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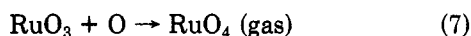
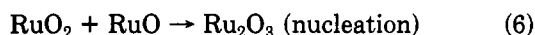
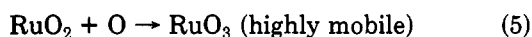
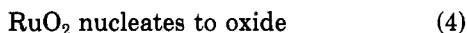
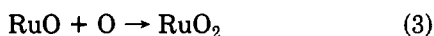
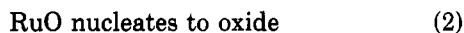
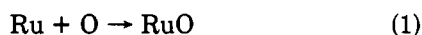
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charged ions are being formed. It would suggest that RuO and RuO₂ are mobile surface species that can nucleate into the growing oxide. RuO₃⁺ and RuO₄⁺ already have substantial partial pressures and are chemically less likely to form oxide. The presence of Ru₂O₃²⁺ and possibly Ru₂O₃⁺ would imply that RuO and RuO₂ are reaction partners contributing to the oxide. However, a more detailed study is needed to confirm the existence of the singly charged species. Should the high mass peak be the dimer (RuO₂)₂⁺, it would confirm the presence of diffusing and reacting RuO₂ molecules analogous to the WO₃ species on oxidizing tungsten. The point will be scrutinized in future studies with a higher resolution instrument. From the above information, the following mechanism is suggested:



Where RuO₃ and RuO₄ are not participants to any great extent in oxide growth, RuO and RuO₂ nucleate to oxide or are precursor to volatile product formation.

The present qualitative study shows the advantage of PFDMS over SIMS which is too destructive a technique to give a complete view of surface intermediates. This should be considered in present efforts to use SIMS for examination of surface reactions.³⁰⁻³³ Correlation with

atom probe results help establish the presence of strongly adsorbed structures or "bulk"-like features. Comparison with the known vapor species observed by sensitive mass spectrometry allows speculation about mobile surface species since the activation energy for diffusion is usually less than that for vaporization.

This work has laid the groundwork for investigations planned with higher resolution PFDMS and photon stimulated field desorption. In these investigations, the kinetics and detailed mechanism of oxidation will be pursued in this very important and presently neglected research area.

Conclusions

General: (a) PFDMS can identify intermediates in metal oxidation reactions and has advantages over SIMS. (b) Interpretation of PFDMS results is aided by thermal vaporization and atom probe results. The former suggests surface species while the latter gives information on bulklike structures.

Specific: (a) RuO and RuO₂ are precursors for RuO₃ and RuO₄. (b) RuO and RuO₂ apparently nucleate to form bulklike surface structures which appear as doubly charged ions. (c) The model of field desorption which predicts singly charged species come from weakly adsorbed species while double charged species come from field evaporation of bulk structure is supported.

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Liquid-Expanded to Liquid-Condensed Transitions in Lipid Monolayers at the Air/Water Interface

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The so-called liquid-expanded to liquid-condensed phase transitions in monolayers of *n*-pentadecanoic and *n*-hexadecanoic acids at the air/aqueous HCl interface and of dihexadecanoylphosphatidylcholine at the air/aqueous NaCl interface have been studied in detail. The experiments followed critical methods for monolayer spreading, surface pressure measurement, and humidity control and used ultrahigh purity lipids. It has been demonstrated unambiguously from the pressure isotherms, and confirmed by surface potential measurements, that the transition is simply first order. The frequently reported "higher order" nature of this transition is the result of inadequate monolayer techniques, poor humidity control, and the use of insufficiently pure monolayer substances or substrates. Some results on temperature effects are also reported. It is proposed that the use of the notation "liquid expanded" and "liquid condensed" be abandoned. Analysis of the published results on phase transitions observed in phospholipid monolayers at the oil/water interface confirms that they are not first order.

It has been shown for numerous lipid monolayers at the air/water (A/W) interface that two prominent phase transitions can occur in the surface pressure (Π)-surface area (A) isotherms at appropriate temperatures. The

transition that occurs at lower pressures corresponds to the change in two dimensions from a liquid to a vapor (l/v), and it is well-accepted that this l/v transition is first order. At higher pressures and densities a second transition is usually described as representing the change from a "liquid-expanded" to a "liquid-condensed" state (le/lc). This transition is regarded as of "higher order" and has been the subject of considerable speculation and theory. In the course of an extended study directed to providing

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a set of standard surface pressures based on the use of phase transitions as thermodynamic reference points,¹⁻³ both the le/lc and l/v transitions have been examined anew. Here we give further results for three monolayer lipids at the le/lc transition showing that this transition is, in fact, first order.

