleus.

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Note added in proof. — After this work was completed, we learned that M. Banville *et al.* have proposed a spin-one model based upon a lattice

Bragg-William's method to explain the surface pressure isotherms of disc-like molecules such as those studied here (BANVILLE, M., CAILLE, A. and ALBINET, G., *J. Physique* **46** (1985) 101). Although their work was apparently initiated by some preliminary, unpublished, data of ours on BH-5, this model is irrelevant to the experimental situation because it assumes that the phase transition is related to molecular interlocking and to the subsequent reduction in lattice vacancies. The possibility

of a cooperative tilting of the aliphatic chains in the vertical direction is completely overlooked. However, the present experiments, performed on several benzene-hexa-*n*-alkanoates, show that this latter mechanism must be taken into consideration. This neglect may help to explain why the authors had to point out in their conclusion that their model was not completely satisfactory and that it predicted values for the slopes of the isotherms at variance with the experimental data.

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