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Monolayer behaviour of a nematogenic phenyl benzoate at the air-water interface†

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The pressure-area characteristics of the monolayers of butyl *p*-(*p*-ethoxyphenoxycarbonyl) phenyl carbonate (BPC) have been studied at various temperatures in the range 10°–31°C. With compression, the film passes from the gaseous (G) to the multilayer (M) state, via the liquid condensed (L) state. The transitions from G to L and L to M states occur over wide plateau regions at lower temperatures. The widths of these regions and also the molecular areas at which they begin decrease linearly with elevation in temperature. A remarkable feature of the isotherms is that, in the G and L regions, as the temperature is lowered, they shift in the direction of higher pressure. This is explained by taking into account the possible molecular orientations with respect to the substrate. The overall surface behaviour of BPC differs from that of some other phenyl benzoates studied earlier. In particular, BPC does not form liquid-crystal-like multilayers. The paper also includes certain results on the surface behaviour of mixtures of BPC and cholesterol; the condensing effect of cholesterol is briefly discussed.

1. Introduction

The behaviour of Langmuir monolayers and multilayers of thermotropic mesogens is a subject of fundamental interest, from the point of view of understanding the structural links that may exist between the surface and bulk mesomorphic states. The first experimental study on this subject was by Dörfler *et al.* [1], who examined the compression behaviour of the films of some smectogenic and nematogenic azoxymethylcinnamates. They noticed that the nature of mesomorphism in bulk could be correlated with the shape of the surface pressure-area (π-A) isotherms. Nevertheless, the isotherms were all of the type encountered with one or the other of classical amphiphiles [2]. In contrast, the π-A curves of two nematogenic phenyl benzoates studied later [3, 4] displayed an unusual feature ascribed to the mesogenic character of the molecules: They showed, in a specific temperature region, a liquid-like collapse of the monolayers, followed by a solid-like crystallization. The occurrence of such 'liquid-crystal-like multilayers' has not been reported for any of the compounds studied subsequently [5–9].

Recent spreading experiments [5–9] with a variety of mesogens have brought out certain other interesting aspects: It has been observed for a cyano derivative [6] that the LB films and the bulk nematic phase have similarities in their local molecular

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order. Some nematic polymers have been found [7] to possess a smectic like conformation in their condensed surface state. Some discotic molecules have been observed [8] to behave differently from conventional amphiphiles in that a few of their hydrophilic groups are expelled from the water surface in the high surface pressure region. Long chain aliphatic esters of cholesterol have been reported [9] to form stable surface films, but with abnormally low molecular areas in the condensed state.

From the diverse results that have emerged so far on the two-dimensional behaviour of mesogens, it appears that much work remains to be done before an overall appreciation of the subject is possible. It is the aim of this paper to describe our observations on the π-A variations for a nematic phenyl benzoate and its mixtures with cholesterol; we shall discuss the results in the light of the earlier work and with particular reference to the results reported for other phenyl benzoates [3].

2. Experimental

2.1. *Materials used*

Butyl *p*-(*p*-ethoxyphenoxycarbonyl) phenyl carbonate (BPC), obtained from Eastman Organic Chemicals, was used as received. It was of the best grade commercially available, and, on heating, became nematic at *c*. 56°C and isotropic at *c*. 87°C. These transition temperatures agree with those observed for recrystallized samples of BPC [10]. Cholesterol, used in mixed monolayer studies, was of purity better than 99 per cent. Cetyl alcohol, used for standardization of the experimental set up, was of purity better than 99·5 per cent. Analar grade benzene was fractionally distilled and the fraction boiling between 77° and 78°C was used as the spreading solvent. The subphase water was twice-distilled. The second distillation was carried out in an all-glass apparatus, on alkaline potassium permanganate. The water so obtained had a pH of 5·9 and surface tension of 72·0 mN/m at 25·0°C.

2.2. *Method*

The π-A characteristics were determined on a Langmuir-type horizontal film pressure balance, using a $70 \times 16 \times 2\,\mathrm{cm}^3$ perspex trough and Teflon barriers. The temperature of the subphase water was kept constant to an accuracy of $\pm 0{\cdot}1$°C, by circulating thermostatted water through a serpentine coil kept in the trough. The actual temperatures of measurement are given in the relevant figures. The samples of BPC and its mixtures with cholestrol were vacuum degassed for a few hours before using. BPC was in storage at *c*. 5°C, prior to degassing. Solutions were prepared in a A-grade 5 ml calibrated flask. The volume of the solution applied to the substrate was measured with a calibrated Agla micrometer syringe with an accuracy of $\pm 0{\cdot}0002$ ml. In each experiment, usually about 5×10^{16} molecules were spread and the initial area per molecule in most of the experiments was about $1{\cdot}2\,\mathrm{nm}^2$. An interval of about 20 min was allowed after spreading the solution and before the commencement of compression. The compression was carried out manually, by moving the barrier in a stepwise manner, with an interval of about 2 min between successive steps. The measurements were repeated at least thrice in each case, using a fresh film for each experiment. The average values were used to plot the isotherms. The pressure sensitivity of the balance was better than $\pm 40\,\mu$N/m. Surface areas at most pressures were reproducible within $\pm 0{\cdot}01\,\mathrm{nm}^2$/molecule.

