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The Effect of Surface Pressure on the Langmuir-Blodgett Polymerization of 2-Pentadecyl Aniline

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The application of the Langmuir-Blodgett (LB) technique to the polymerization of 2-pentadecyl aniline on the LB trough is discussed in this paper. The changes in the mean molecular area (Mma) during the polymerization is mainly due to the change of the alkyl sidechain conformation. The polymerization rate (PR) is deduced from the change of the Mma. The effect of the surface pressure on the polymerization is investigated. It is found that the effect of the surface pressure is mainly on the reaction rate constant, not on the surface concentration.

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The Effect of Surface Pressure on the Langmuir Blodgett Polymerization of 2-Pentadecyl Aniline

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The application of the Langmuir Blodgett (LB) technique to the polymerization of 2-pentadecyl aniline on the LB trough is discussed in this paper. The changes in the mean molecular area (Mma) during the polymerization is mainly due to the change of the alkyl sidechain conformation. The polymerization rate (PR) is deduced from the change of the Mma. The effect of the surface pressure on the polymerization is investigated. It is found that the effect of the surface pressure is mainly on the reaction rate constant, not on the surface concentration.

The interest in LB techniques has increased in recent years due to the special nonlinear optical and electronic characteristics of LB films (*1*,*2*). Because polyaniline is conductive and air stable, polymerizations of substituted anilines on LB troughs were tried and successfully realized (*3-6*).

Meanwhile, it was found that the mean molecular area was decreasing during the polymerization of 2-pentadecyl aniline. Also no polymer was found when the reaction was run at low applied surface pressure, such as 1 mN/m (*4*). However, it was not clear why Mma decreased during the reaction and why no polymer was formed at lower surface pressure. In this paper, the cause of Mma decrease is revealed and the effect of surface pressure is discussed. Moreover, it is shown that LB techniques may be a good probe to observe and to monitor polymerizations confined to surfaces on LB troughs, like dilatometry which is used to observe bulk polymerizations (*7*).

In the first section we present results from the monomer and selected model compounds at the air/water interface which are useful in interpreting the subsequent polymerization reaction. The second section describes the polymerization reaction and how the LB techniques are used to monitor the polymerization rate. The third section describes the effect of applied surface pressure on the polymerization reaction.

The experimental part is described in detail in the previous paper (*5*).

Results and Discussions

Isotherms of 2-Pentadecyl Aniline, Stearic Acid and 4-Hexadecyl Aniline. It was shown in a previous paper (*4*) that the onset Mma of the monomer (2-pentadecyl aniline) is about 80 Å^2 on a 0.5 M sulfuric acid subphase. However, the area of poly (2-pentadecyl aniline) per unit was only about 40 Å^2 (unpublished data). The area difference per unit between monomer and polymer, we suppose, is the cause of Mma decrease during the polymerization of 2-pentadecyl aniline. Compared with the area of a long alkyl sidechain or a benzene ring, the onset Mma of the monomer was exceptionally large. To understand this behavior, stearic acid and 4-pentadecyl aniline are used as model compounds for comparison.

The structures of 2-pentadecyl aniline, stearic acid and 4-hexadecyl aniline are shown in Figure 1.

Figures 2 and 3 show surface pressure vs surface area isotherms of 2-pentadecyl aniline on water (Fig. 2a) and on 0.5 M sulfuric acid (Fig. 3a). These are compared with stearic acid (Figs. 2b and 3b) and 4-hexadecyl aniline (Figs. 2c and 3c). All three compounds spread on both subphases to give repeatable isotherms which show little hysteresis upon subsequent decompression. The monolayers of these compounds are also stable as indicated by very small changes in mean molecular area with time under various constant applied surface pressures. From Figure 2 it can be seen that the 2-pentadecyl aniline isotherm is shifted to substantially higher surface areas than the other two isotherms on water, while its collapse pressure is considerably less than those of both stearic acid and 4-hexadecyl aniline. Additionally, on the acidic subphase the isotherm of 2-pentadecyl aniline is shifted to still higher surface areas. Both the surface pressure onset areas and collapse points of the other compounds are considerably less effected by the acidity of the subphase.

It is well known that at high applied surface pressures, stearic acid side chains are largely in a *trans* conformation, close packed, and rather well ordered (*2*). Similarly, one can expect that the 4-hexadecyl aniline side chains are ordered at high pressures, but not as well packed as stearic acid due to the bulky aromatic head group. The surface pressure onsets and collapse points of stearic acid and 4-hexadecyl aniline on 0.5M sulfuric acid subphase are 24.6 Å^2 / 25.2 Å^2 and 19.8 Å^2 / 23.3 Å^2 respectively, which are nearly the same as those on the water subphase, 24.5 Å^2 / 25.1 Å^2 and 19.8 Å^2 / 23.0 Å^2. We suppose, this indicates that the conformation of the stearic acid or 4-hexadecyl aniline molecules is basically not effected by the acidity of the subphase. The proximity of the onsets also indicates that the head group of the 4-hexadecyl aniline is not strongly hydrated. For steric reasons, the aromatic head group is expected to be rather perpendicular to the air/water interface instead of laying flat at the surface. Figure 4a shows a pictorial representation of the conformation expected to be assumed by the 4-hexadecyl aniline.

The 2-pentadecyl aniline behaved entirely different from the other two compounds. The onset point of 2-pentadecyl aniline on 0.5M sulfuric acid, 76.5 Å^2, is much greater (27.6 Å^2 larger) than that on the water subphase, 48.9 Å^2. The collapse point of 2-pentadecyl aniline on 0.5M sulfuric acid, 35.8 Å^2, however, is only slightly larger (2.9 Å^2) than that on water, 32.9 Å^2. As 4-hexadecyl aniline and 2-pentadecyl aniline are chemically similar, the difference in the surface pressure onset is expected to be due largely to the substitution position rather than hydration. Additional insight into the behavior of 2-pentadecyl aniline was obtained by a study of the isotherms as a function of the subphase acid concentration shown in Figure 5.

From Figure 5, it is seen that there is little difference in the isotherms at pH 4 or higher. Below pH 4 the surface pressure onset points obviously increase to higher areas with decreasing pH. We suppose that the increase in the onset point may result from the dissociation of the amine group and its protonation reaction. Assuming that the onset point becomes larger as the concentration of protonated species increases, one can deduce that the maximum of ∂Mma/∂pH, the maximum of Mma change/acidity change, occurs at pK_a = pH. From Figure 5 it can be qualitatively estimated that the maximum of ∂Mma/∂pH is in the range of pH 2 ~ 3. This is to say that the K_a of the 2-pentadecyl aniline monolayer is about $10^{-2} \sim 10^{-3}$ which is about 10^2 higher than that of aniline in solution(8) After the protonated species form, the conformation of 2-pentadecyl aniline molecules may change due to the static effect which pulls the amine cation downward as shown pictorially in Figure 4b. As shown in Figure 4b, as the amine group is tilted down towards the water, *gauche* conformations must be introduced in the alkyl side chain and a portion of the side chain may occupy the interface with the aromatic groups. This accounts for the large increase in the mean molecular areas between the isotherms of 2- and 4-substituted anilines. The large onset area of 76.5 Å^2 for 2-pentadecyl aniline on the 0.5M sulfuric acid surface, 51.3 Å^2 more than that of 4-hexadecyl aniline, means that in addition to the aromatic ring, at least several CH_2 units of the pentadecyl side chain contribute to the steric interactions on the surface.

In both Figures 2 and 3, the isotherms of 2-pentadecyl aniline have a considerably different shape than those of the other compounds. The long gentle curved shapes of these isotherms are in contrast to the sharply sloped, nearly linear isotherms of the other compounds. It is expected that as the monolayer of 2-pentadecyl aniline is compressed on 0.5M sulfuric acid, the benzene ring is turned and the side chain is somewhat straightened. In other words, as the molecule is compressed, considerable energy is put into changing its conformation at the surface.

In the case of 2-pentadecyl aniline, the work done upon compressing the monolayer, we suppose, is basically contributed to the "twist energy" due to straigtening of the pentadecyl chain. From Figure 2a, the twist energy is estimated in the range of one to several kilocalories per mole. However, in the cases of stearic acid and 4-hexadecyl aniline, the long side chain is supposed to be basically perpendicular during compressing.