Long-chain carboxylic acid monolayers were the subject of the classical studies of Adam,⁴ Harkins et al.,⁵⁻⁸ Stenhagen,⁹ and Dervichian,^{10,11} all showing the le/lc transition as degenerate or higher order, characterized by an isotherm in which the surface pressure rises across the transition as the density increases. This pattern has been repeatedly found by later workers,¹² and numerous suggestions on two-dimensional micellization,²⁷ polymorphism,¹³ nonequilibrium states, and configurational changes^{11,14,16} have been made, with the order of the transition being put as high as three.¹⁷ The considerable theoretical literature on the transitions has recently been reviewed,¹⁸ both for the fatty acids and for phospholipid monolayers which have been much examined recently for their biophysical significance.^{16,29} It is interesting to note that Adam and Harding¹⁹ reported in 1932 observing fluctuations in the surface potential (ΔV) in the le/lc region. These fluctuations could indicate large regions with differing densities in the monolayer, as would be expected for a first-order transition, but Adam and Harding regarded them as evidence of film collapse. Demel and Joos²⁰ reported that no le/lc region was found in a phospholipid monolayer using an impure sample but that a degenerate transition was observed when the sample was somewhat purified. More recently, substantial ΔV fluctuations were observed in *n*-pentadecanoic acid monolayers in the le/lc region.^{21,28} A corresponding pressure-area isotherm²¹ was not quite flat through the region although much flatter than those

previously reported.

Horn and Gershfeld³⁰ examined several features of the le/lc transition in phospholipid monolayers and pointed out that the isotherms obtained by solvent spreading can exhibit the transition at pressures well above the equilibrium spreading pressure of crystals of the monolayer substances. When films were spread from crystals at temperatures above the gel-liquid transition point, corresponding to the temperature at which the spreading pressure becomes large, and then cooled to lower temperatures and compressed the le/lc transition again appeared. Monolayers at pressures above the spreading pressure are plainly thermodynamically metastable, but the nucleation process in the monolayer is so slow that the isotherms can appear stable over the period of a typical published experiment. The le/lc transition in fatty acid monolayers occurs frequently at pressures below the spreading pressure so that the transition can occur in both equilibrium or metastable monolayers. All the results given here for the fatty acid monolayers are for equilibrium films at pressures below the spreading pressures. The results for the phospholipid monolayers are for metastable films at pressures above the spreading pressure, which is reported as not measurable for dihexadecanoylphosphatidylcholine at 25 °C.²³⁻²⁵ From our experiments, the spreading pressure is certainly not greater than 13 $\mu\text{N m}^{-1}$.²⁶

Experimental Section

The surface balances, humidity and temperature controls, methods for surface pressure and surface potential measurements, and the spreading techniques were as described in detail earlier.^{1-3,21} The preparation of water and HCl solutions and the purification and analyses of the *n*-pentadecanoic and *n*-hexadecanoic acids have also been reported fully.¹⁻³ Fatty acid monolayers were spread from purified *n*-hexane on 10⁻² M HCl.

Anhydrous dihexadecanoylphosphatidylcholine (DHPC) was obtained from Avanti Biochemicals Inc. and was claimed to be better than 99% pure. A portion was purified by six successive recrystallisations from dry chloroform by cooling a solution from 50 °C to below room temperature over about 20 h. The chloroform was redistilled and treated with charcoal. No analysis of the resultant phospholipid is available, but from comparable previous work,^{2,3,34} the purity is expected to be in the 99.9% region. The phospholipid monolayers were spread from chloroform solution onto aqueous 0.1 M NaCl. The sodium chloride was analytical grade, recrystallized, and roasted to 800 °C prior to use to destroy trace organic contaminants.

For the fatty acid results, complete equivalence was obtained with horizontal surface balances using threads coated with purified wax or Vaseline and with Wilhelmy plate assemblies using no threads. Since the troughs and movable barriers were of clear silica made hydrophobic through the vapor phase with dimethyldichlorosilane, contaminant or spreading solvent effects from waxes and Vaseline can be ruled out. For the DHPC monolayers, only the Wilhelmy technique without use of wax or Vaseline was employed.