3. Results and discussion

3.1. *Pure compound: BPC*

Figure 1 shows some representative π-A curves of BPC in the temperature region 10°–31°C. The isotherms below 25°C display the following common features: Towards the high density side, from about 1·2 nm^2/molecule, the pressure rises slowly, and the isotherms are convex to the π-A axes, until a sharp break occurs in the isotherms; this region (R_1) is followed by a highly compressible plateau-like region (P_1); P_1 leads smoothly into a region (R_2) where the pressure rise is rapid; then a continuous transition into a second plateau (P_2) takes place; finally, at high surface densities, there occurs a rapid and unstable pressure rise (R_3). These regions are interpreted in what follows, at the molecular level.

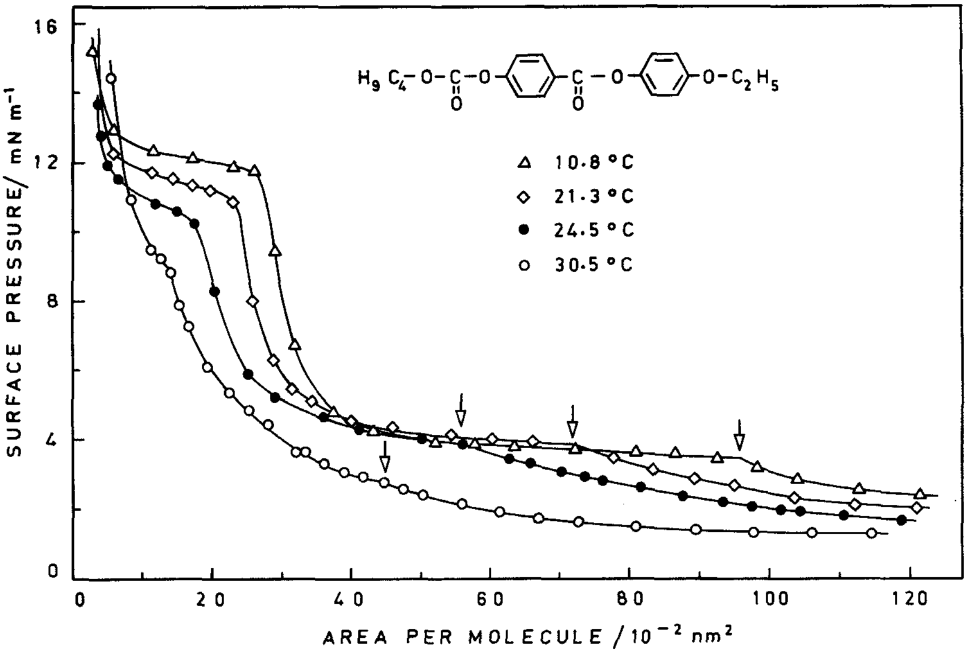

Figure 1. Pressure-area isotherms for BPC at different temperatures. The arrows indicate the positions of transition between the gaseous and liquid states.

Certain features of the iostherms are suggestive of the gaseous state for the film in region R_1. The first concerns the rate of change of π; for instance, when the molecular area is halved from 3·0 nm^2, the pressure is found to increase by less than 20 per cent of its initial value. In other words, the surface pressure approaches the zero value asymptotically and this is a distinguishing feature of the gaseous phase. Secondly, the surface pressures observed in the region R_1 are too large for the R_1 film to be coherent; coherent films, as Adam points out [2], rarely give a pressure exceeding their surface vapour pressure at areas above 1 to 2 nm^2 per molecule. Further, it is well known that amphiphatic molecules with widely separated polar groups are apt to form gaseous monolayers [1, 11]. Yet, the molecular areas at which the break occurs in the isotherms do not seem to favour a flat molecular disposition in the films of BPC, near the transition point. While precise dimensions of BPC molecules are not available, keeping in mind the data for certain other molecules with similar aromatic cores