From the above discussion one can see that the isotherms of all the compounds varied with different environmental conditions, especially those of 2-pentadecyl aniline. The changes in the isotherms may be related with the structure of monolayer.

The LB Polymerization of 2-Pentadecyl Aniline. When 2-pentadecyl aniline polymerizes, two hydrogen atoms per monomer are lost and covalent bonds link the monomers together. Analogous to vinyl polymerizations, the replacement of the two Van der Waals distances between unreacted monomer molecules by two shorter covalent bond distances results in a net densification of the compound upon polymerization. This allows for the polymerization reaction to be studied by the technique of dilatometry (*7*). Similar densification occurs in a monolayer at the Langmuir trough, allowing the polymerization to be studied by monitoring the mean molecular area or barrier speed as a function of reaction time. Typical curves obtained in the LB polymerization of 2-pentadecyl aniline are shown in Figure 6.

This polymerization reaction was performed at 27°C and under a constant applied surface pressure of 30 mN/m. The isotherm of the polymerized material is reproducible with little hysteresis upon subsequent decompression. During the reaction, the mean molecular area is observed to decrease monotonically from approximately 42 $Å^2$ to a value of 22 $Å^2$ after 34 min at the end of the polymerization as shown in Figure 6. This change in surface area is much larger than the bulk density change normally associated with a polymerization. We suppose that the surface area change consists of two components. One is the densification associated with forming covalent bonds and the other is due to conformation changes of the monomer upon polymerization. Aniline polymerizes primarily in the 1 and 4 positions. To polymerize, 2-pentadecyl aniline monomers must change conformation. Upon polymerization, the side chain tilt associated with the monomer conformation can easily straighten to form a more tightly packed conformation with more *trans* content.

The initial mean molecular area (Mma_o) on a rectangular trough can be expressed as follows:

$$Mma_o = 1.66\times10^{-10}\,(L \times W)/\,M \quad (Å^2/\text{molecule}) \qquad (1)$$

where L is the length of the subphase on the LB trough covered by the monomer in mm, W is the width of the subphase on the LB trough covered by the monolayer in mm, and M is the number of moles of monomer spread.

Assuming the Mma change is only due to polymerization and to simplify calculations assuming this change is a constant for all reaction steps under same polymerization conditions, the Mma (in Å^2/molecule) at a given reaction time may be calculated by:

$$\mathrm{Mma}(t) = 1.66\times10^{-10}(L \times W - 10^{-14} n_t \times \Delta\mathrm{Mma})/\ M \qquad (2)$$

Where n_t is the number of the monomer molecules having polymerized at time, t, and ΔMma is the change in Mma (Å^2/molecule) due to polymerization.

The average barrier speed (BS), the time derivative of the barrier displacement needed to maintain constant pressure, is also shown in Figure 6. BS increases at the beginning of the reaction, then subsequently decreases to zero as the polymerization terminates.

BS can be written in the following form:

$$BS = \Delta l/\Delta t \qquad (\mathrm{mm/min}) \qquad (3)$$

Where Δl represents the distance the barrier has moved in the time interval Δt. From equations 2 and 3, one may deduce the relationship between BS and Mma as follows The relationship between BS and Mma is differential:

$$BS = (L/\mathrm{Mma}_0)\ \partial\mathrm{Mma}/\partial t \qquad (4)$$

BS is proportional to ∂Mma/∂t and inversely proportional to the Mma_0 on a given trough. Figure 7 shows experimental data from the polymerization of three different spread volumes of 2-pentadecyl aniline. From Figure 7, it is seen that ∂Mma/∂t is independent of the amount of spread monomer, which is in accordance with equation 2.

The PR can then be written in the following form:

$$PR = \Delta n/\Delta t \qquad (\mathrm{molecule/min}) \qquad (5)$$

where Δn represents the number of the monomer molecules having polymerized in Δt. From equations 2, 3 and 5, one may have

$$PR = -(10^{14}\ W)\ BS/\Delta Mma = -(6.025\times10^{23}\ M/\Delta Mma)\ \partial Mma/\partial t \quad (6)$$

Equation 6 expresses the relationship between the polymerization rate, barrier speed and mean molecular area. As a check on the relationship between BS and the Mma_0 in equation 4, the barrier speed values from Figure 7 can be compared; if equation 4 is obeyed, a constant should be observed. The peak barrier speed values of curves a, b, and c in Figure 7 are 2.42, 4.86 and 7.13 mm/min respectively. The Mma_0 values for these curves are 168.63, 84.31 and 56.21 $Å^2$ respectively. The products of the peak barrier speeds and Mma_0's for the curves in Figure 7 are 408, 410 and 401 $Å^2$ mm/min, which are in very close agreement with the constant predicted by equation 4.

Furthermore, from equation 6, one may estimate the polymerization rate. In the case of Curve b in Figure 7, the ΔMma is approximately 20 $Å^2$, as determined from the difference between Mma_0 and the Mma at time 40 min. (W is 150mm for this trough). Then the polymerization rate at the peak barrier speed is 5.3×10^{15} (molecule/min).

The information such as that shown in Figure 6 may be useful in studying many other polymerization reactions. Assuming the ΔMma is constant under a given set of conditions and due only to polymerization, the polymerization rate is directly proportional to BS and can be conveniently estimated. Therefore, information about when a polymerization starts and finishes, when and how much the highest polymerization rate is, and how the polymerization rate changes during the polymerization may be gained from the barrier speed curves. The Mma change may be also used as a convenient measure of the conversion of monomer to polymer as a function of reaction time. Furthermore, LB polymerizations of monomers such as 2-pentadecyl aniline use only tens of micrograms of monomer per experiment and are fast, convenient, and highly reproducible.

The LB polymerization of 2-pentadecyl aniline also has some fundamental differences compared to typical bulk polymerization reactions. The first of these is that the reaction is confined to a surface. The reaction is not expected to be strictly two-dimensional in nature, however, as the ammonium peroxydisulfate oxidizing agent diffuses to the monolayer from the bulk subphase. The monomers are also likely to undergo significant vertical displacement at the surface due to thermal motion and other surface perturbations. Nonetheless, the initial conformation of the compressed monomer monolayer before polymerization starts is both considerably more anisotropic and ordered than that attained in a classical polymerization.

The different monomer conformation on the LB trough may affect the polymerization process. For example, in the solution polymerization of 2-alkyl anilines under the same polymerization conditions, the yields of poly(2-methylaniline), poly(2-ethylaniline) and poly(2-propylaniline) were observed to be 80%, 16% and 2% respectively (*9*). The cause of this big difference in yields was steric hindrance from the side chain. On the other hand, the yield of the LB polymerization of 2-pentadecyl aniline is larger than 90%. This may be due to the fact that the monomer is "pre-oriented" in sterically favorable conformations before the polymerization.

Finally, once the LB polymerization is in progress, the topological constraints on the growing chains are considerably different from what would be seen in a bulk polymerization reaction. This may affect the polymerization process.

Further investigations are in progress to investigate the above effects.

The Effect of Applied Surface Pressure. Previous studies (*4*) have found that the polymerization of 2-pentadecyl aniline occurred at high surface pressure, 30mN/m, but no polymer was found at lower surface pressure, 1 mN/m, in 34 min. The LB polymerization of 2-pentadecyl aniline can be done under conditions of certain constant applied surface pressure. It is therefore interesting to study the effect of surface pressure upon the polymerization reaction. Figure 8 shows the effect of different applied surface pressures on the Mma vs reaction time curves. The Mma change upon polymerization is seen to depend strongly on the applied surface pressure.

Figure 9 shows plots of BS vs reaction time for the polymerization at different applied surface pressure, π. It is seen that the peak values of the barrier speed, BS(P), increase, go through a maximum, and then decrease as a function of increasing surface pressure. However, as shown in equation 6, PR depends not only on the barrier speed, but also on ΔMma. Here, the change in ΔMma under different applied surface pressures is not negligible. The different ΔMma values were taken from Figure 8 and the peak polymerization rates, PR(P), are collected in Table I. This table shows that PR(P) do increase with the increase of surface pressure over the entire experimental range.