Results and Discussion

By use of the results of previous experiments from this laboratory,^{2,21} the monolayer densities were established

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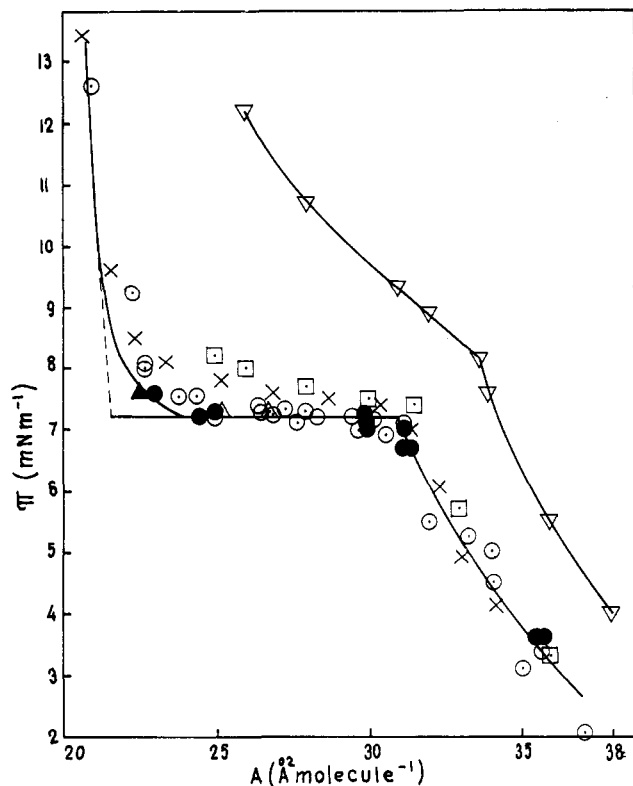


Figure 1. Π - A isotherms for *n*-pentadecanoic acid monolayers on 10^{-2} M HCl at 25 °C with highest purity samples. (●) Single spreadings; (○) successive additions; (×) discontinuous compression; (▲) single shot followed by (Δ) discontinuous expansion (note point at $26.8 \text{ Å}^2 \text{ molecule}^{-1}$). Isotherm from an as-received sample (□) by successive additions. (▽) Isotherm from ref 8. The horizontal line representing the transition is extended to the left to show the dense end of the transition as determined by surface potentials.²¹

either by single-shot or successive additions of spreading solutions or by expansion of a single-shot spread film by moving a restraining barrier. Most previous published results have been obtained by continuous or discontinuous compression of a spread film. In the compression method a film is spread between barriers and usually one barrier is moved to reduce the available area. On some balances the barrier is moved continuously and the force on the sensor is simultaneously recorded. These forces depend on the compression rate. In the discontinuous method, a barrier is moved to prearranged positions and the force observed until it becomes constant and equal to the homogeneous pressure in the film. With the compression method, we have shown that it is very difficult to avoid effects from impurities concomitantly compressed.² Figures 1 and 2 give results for *n*-pentadecanoic acid monolayers at 25 and 30 °C with the highest purity samples (99.95%). The results at 25 °C are compared with those using an as-received sample (99.85%) by the method of successive addition as reported previously.²¹ The *le/lc* region shows a constant pressure within experimental error for the purest sample, as distinct from the definite increase of pressure with density shown by the as-received material. Figure 1 also gives results obtained by discontinuous compression following a single-shot spreading of a highest purity sample, showing a slight rise in pressure across the transition region and illustrating the difficulties with this method.² Undoubtedly, further improvement in the purity control of water, air, and fatty acid could extend the measured flat region to higher densities. The anticipated dense end of the *le/lc* transition for the perfect case is indicated at 25 °C from the density range of the observed

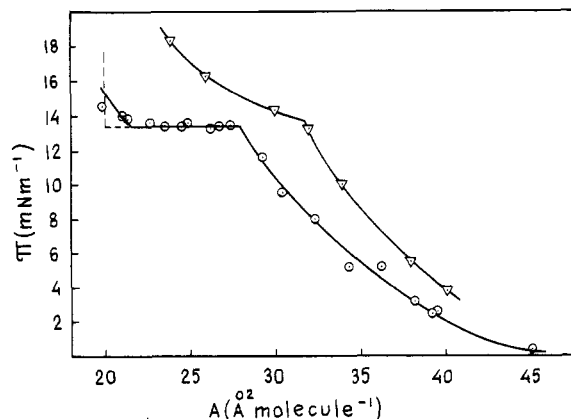


Figure 2. Π - A isotherm with highest purity samples for *n*-pentadecanoic acid monolayers on 10^{-2} M HCl at 30 °C; (○) successive spreadings. (▽) Isotherm from ref 8. The dashed line extension gives the probable form of the transition for a perfectly pure monolayer.