[7, 12, 13], a rough estimate of the dimensions can be made. Thus, ignoring the alkyl end groups, we may consider the size of BPC molecule to be about $1{\cdot}45 \times 0{\cdot}67 \times 0{\cdot}36\,\mathrm{nm}^3$. Therefore, the minimum area to be expected for the molecules lying with their aromatic planes parallel to the water surface (configuration A) is about $0{\cdot}97\,\mathrm{nm}^2$. But the observed values at higher temperatures are not compatible with this estimate: between 10·8°C and 24·5°C, the transition point shifts from $0{\cdot}96\,\mathrm{nm}^2$ to $0{\cdot}56\,\mathrm{nm}^2$. If the R_l films are gaseous, as they appear to be, they must be composed of molecules with their length and thickness both parallel to the water surface (configuration B). In that case, the minimum area would be about $0{\cdot}51\,\mathrm{nm}^2$/molecule.

It is pertinent to mention here that the isotherms of another phenyl benzoate, 4-*n*-heptylphenyl(4′-*n*-hexanoyloxy) benzoate, HPB (see figure 7 for the structural formula), also display similar features as those of BPC [3]. But the transition point in the low density region is significantly unaffected by temperature for HPB. It seems, therefore, that the addition of a third polar group at the *n*-alkyl end of HPB could remarkably affect the molecular orientation in the region R_l.

The π-A plots in the region R_l show a negative thermal expansion or the so-called isotherm reversal [14]. This phenomenon could arise due to one or a combination of three causes: Enhanced film dissolution at elevated temperatures; existence of various molecular conformations of temperature dependent stabilities; and the occurrence of different types of temperature dependent molecular reorientations. We may discount the first possibility as the sole reason for the thermal anomaly in BPC, since increased solubility would just shift the isotherm to high density side without affecting its shape, whereas, for BPC, the form of iostherms does alter with temperature (figure 1). Isotherm reversal in several amphiphatic compounds observed earlier [11, 14] have been attributed to the second cause, but conformational changes which could explain the reversal are difficult to envisage for the R_l film of BPC. Of course, conformational changes could occur in BPC due to the flexibility of the alkyl end groups. But these groups, in the compressed gaseous state, project out of the water surface due to their hydrophobic nature, and their enhanced thermal agitation at higher temperatures could only lead to an increase in molecular area at a given pressure. Thus when the

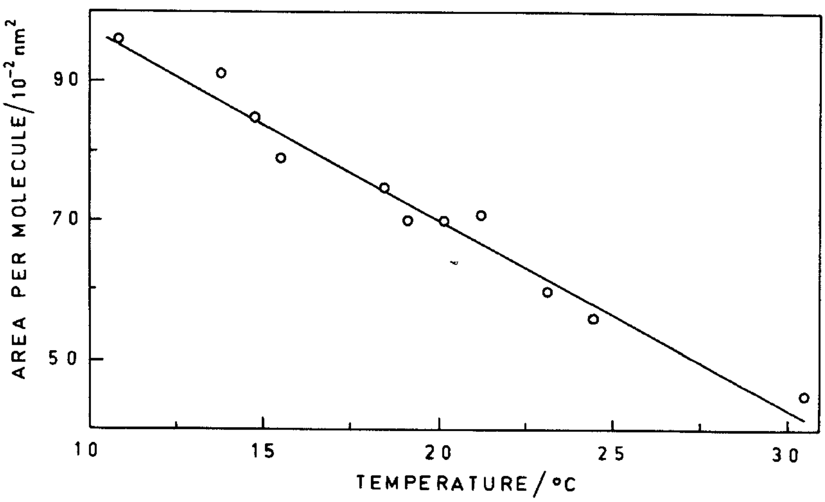

Figure 2. Temperature variation of the molecular area at which the transition from the gaseous to the liquid state begins.

rigid aromatic core lies on the water surface with its terminal polar groups pinned to the substrate, conformational changes in the alkyl end groups cannot account for the isotherm reversal. Therefore we are left with the configurational change to explain the reversal. As earlier mentioned, the molecules in the gas state could assume one of the two configurations, A and B. If we assume that the configuration B is more probable at elevated temperatures and under isobaric conditions, the isotherm reversal follows.

The plateau P_1 is the region of coexistence of the gaseous and liquid states. The area at which it begins varies nearly linearly with temperature (figure 2). The temperature dependence of the transition point is only to be expected since it marks the onset of molecular reorientation, which in turn calls for expulsion of an end polar group out of water [3, 15]. In fact, in the case of HPB mentioned earlier, the constancy of position of the kink point for various temperatures has been taken as an evidence for the absence of molecular reorientation for the compound [3].

The width of the plateau P_1 decreases with rise in temperature as shown in figure 3. This is only to be expected since molecular reorientation is facilitated at higher temperatures.