Table I Polymerization data at different surface pressures

π (mN/m)	0.5	1	2	3	5	10	20	30	35
ΔMma ($-Å^2$)	34.8	33.1	31.3	32.8	33.3	28.1	24.6	20.1	17.5
BS(P)(mm/min)	0.74	0.99	2.36	4.20	5.85	5.79	5.34	4.89	4.62
PR(P)*	3.20	4.50	11.3	19.2	26.3	30.9	32.5	36.6	39.5
tc (min)	403	312	129	81.5	62.6	48.4	37.8	33.6	28.6
BS(S)(mm/min)	0.30	0.30	0.30	0.32	0.44	0.69	1.41	2.15	2.17
PR(S)*	1.29	1.36	1.44	1.45	1.98	3.68	8.60	16.1	18.6

* The units of PR(P) and PR(S) are 10^{14} molecules/min.

The time to complete the polymerization, t_c, was obtained from Figure 9 as the intercept of the tangent to the inflection point and a line through the baseline after complete reaction. These values are shown in Table I. The t_c increases as the surface pressure decreases , especially at low values of π. The initial barrier speed, BS(S), is also shown in Table I and increases with increasing π. All of the above trends may be expecte

The π is somewhat analogous to the pressure, P, in the bulk. The P has the unit of "force/area" in three dimensions while π has the unit of "force/length" in two dimensions. In common gas state reactions, the effect of pressure changes is mainly one of changing the reactant concentrations. However, in the LB polymerization of 2-pentadecyl aniline, the observed effect of applied surface pressure on the polymerization rate might not be primarily due to changing the average distance between reacting monomers and thus their collision frequency. Here on a trough, the surface area changes under the constant applied surface pressure during the polymerization. This indicates that the apparent activation energy for the polymerization reaction could be affected.

Polymerization experiments were performed on mixed monolayers to investigate these effects. From isotherm studies (*8*), stearic acid appeared to form a compatible mixture with 2-pentadecyl aniline. Furthermore, when stearic acid was spread on the Langmuir trough under conditions that would result in the polymerization of 2-pentadecyl aniline, no measurable surface area change was observed. Stearic acid was thus considered to be an "inert" blending agent.

A first mixture experiment involved polymerizing pure monomer and a mixture at the same applied surface pressure. If the polymerization rate were dominated by the average distance between aniline monomers, the polymerization rates would be expected to differ substantially. Figure 10 shows that the effect of polymerizing a 3:1 mol ratio (2-pentadecyl aniline : stearic acid) mixture compared to the pure monomer at a constant surface pressure of 30 mN/m. Both the mean molecular area curves and the barrier speed curves indicate that the difference in the polymerization rate is very small. Similar results were also seen for a 3:2 mol ratio mixture. The shift seen between the mean molecular areas of the mixture and the pure 2-pentadecyl aniline curves is due simply to the different areas occupied by the two components at the surface.

Another mixture experiment performed is shown in Figure 11. In this reaction, the applied surface pressure of the mixture was adjusted to be higher than that of the pure monomer so that the average distance between 2-pentadecyl aniline molecules in the pure monomer and mixture was nearly the same at the beginning of the reaction. If the polymerization reaction were dominated by concentration, the initial rates of both curves, as indicated by $\partial Mma/\partial t$, would be nearly the same. It is clearly observed, however that the initial rates are significantly different from each other.

The above mixture experiments indicate that the effect of applied surface pressure on the LB polymerization of 2-pentadecyl aniline is not dominated by simple concentration differences.

As discussed in the first section, the conformations adopted by 2-pentadecyl aniline may vary substantially with the applied surface pressure. As the surface pressure increases, the alkyl side chain is likely to be more perpendicular. This may help to overcome the steric hindrance of the long side chain and help the para position polymerization.

However, the relationships between the barrier speed, applied surface pressure, and t_c are not quantitatively simple. As discussed above and shown in Figure 10, the polymerization rate at constant π and different Mma does not change appreciably. It is useful to discuss these relationships from a kinetics point of view. For example, the relationship between BS(S), the average barrier speed at the start of the polymerization, and applied surface pressure will be discussed below.

In general, under constant surface pressure and constant temperature one may have:

$$d[M]/dt = -K[M]^X \tag{7}$$

where [M] is the surface concentration of the monomer in molecules/Å^2, K is a reaction rate constant and X is the number of the reactant monomer molecules. As is known, K is dependent on the activation energy. Here, the polymerization is carried out under given applied surface pressure and the surface area is changing as the polymerization proceeds. Thus the work, defined by the applied surface pressure times the change in surface area during the polymerization, will contribute to the reaction rate constant like the activation energy term. Then, one may have:

$$K = A\exp(W/kT) \tag{8}$$

where A is a constant and W is the work done during the polymerization. At the starting step of the polymerization, the change in [M] may be negligible and from equations 7 and 8 one may obtain:

$$d[M]/dt = -A[M]_o^X\exp(W/kT). \tag{9}$$

Then from equations 4 and 9:

$$BS(S) = LA[M]_o^{X-1}\exp(W/kT)$$

and
$$\ln(BS(S)[M]_o^{1-X}) = \ln(LA) + W/kT \tag{10}$$

Figure 12 shows the plot of $\ln(BS(S)[M]_0^{1-X})$ vs W at X = 1, 2 and 3. Higher values of X are not necessary because usually few reactions are of three or more molecules. From Figure 12, one may see that the relationship between $\ln(BS(S)[M]_0^{-2})$ and W is not linear at X = 3. The curves for both X = 1 and 2 are much more linear. Because of the experimental error one can not be sure whether the polymerization initiation reaction involves one monomer molecule or two. However, by comparing the curves in Figure 12, X=1 is preferable.

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Captions

Figure 1. The structures of 2-pentadecyl aniline (a), stearic acid (b) and 4-hexadecyl aniline (c)

Figure 2. Surface pressure vs Mma isotherms of the three compounds on a pure water subphase, T = 23 °C, Barrier speed = 50 mm/min..

Figure 3. Surface pressure vs Mma isotherms of the three compounds on a 0.5 M H_2SO_4 subphase, T = 23 °C, Barrier speed = 50 mm/min.

Figure 4. Pictorial view of the conformation of the substituted anilines at the air/aqueous interface.

Figure 5. Surface pressure vs Mma isotherms of 2-pentadecyl aniline on different pH subphases, T = 23°C, Barrier speed = 50 mm/min.

Figure 6. Surface pressure, mean molecular area and average barrier speed vs reaction time during the polymerization of 2-pentadecyl aniline, T = 27 °C, 0.5 M H2SO4, 0.05 M ammonium peroxydisulfate.

Figure 7. Mean molecular area and average barrier speed vs time for different spread amounts of 2-pentadecyl aniline, T = 27 °C, 0.5 M H2SO4, 0.05 M ammonium peroxydisulfate.

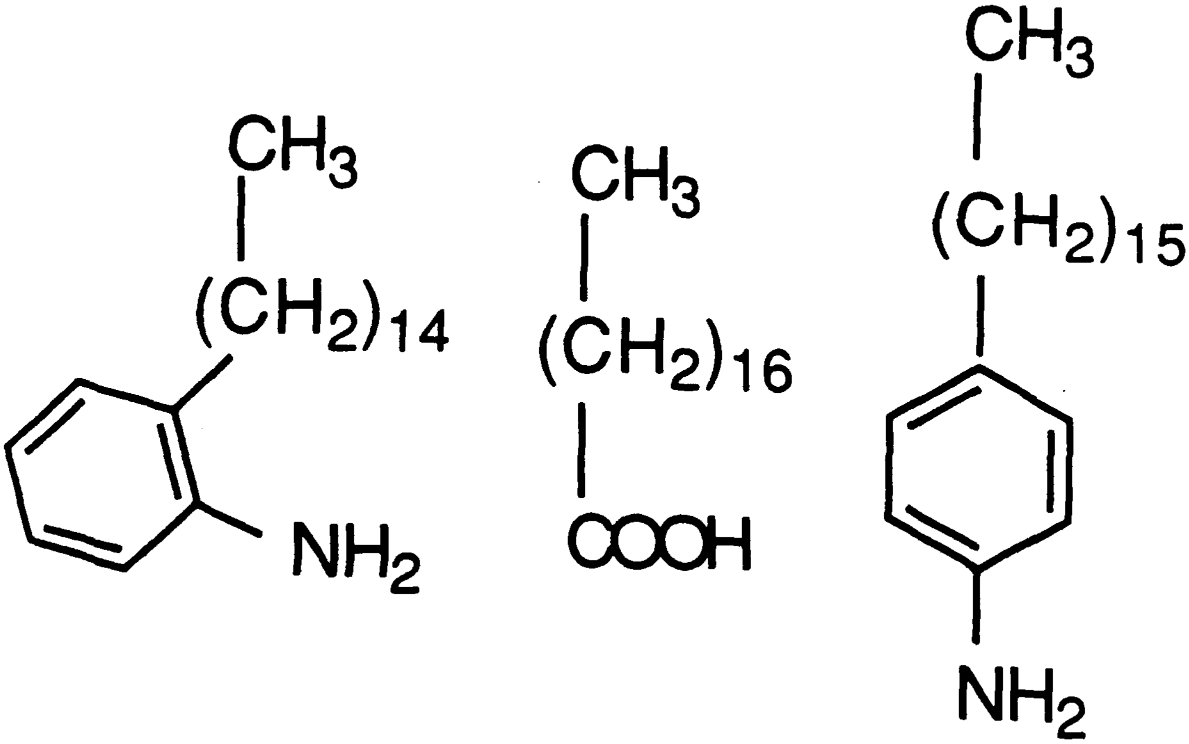
Figure 8. Mean molecular area vs time at different applied surface pressures during the polymerization, T = 27 °C, 0.5 M H2SO4, 0.05 M ammonium peroxydisulfate.