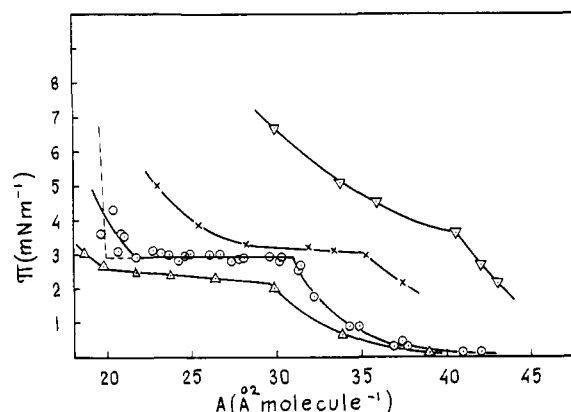


Figure 3. Π - A isotherms for *n*-hexadecanoic acid monolayers on 10^{-2} M HCl at 30 °C by successive spreading: (×) as received; (○) purified; (Δ) estimated 65% relative humidity. (▽) Isotherm from ref 8. The dashed line extension gives the probable form of the transition for a perfectly pure monolayer.

fluctuations in surface potential with the as-received *n*-pentadecanoic acid sample.²¹ Figures 1 and 2 also show the Harkins result for comparison,⁸ the differences probably being due to the use of less pure fatty acid and substrate in the earlier study and to the use of the monolayer compression method. From the transition pressures at 25 and 30 °C (7.2 and $13.2 \pm 0.1 \text{ mN m}^{-1}$) and by use of the two-dimensional Clapeyron equation, the enthalpy of condensation at the transition for *n*-pentadecanoic acid is 18 kJ mol^{-1} subject to an error of $\pm 10\%$ from the known errors in the area and pressure measurements.² The corresponding entropy is $7.5R$, where R is the gas constant.

Figure 3 gives the Π - A isotherm for *n*-hexadecanoic acid at 30 °C, and the corresponding surface potentials are presented in Figure 4. Again, it is adequately clear from the constancy of Π and the observed large fluctuations in surface potential that the transition is first order. Figure 3 also shows the striking effect on the transition when the relative humidity is not controlled to the 98–100% used for all the other measurements presented here. It was found difficult to maintain an enclosed trough assembly at a steady low relative humidity. The relevant isotherm shown in the figure was measured at an estimated 65% relative humidity at the monolayer, with the humidity varying to below this in other parts of the thermoregulated enclosure.

Reduction in humidity cools the surface region by evaporation. Barnes and Cammenga have estimated this

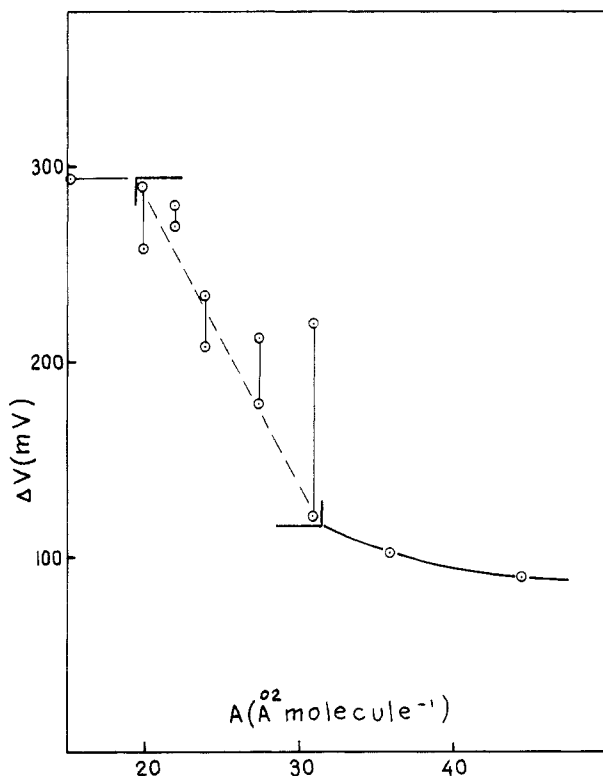


Figure 4. Surface potentials for highest purity *n*-hexadecanoic acid monolayers on 10^{-2} M HCl at 30°C . Vertical lines between points indicate observed fluctuations. The two-phase region is indicated by the dashed line and the corner brackets.