Region R_2 corresponds to the liquid condensed state. As is well known, the surface pressure in this region has a linear dependence on area, being expressible as $\pi = a - bA$. The table gives the limiting areas (A_0) and the compressibility coefficients (K) for this state, at various temperatures. The values are quite characteristic of the liquid condensed state.

Limiting area (A_0) and compressibility (K) data for the liquid condensed state in BPC. The values of a and b are from $\pi = a - bA$.

Temp./°C	a/m mN^{-1}	b/mN m^{-1} nm^{-2}	A_0/nm^2	K/m mN^{-1}
10·8	56·49	162·8	0·347	0·018
18·5	42·80	133·7	0·320	0·023
21·3	37·53	119·1	0·315	0·027
24·5	28·20	95·6	0·295	0·035
27·2	18·80	72·3	0·260	0·052

The K value increases with temperature (figure 3), as may be expected. However, the area variation seems unusual. For a close-packed arrangement of the vertically oriented molecules of BPC, the molecular area to be expected is about 0·24 nm^2. Whereas the A_0 values are greater than this value, the order in which they vary with temperature is rather unusual. This is a result of the isotherm reversal occurring in the region R_2. As mentioned earlier, thermal anomalies in the monolayer behaviour have been observed in the past with different types of amphiphatic molecules, but their explanation does not apply to the case of BPC. For instance, Cadenhead and coworkers [11, 14, 15] have reported negative thermal expansion for some nitroxide fatty acids and esters, and also some isomers of hydroxyhexadecanoic acid. They explain it by supposing the existence of a bent molecular conformation, in addition to the erect one; the equilibrium between the two configurations is such that the erect one is stabler at higher pressures and temperatures. For BPC, a similar reasoning is not possible since the rigidity of the aromatic cores obviates the existence of a bent conformation. Similarly, the isotherm reversals in hexadecyl and octadecyl urea are thought to arise from hydrogen bonding between the polar groups [16], and such is unlikely to be the case with BPC. The behaviour of BPC is somewhat similar to that

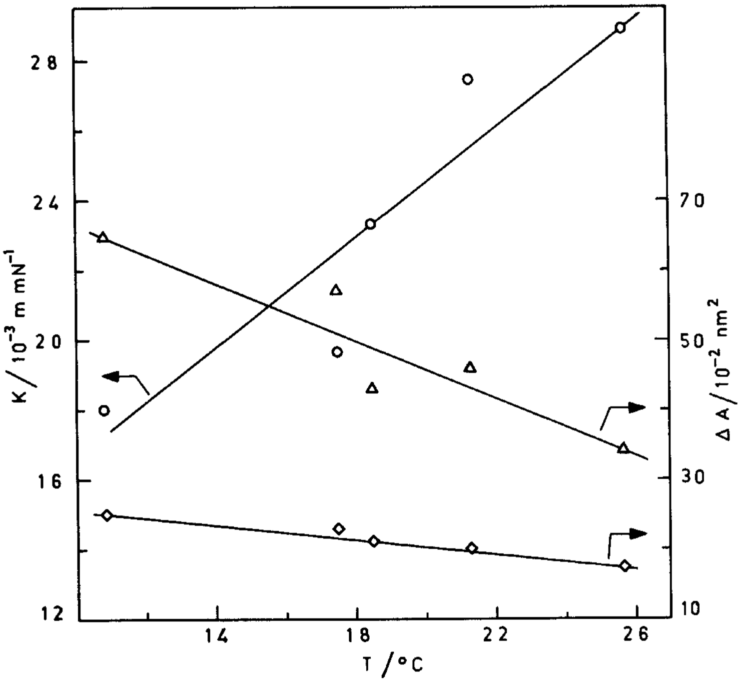

Figure 3. Effect of temperature on (i) the widths (ΔA) of transitional regions between the gaseous and liquid states (triangles), and between the liquid condensed and multilayer states (squares); (ii) the compressibility (K) in the liquid condensed state (circles).

of β-estradiol diacetate [14, 17]; the rigid bipolar diacetate molecules exhibit the reversal on the high density side of the isotherms and there does not seem to be an adequate explanation of this effect [14].