Figure 9. Barrier speed vs time at different applied surface pressures during the polymerization, T = 27 °C, 0.5 M H2SO4, 0.05 M ammonium peroxydisulfate.

Figure 10. Mean molecular area and average barrier speed vs time during the polymerizations of 2-pentadecyl aniline and a 3 : 1 mole ratio blend with stearic acid, π = 30 mN/m, T = 27 °C, 0.5 M H2SO4, 0.05 M ammonium peroxydisulfate.

Figure 11. Mean molecular area vs time during the polymerizations of 2-pentadecyl aniline and a 3 : 2 mole ratio blend with stearic acid, T = 27 °C, 0.5 M H2SO4, 0.05 M ammonium peroxydisulfate.

Figure 12. Kinetics plot of 2-pentadecyl aniline polymerizations.



a b c

a: 2-pentadecyl aniline

b: stearic acid

c: 4-hexadecyl aniline

Figure 1

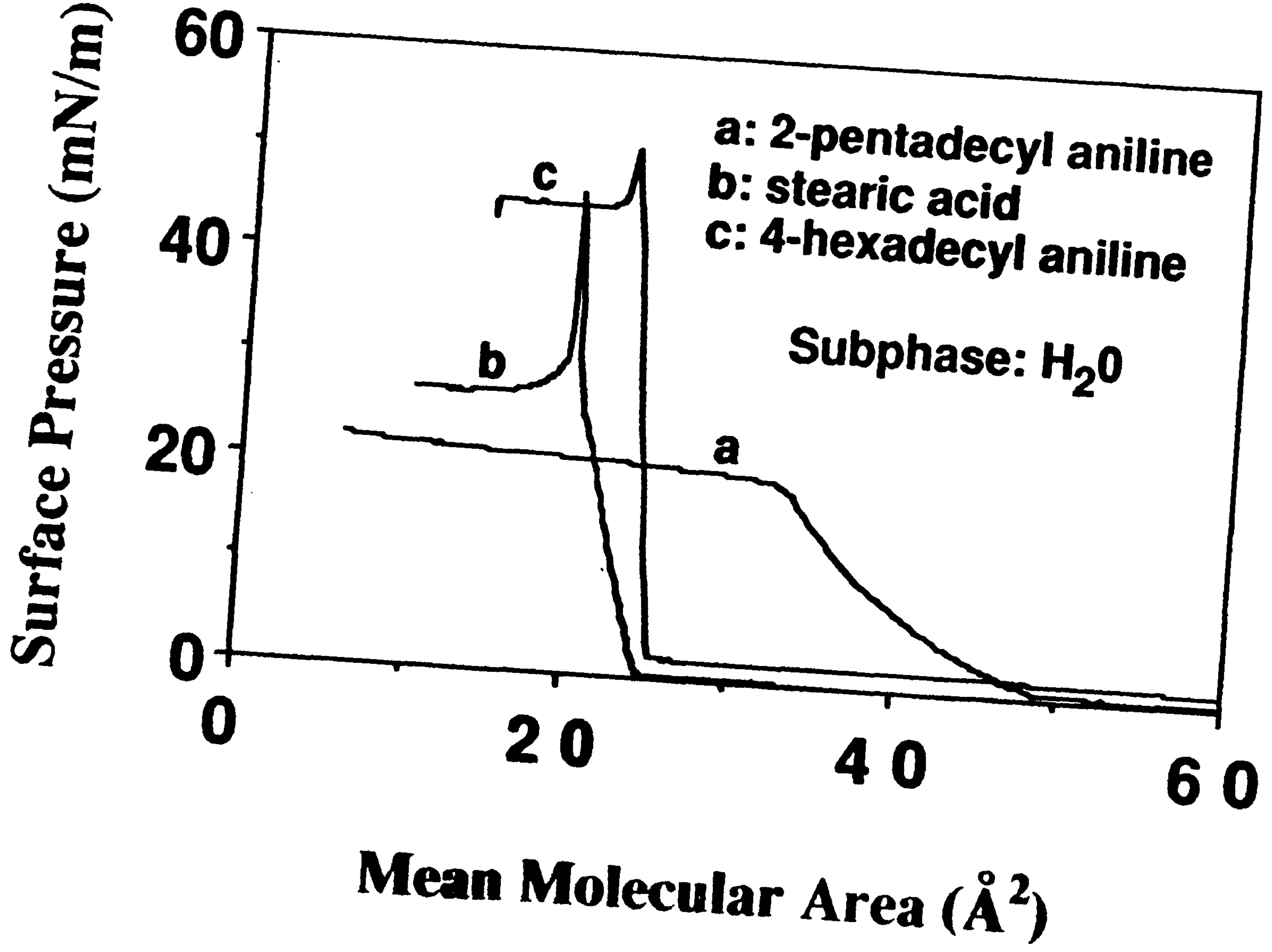

Surface Pressure (mN/m)
60
40
20
0
0
20
40
60
Mean Molecular Area (Å^2)
a: 2-pentadecyl aniline
b: stearic acid
c: 4-hexadecyl aniline
Subphase: H_20
a
b
c