cooling for a film-free water surface.²² The anticipated cooling at 65% relative humidity would be approximately 0.3°C , which would bring the surface temperature closer to the monolayer triple point of approximately 29°C ,^{8,11} at which Π is less than 0.1 mN m^{-1} .²⁶ However, the evaporation will be increasingly retarded by the presence of film as the monolayer density increases. The rising value of Π across the transition for the isotherm at low humidity as shown in Figure 3 may partly reflect the correspondingly rising temperature at the surface as the monolayer density increases. The results shown were, in fact, obtained with a Wilhelmy plate and one effect of a change in surface temperature will be to alter the base-line surface tension, which further complicates the situation. We may note that measurements with a horizontal surface balance will also be affected at low humidities by a difference in temperature on the two sides of the barrier confining the film. Further studies of the effects of humidity control on monolayer behavior are clearly desirable, and reported monolayer results for which humidity control was neglected or not reported must be treated with reserve, particularly at or near phase transitions and triple points.

Figure 5 gives the Π - A isotherm at 25°C on aqueous 10^{-2} M NaCl from one set of successive spreadings with the as-received DHPC, together with some results from the literature for comparison. The "degenerate" character of the transition appears in these cases. Figure 6 shows the isotherm for the purified sample from two series of successive spreadings using a Wilhelmy plate. The scatter of the points about the line at areas above the transition region primarily reflects errors in the area determination, not the pressure, as discussed previously.² The results indicate clearly that this metastable monolayer exhibits a first-order transition when purity and technique are well controlled. In confirmation, the surface potentials of monolayers of pure DHPC in the phase-transition region exhibit small but definite fluctuations, as shown in Figure

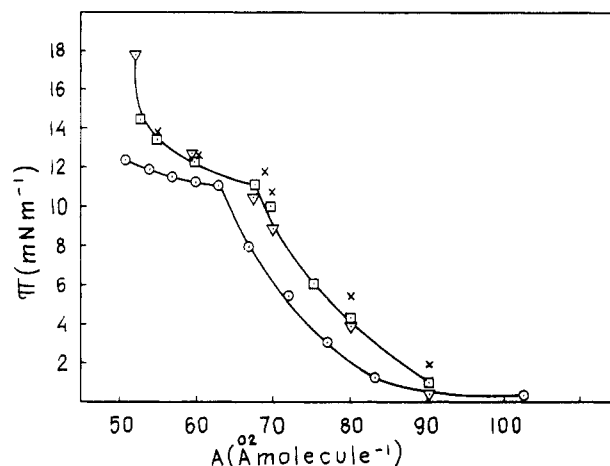


Figure 5. Π - A isotherms for various samples of dihexadecanoylphosphatidylcholine monolayers on 10^{-2} M NaCl at 25°C . (○) This study, successive spreading, as-received sample. Literature results by discontinuous compression: (□) ref 31; (▽) ref 23; (×) ref 32.

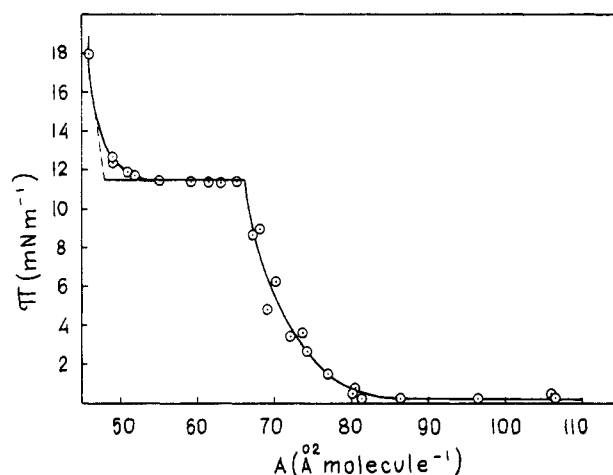


Figure 6. Π - A isotherm by successive spreading for the monolayer of purified dihexadecanoylphosphatidylcholine on 10^{-2} M NaCl at 25°C . The horizontal line representing the phase transition is extended to the probable limit for a perfectly pure monolayer.