In general, to explain the isotherm reversal, the existence of a minimum energy configuration occupying greater space than more compact configurations of higher energy will have to be supposed [14]. As regards the possible configurations in the R_2 state of BPC, we may consider the following: while the long axes of the molecules remain perpendicular to the substrate, the planes of their aromatic cores may be either randomly oriented or arranged 'face-to-face'. The minimum molecular areas for these two arrangements are about 0·35 and 0·24 nm^2, respectively. Thus, to explain the isotherm reversal, we may suppose the aromatic planes of the molecules to be randomly oriented at lower temperatures and to be in register, face-to-face, at higher temperatures. In other words, an energy barrier exists between the orientationally disordered and ordered arrangements, and this is overcome at higher temperatures due to the weakening of the adhesion to the water of the polar headgroups. Another way of explaining the reversal is to suppose the molecules to be tilted to the vertical at lower temperatures, the extent of tilt being determined by the way the polar headgroup is disposed with respect to the water surface; with increase in temperature, the molecules tend towards a vertical configuration. Both of these explanations are tentative in as much as the true cause of the unusual energy gap between the higher and lower area configurations remains to be fully understood. Further work using ellipsometric and surface potential measurements might reveal the structure of R_2 films and help understanding the thermal anomaly.

The films of BPC collapse from the liquid condensed state and form multilayers as indicated by the isotherms in the region P_2 . The collapse takes place at lower pressures as the temperature increases. At very high surface concentrations, the pressure rises steeply soon after compression, but drops back in a continuous manner. More precisely, the pressure in the multilayer region remains somewhat steady until 4–5 layers pile up, but thereafter becomes very unsteady.

The point of intersection X, of the extrapolated linear portions of the curves in R_2 and P_2 varies with temperature as shown in figure 4. The R_2 to P_2 transition is not abrupt and the collapse starts at a greater area than corresponding to the point X; the areas in figure 4 correspond really to a situation where the multilayer state starts becoming more dominant than the liquid condensed state. In view of this continuous change from R_2 to P_2, the scatter of points in figure 4 is understandable.

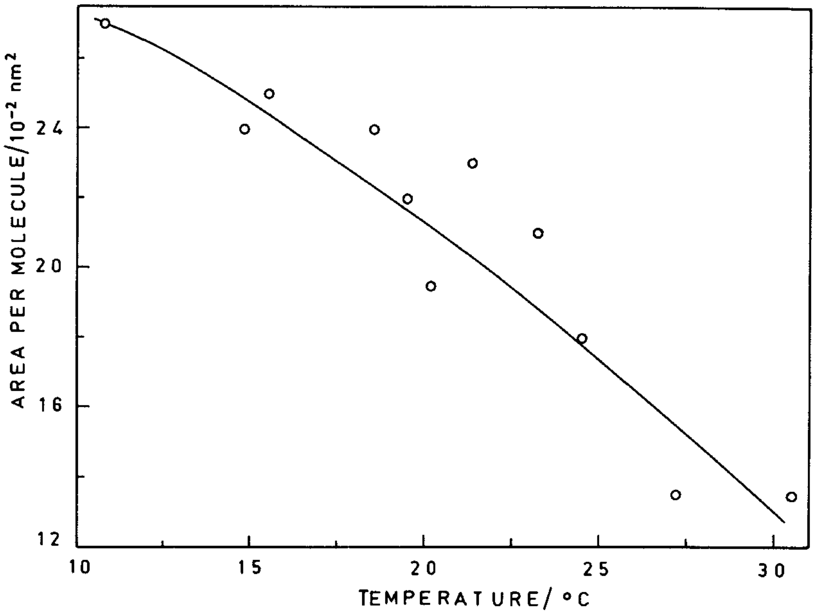

Figure 4. Temperature variation of the molecular area at which the transition from the liquid condensed to multilayer state begins.

The transition between the P_2 and R_3 states is also very gradual. If the linear portions of the isotherms for these states are extrapolated to intersect at Y, the area-interval between X and Y would be a measure of the extent of P_2 zone. We shall refer to this interval as the 'width' of P_2 for convenience, although this term may be less appropriate in view of the slope of P_2 isotherm. Figure 3 shows the temperature variation of the 'width' of P_2 which is linear and similar to that of P_1.

It may be mentioned here that monolayer collapse leading to a P_2-type isotherm is unusual in conventional amphiphiles. Such 'plateaus' have earlier been reported for two liquid crystal forming compounds [4, 6]. In one case [6], the transition to multilayer state is continuous and the P_2 isotherm is smooth, as in BPC. In the other case [4], the change from R_2 to P_2 is marked by a sharp break and the P_2 isotherm shows steps corresponding to the onset of different multilayer states. It appears that a detailed examination of the structure of the P_2 film exhibited by different mesomorphic materials is needed for an appreciation of the possible significance of this region in relation to the mesogenic character of the molecules.

In the higher temperature region (above 30°C), the isotherms of BPC show a practically smooth and continuous rise in pressure with compression. Slight inflections occur in place of the well marked plateaus P_1 and P_2 seen at lower temperatures. These do not evidently indicate the onset of a change from one physical state to another, but correspond to the positions where one state predominates over the other, or the rate of transformation between the states is maximum. It may as well be said that the critical temperature for gas to liquid transformation in BPC is about 30°C, and above this temperature the transformation is continuous.