Figure 2

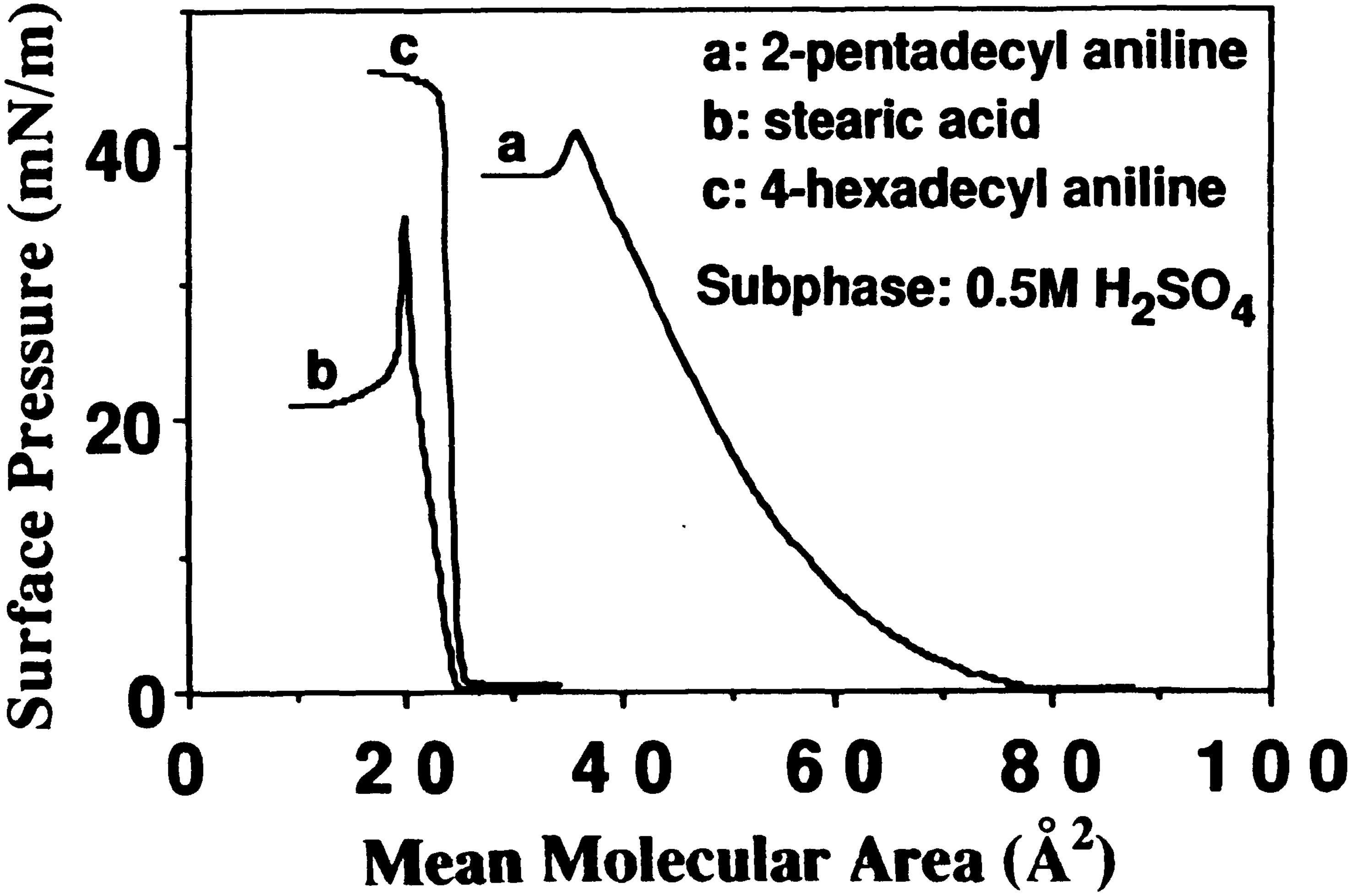
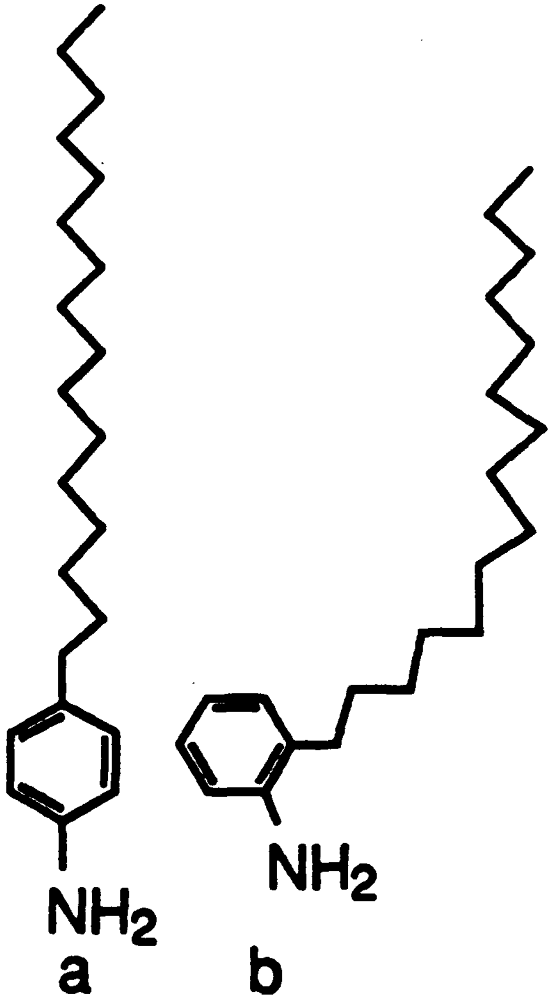

a: 2-pentadecyl aniline
b: stearic acid
c: 4-hexadecyl aniline
Subphase: 0.5M H_2SO_4
a
b
c
Surface Pressure (mN/m)
0
20
40
Mean Molecular Area (Å^2)
0
20
40
60
80
100

Figure 3



a: 4-hexadecyl aniline
b: 2-pentadecyl aniline

Figure 4

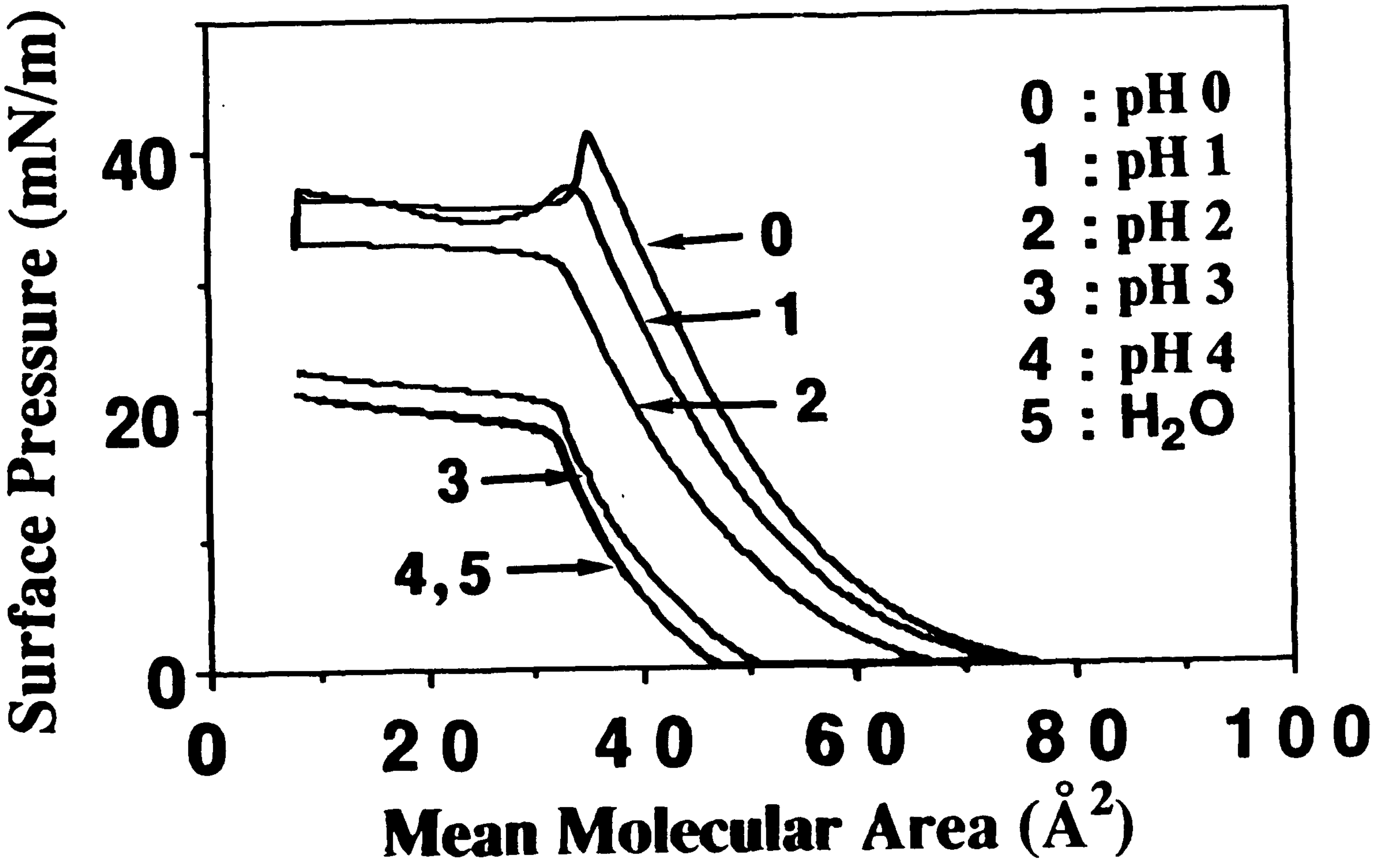

Surface Pressure (mN/m)
40
20
0
0
20
40
60
80
100
Mean Molecular Area (Å^2)
0 : pH 0
1 : pH 1
2 : pH 2
3 : pH 3
4 : pH 4
5 : H_2O
0
1
2
3
4,5