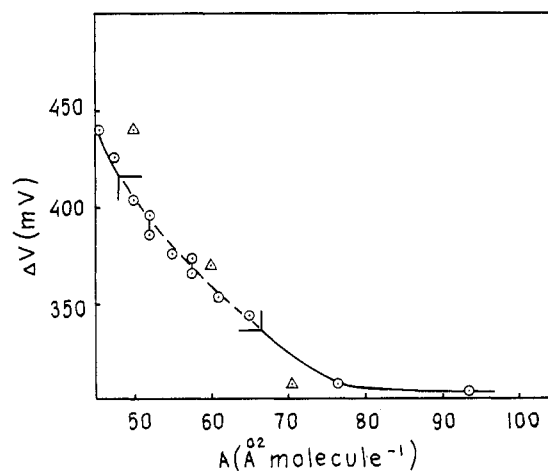


Figure 7. Surface potentials for purified dihexadecanoylphosphatidylcholine monolayers on 10^{-2} M NaCl at 25°C . Vertical lines between points indicate observed fluctuations. The two-phase region as given in Figure 6 is indicated by corner brackets. Also shown (Δ) are results from ref 23 at 25°C on water.

7. These fluctuations are as large as 10 times the experimental error ($\pm 1 \text{ mV}$) in the surface potential and

would seem to be the first observed with a phospholipid film. Previous studies on phospholipid surface potentials may have missed these fluctuations either because of impurity effects or because of inadequate sensitivity in the methods used. It should be noted that the surface potential fluctuations were observed with an electrode of 1-cm diameter for the three monolayers studied, so that the inhomogeneities in monolayer density causing the fluctuations are at least of the order of millimeters. Neuman et al.³⁹ report inhomogeneities in Langmuir-Blodgett films withdrawn from DHPC monolayers on 10^{-2} M NaCl at 22 °C in the le/lc region. The scale of these inhomogeneities is approximately 0.5 μ m, which would not be observable by surface potential fluctuations. The Π -A isotherm given by Neuman et al.³⁹ shows a degenerate transition region. Their experiments used as-received phospholipid, water from reverse osmosis, and a Lucite trough. The isotherm was obtained by the continuous compression method. Lösche and Möhwald⁴⁰ have reported inhomogeneities on a scale of a few microns in DHPC monolayers in the le/lc region when a fluorescent tracer was spread with the film at 17.5 °C. Their Π -A isotherm is also degenerate in the transition region and was obtained by continuous compression with an as-received sample.

Generalizing on the basis of our results with these three monolayers at the A/W interface, we propose that until proof to the contrary be offered for a particular substance the le/lc transition should be regarded as first order for both stable and metastable films, and that results suggesting degenerate phase behavior result from inadequate monolayer methods or from impurities, as proposed on theoretical grounds by Marcelja.³⁵

For the oil/water (O/W) interface the situation appears to be different. From an extended set of experiments on a homologous series of saturated 1:2 diacylphosphatidylcholines at the *n*-heptane/aqueous NaCl interface it was shown that phase transitions occur in the high-density regions of the isotherms.^{36,37} Although the results were obtained with high-quality compounds and by critically examined methods,^{3,38} none of these phase transitions show constant Π across the transitions, although with the longest

chains and lowest temperatures the rise in Π with increasing monolayer density is small.

Bell and Mingins and Taylor²⁴ have discussed whether impurities could explain the behavior of these phospholipid monolayer transitions at the O/W interface and conclude that the transitions are degenerate. The overall set of results is consistent with the view that in the presence of the *n*-heptane phase, the condensation process at the transition consists of two-dimensional micelle formation with aggregation number increasing with chain length and decreasing with temperature. At the A/W interface the corresponding aggregation is essentially infinite, corresponding to the first-order transitions observed. This difference between the phase changes of the phospholipid monolayers at the A/W and O/W interfaces has a parallel in the behavior of the chain-melting transitions for crystals of phospholipids in the presence of water and heptane.³³ The sharp thermal transitions for crystals alone are also observed in the presence of water or heptane separately. When both liquids are present, the transition temperature decreases and the transition is diffuse, suggesting a more disordered or solvent-swollen structure in the crystals.

In conclusion, we note that the original reason for describing the transition as liquid expanded to liquid condensed was that the monolayers were fluid at densities above the transition point, with this fluid range merging into viscous and solid regions as the density increased. We have not examined the rheological state of the condensed monolayers at or above the transition pressures, but we may anticipate that the condensed phases will often be solid in character. Below the triple point, the condensation of the vapor will go directly to the condensed phase with densities near to close packed. The "le/lc" transition is probably best described in general as liquid to close packed or in many cases simply as liquid to solid.

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Registry No. *n*-Pentadecanoic acid, 1002-84-2; *n*-hexadecanoic acid, 57-10-3; dihexadecanoylphosphatidylcholine, 2644-64-6.

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