Even after the collapse, the films of BPC could be expanded and recompressed to show all the essential features. This is clear from the hysteresis results in figure 5. Plot (*a*) represents the initial compression carried just past the collapse point. Plots (*b*) and (*c*) show the expansion and recompression behaviour. The collapse on recompression occurs at about the same pressure as before. This is unlike the behaviour of HPB, where the collapse takes place prematurely, at a much reduced surface pressure than in the initial compression [3]. In the case of HPB the effect is said to be due to the presence of microcrystallites in a metastable condition, in the film.

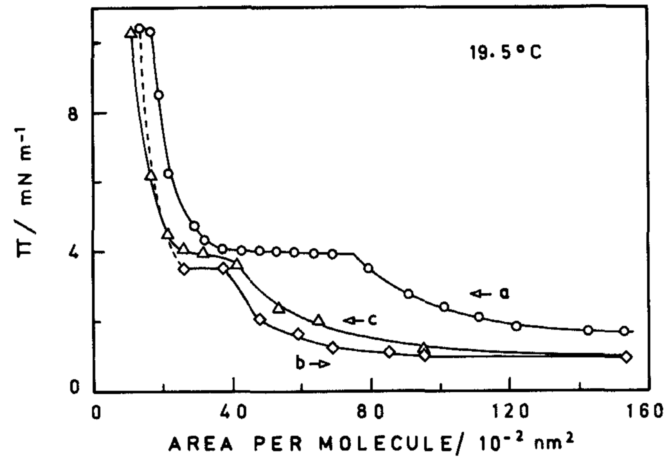

Figure 5. Pressure-area isotherms for a film of BPC under compression (*a*), decompression (*b*) and recompression (*c*).

BPC does not exhibit the liquid-crystal-like behaviour in its multilayer state unlike some other phenyl benzoates [3]. To make this point clear, we must describe first the dependence of isotherm shapes for BPC on the rate of compression. Significant dependence is found only in the L to M transformation region (figure 6). At the onset of the transition, the pressure rises sharply on compression of the film, but drops to a steady lower value in a couple of minutes. The pressure fluctuations are greater at the beginning of transition, but die down as the transition nears completion. The fluctuations are lesser in extent for higher temperatures. The initial and final pressures are shown in figure 6 for two temperatures. It is evident that, if the compression is rapid, the isotherms could display peaks and humps as indicated by dotted lines in the figure.

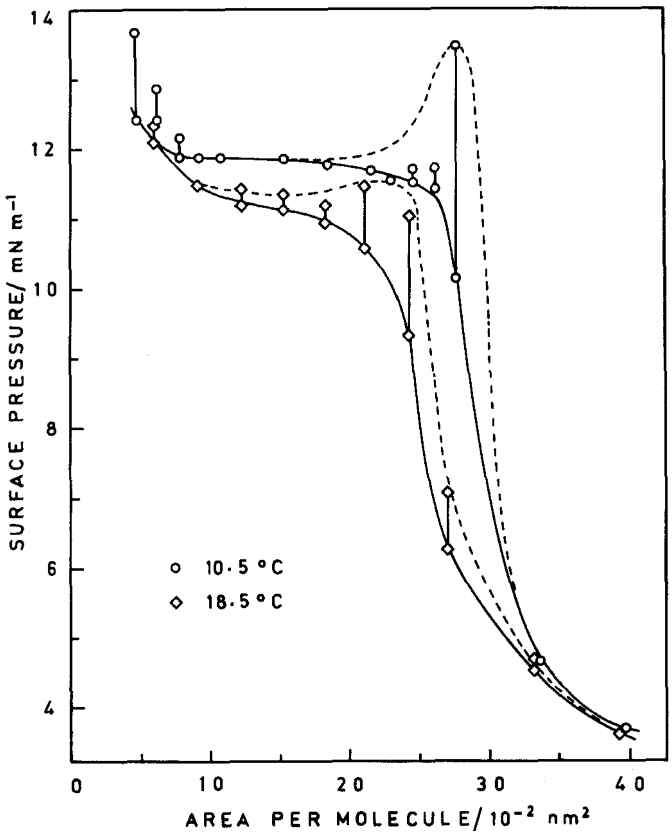

Figure 6. Surface pressure fluctuations occurring in the collapse region of the isotherms for BPC. The fluctuations are indicated by the vertical lines drawn between the initial unsteady and final steady pressures.