Figure 5

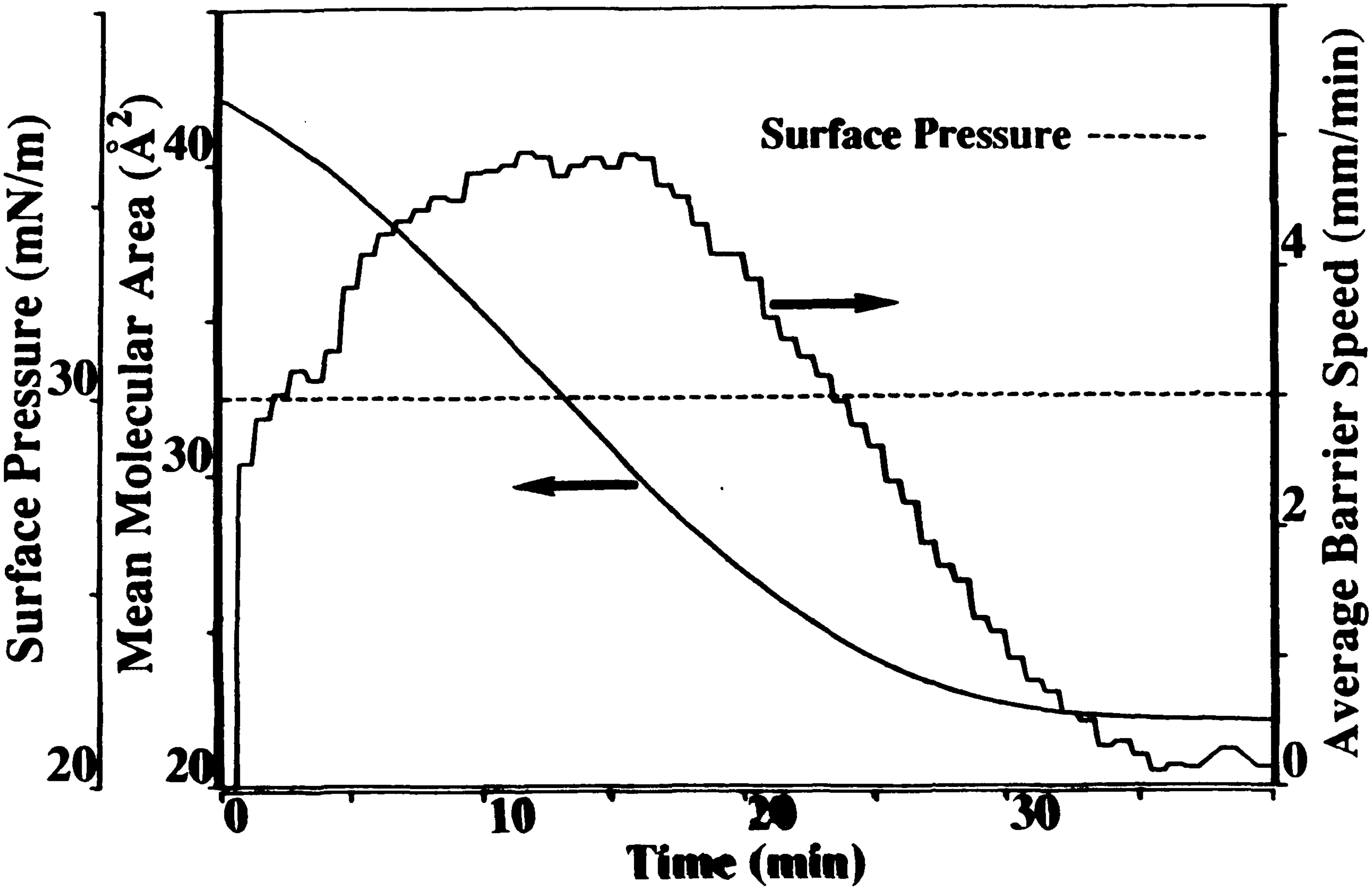

Surface Pressure (mN/m)
20
30
Mean Molecular Area (Å^2)
20
30
40
Surface Pressure --------
Average Barrier Speed (mm/min)
0
2
4
0
10
20
30
Time (min)

Figure 6

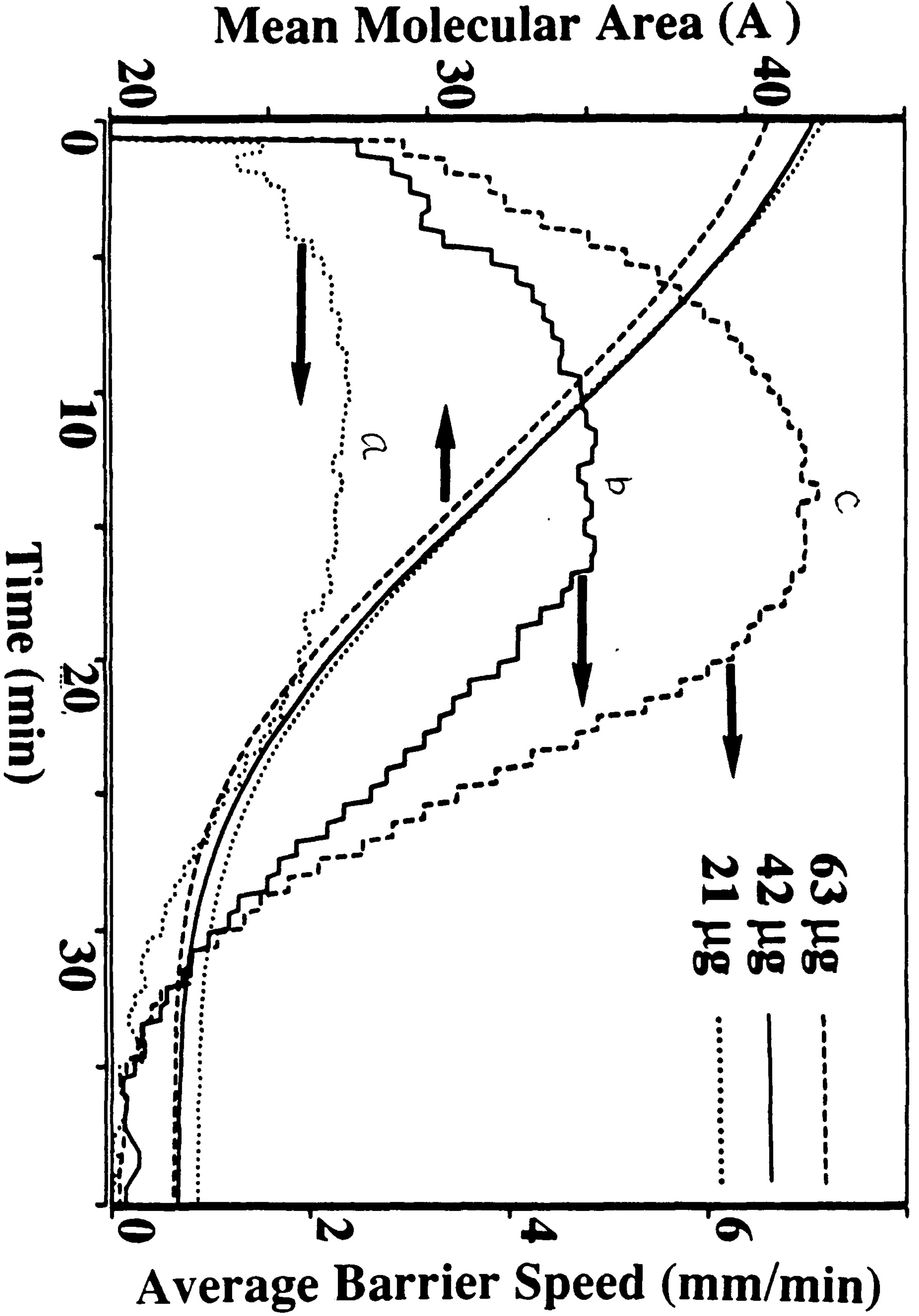

Mean Molecular Area (Å)
20
30
40
0
10
20
30
Time (min)
0
2
4
6
Average Barrier Speed (mm/min)
63 µg
42 µg
21 µg
a
b
c