Now we turn to the results on liquid-crystal-like multilayers. To facilitate the discussion, the earlier results [3] are schematically represented in figure 7. The curves show collapse of the monolayers beginning at area A. The collapse point is the same at different temperatures. This is taken to suggest a 'roll-over' collapse process of horizontal molecules to form multilayers. The collapse is liquid-like at T_1 and crystal-like at T_4. The smaller elevated plateaus at T_2 and T_3 are interpreted as beginning with a liquid-like collapse and ending at the crystallization point. This elevated plateau is considered to characterise liquid-crystal-like multilayers and its appearance does not depend on the rate of compression.

Evidently, what is seen in BPC is a different behaviour. Firstly, the collapse is gradual and the corresponding inflection is affected strongly by temperature changes. Secondly, the molecules of BPC cannot collapse by 'rolling-over', since they are already vertical in the liquid condensed state. Finally, at no temperature does the steady state isotherm of BPC show such raised minor plateaus as are shown by compounds I and II (figure 7).

Further, there are some points that seem to need a closer look regarding the interpretation of the surface behaviour of the compounds I and II: For instance, the A values at which the multilayers are supposed to form are, surprisingly, very different for the two compounds. More importantly, the isotherms of compound I are exactly

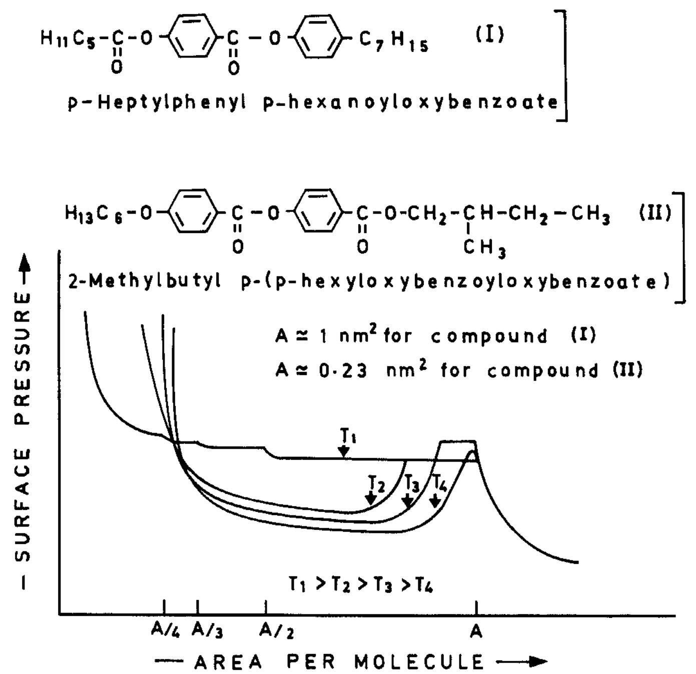

Figure 7. Schematic representation of the pressure-area behaviour for two phenyl benzoates studied earlier by Diep-Quang and Ueberreiter [3]. Temperatures are denoted by '*T*'.

like those of BPC at lower temperatures in all the details, except for the elevated plateau mentioned earlier. Therefore, if the P_1 region is viewed as a multilayer region, what does P_2 signify? It seems that the molecules in compound I undergo reorientations as in BPC. A similar view has also been expressed by other workers [7].

3.2. *Mixtures of BPC and cholesterol*

As is well known [2, 18–21] mixed monolayer studies provide information on the miscibility and the nature of interaction between the component molecules. If at a given pressure, the component molecules of a binary mixture do not occupy the same area as they do in their individual monolayers, i.e. if the observed area per molecule for a mixture is not the molar average of the individual areas of the component molecules, presence of an interaction between the component molecules is indicated [19]. Further, the absence of two separate collapse pressures independent of mixing-ratio of the mixture shows compatibility between the component molecules [21].

It was considered interesting to verify the compatibility of cholesterol and BPC molecules in their two dimensional state, since they are both capable of assuming horizontal (H) and vertical (V) orientations. Figures 8 and 9 show the results for the mixtures in two different compositions. In both the figures, the experimental isotherms of the monolayers show a shift to the lower area side of the curve calculated from the additivity rule [18]. In other words, cholesterol has a condensing effect on the films of BPC. The negative area deviations indicate an attraction between the molecules of BPC and cholesterol.

It is interesting to note that the plateau region P_1 for BPC at 10·8°C is also the two phase region for cholesterol [20]. The molecules of both the components in this region

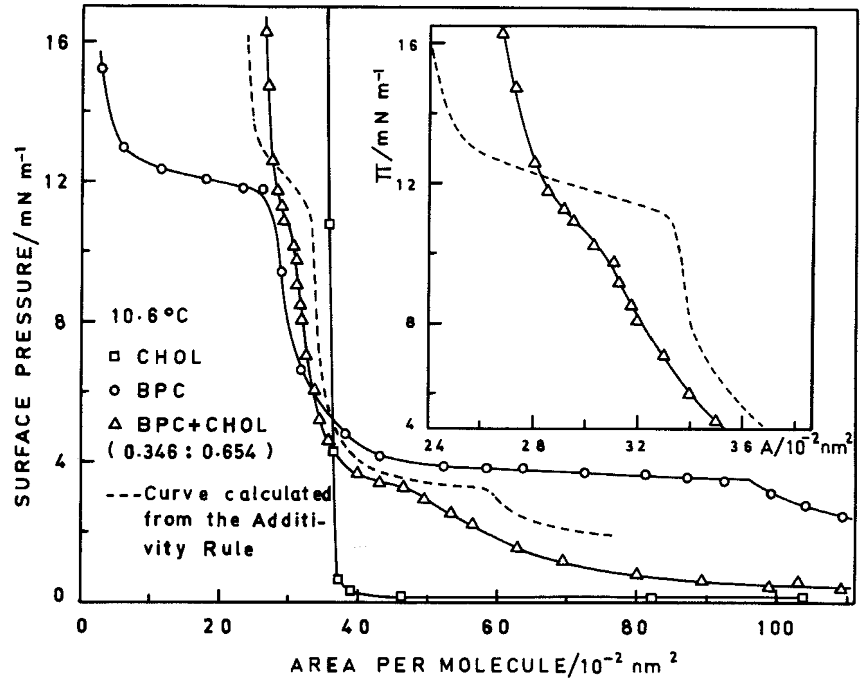

Figure 8. Pressure-area isotherms for BPC, cholesterol and their mixture in the molar ratio 0·346 : 0·654 at 10·6°C. The experimental and calculated curves for the films in the region of collapse are shown enlarged in the inset.

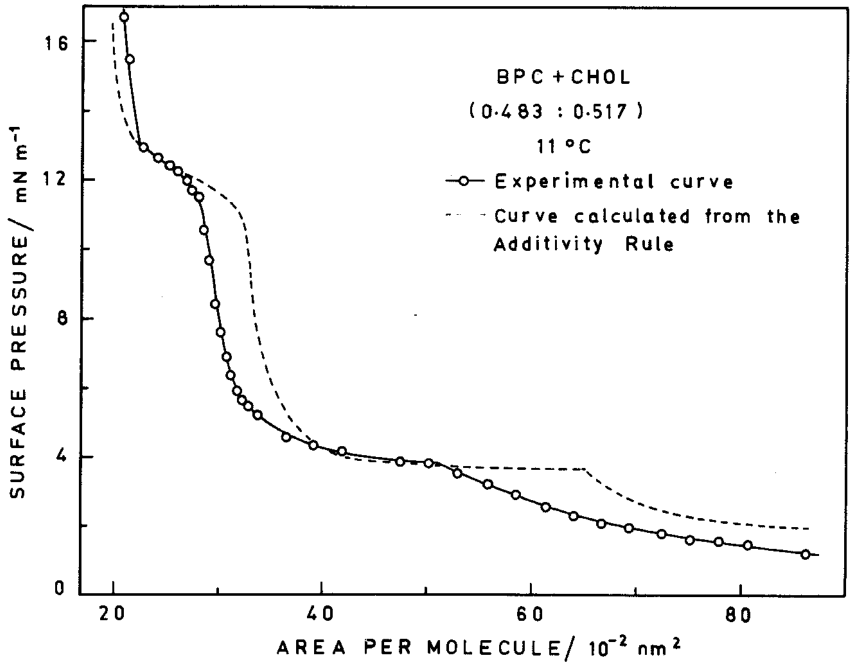

Figure 9. The experimental and calculated isotherms for the mixture of BPC and cholesterol in the molar ratio 0·483 : 0·517.

are thus capable of being in the H or V configurations. Hence an interaction between the molecules can exist; it is only when one of the component molecules is in the H configuration, while the other is in the V, that the mixture is incompatible [21]. Again in the vicinity of 0·4 nm^2/molecule, both BPC and cholesterol show condensed phases with their molecules in the V configuration. The condensing effect of cholesterol for this region too is hence understandable.

The surface pressures observed after the collapse were very unsteady and continuously dropping. The isotherms in figures 7 and 8 show the average values of the pressures observed over two minutes. It appears that only one collapse pressure exists for the mixed films, confirming non-ideality. However, a closer examination of the collapse region for different mixture compositions is required for arriving at more definite conclusions.

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