Figure 7

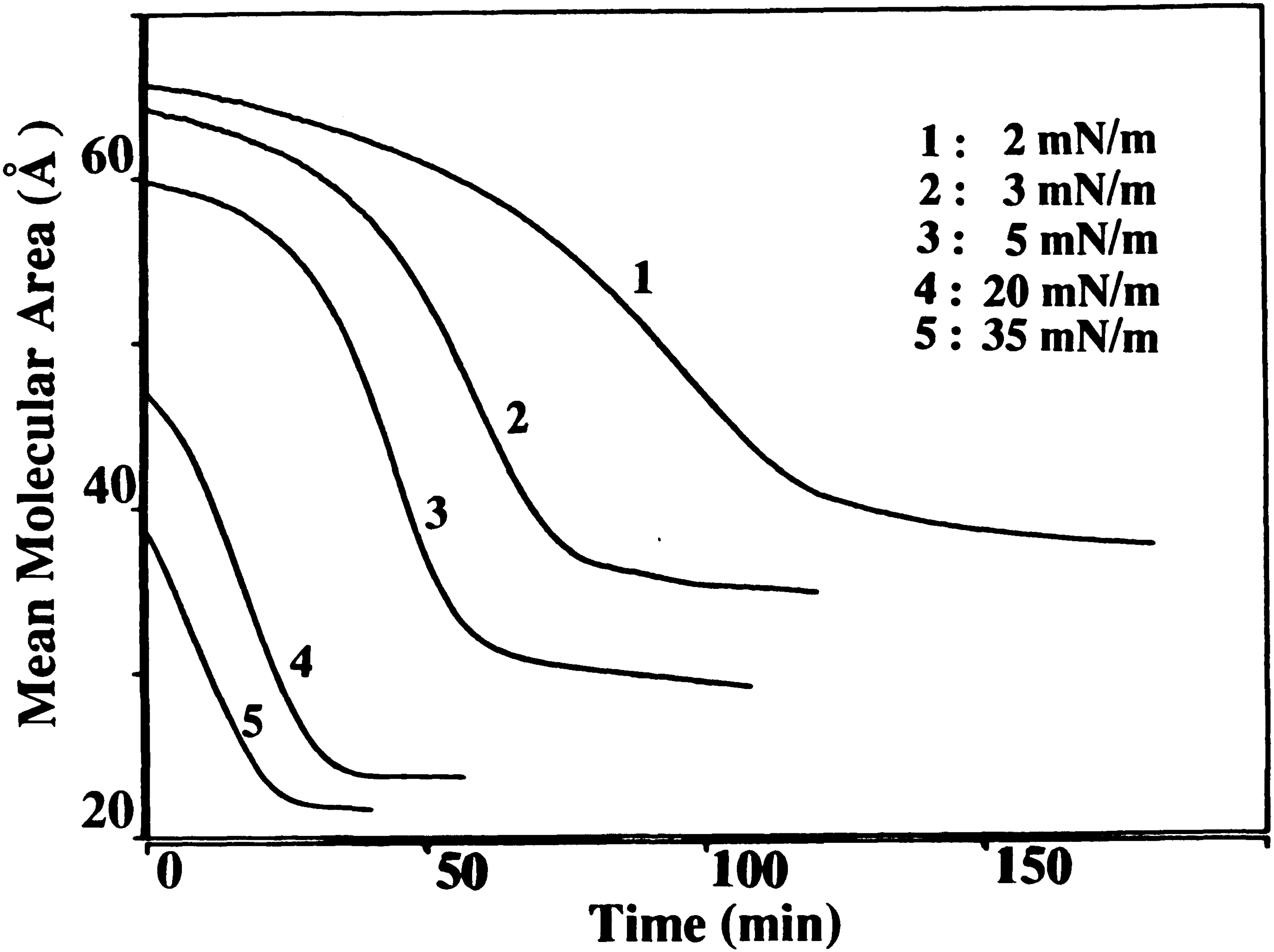

1 : 2 mN/m
2 : 3 mN/m
3 : 5 mN/m
4 : 20 mN/m
5 : 35 mN/m
1
2
3
4
5
Mean Molecular Area (Å)
60
40
20
0
50
100
150
Time (min)

Figure 8

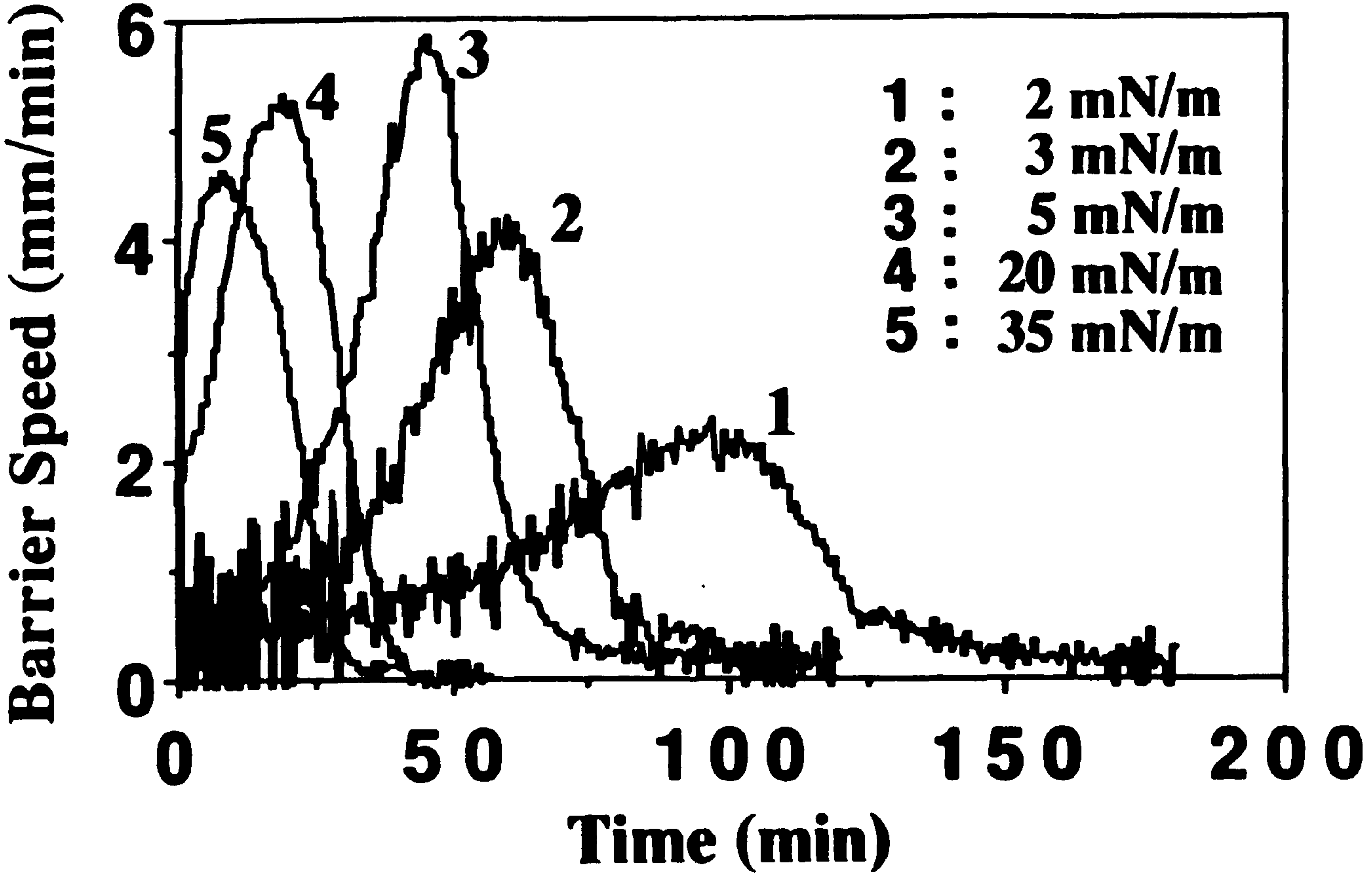

Barrier Speed (mm/min)
6
4
2
0
0
50
100
150
200
Time (min)
1 : 2 mN/m
2 : 3 mN/m
3 : 5 mN/m
4 : 20 mN/m
5 : 35 mN/m
1
2
3
4
5

Figure 9

Table I

π (mN/m)	0.5	1	2	3	5	10	20	30	35
ΔMma (-Å^2)	34.8	33.1	31.3	32.8	33.3	28.1	24.6	20.1	17.5
BS(P)(mm/min)	0.74	0.99	2.36	4.20	5.85	5.79	5.34	4.89	4.62
PR(P)*	3.20	4.50	11.3	19.2	26.3	30.9	32.5	36.6	39.5
t_c (min)	403	312	129	81.5	62.6	48.4	37.8	33.6	28.6
BS(S)(mm/min)	0.30	0.30	0.30	0.32	0.44	0.69	1.41	2.15	2.17
PR(S)*	1.29	1.36	1.44	1.45	1.98	3.68	8.60	16.1	18.6

* The units of PR(P) and PR(S) are 10^{14} molecules/min.

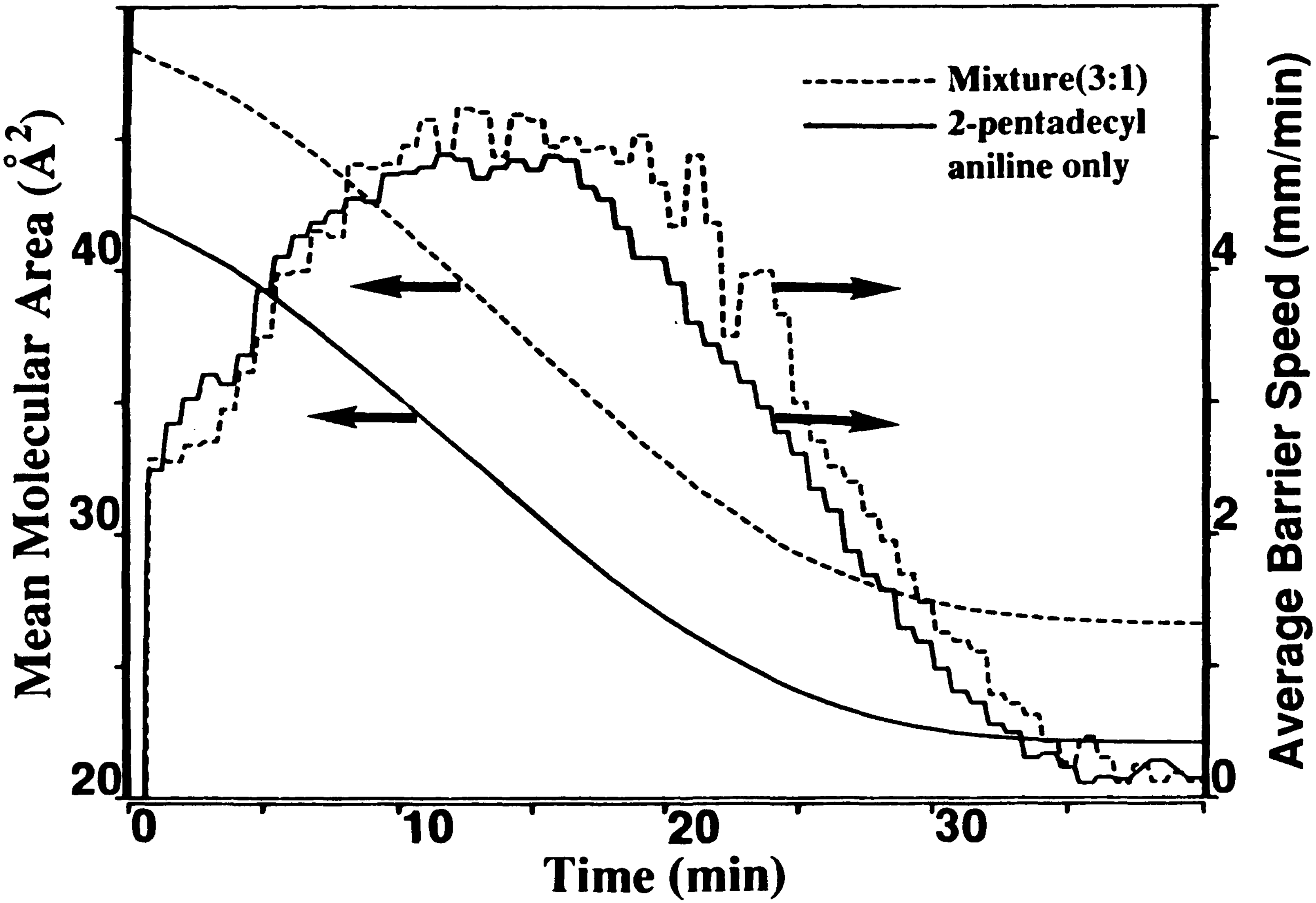
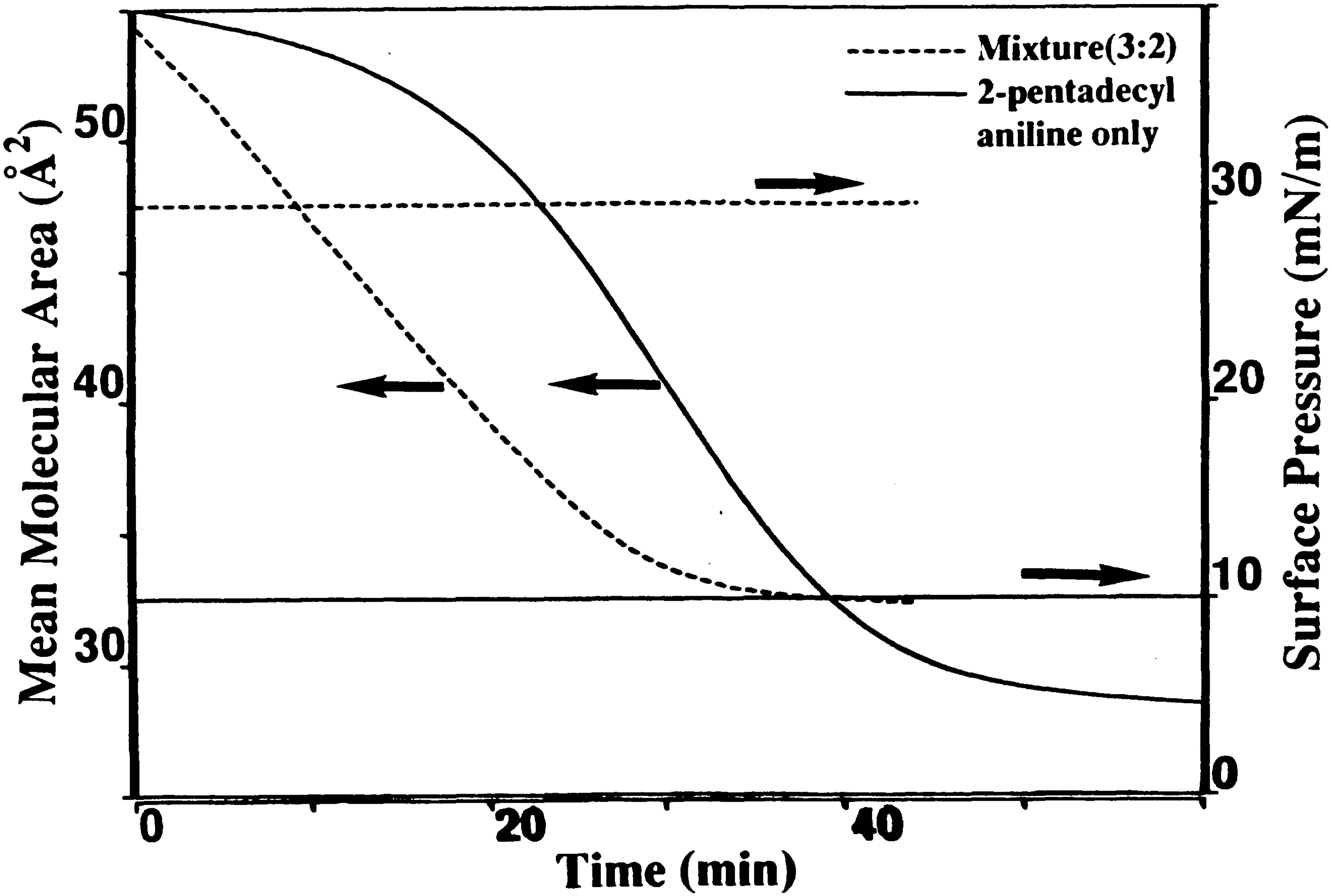

Mixture(3:1)
2-pentadecyl aniline only
Mean Molecular Area ($\mathring{A}^2$)
20
30
40
Average Barrier Speed (mm/min)
0
2
4
0
10
20
30
Time (min)

Figure 10



Mixture(3:2)
2-pentadecyl aniline only
Mean Molecular Area ($\mathring{A}^2$)
50
40
30
Surface Pressure (mN/m)
30
20
10
0
0
20
40
Time (min)

Figure 11

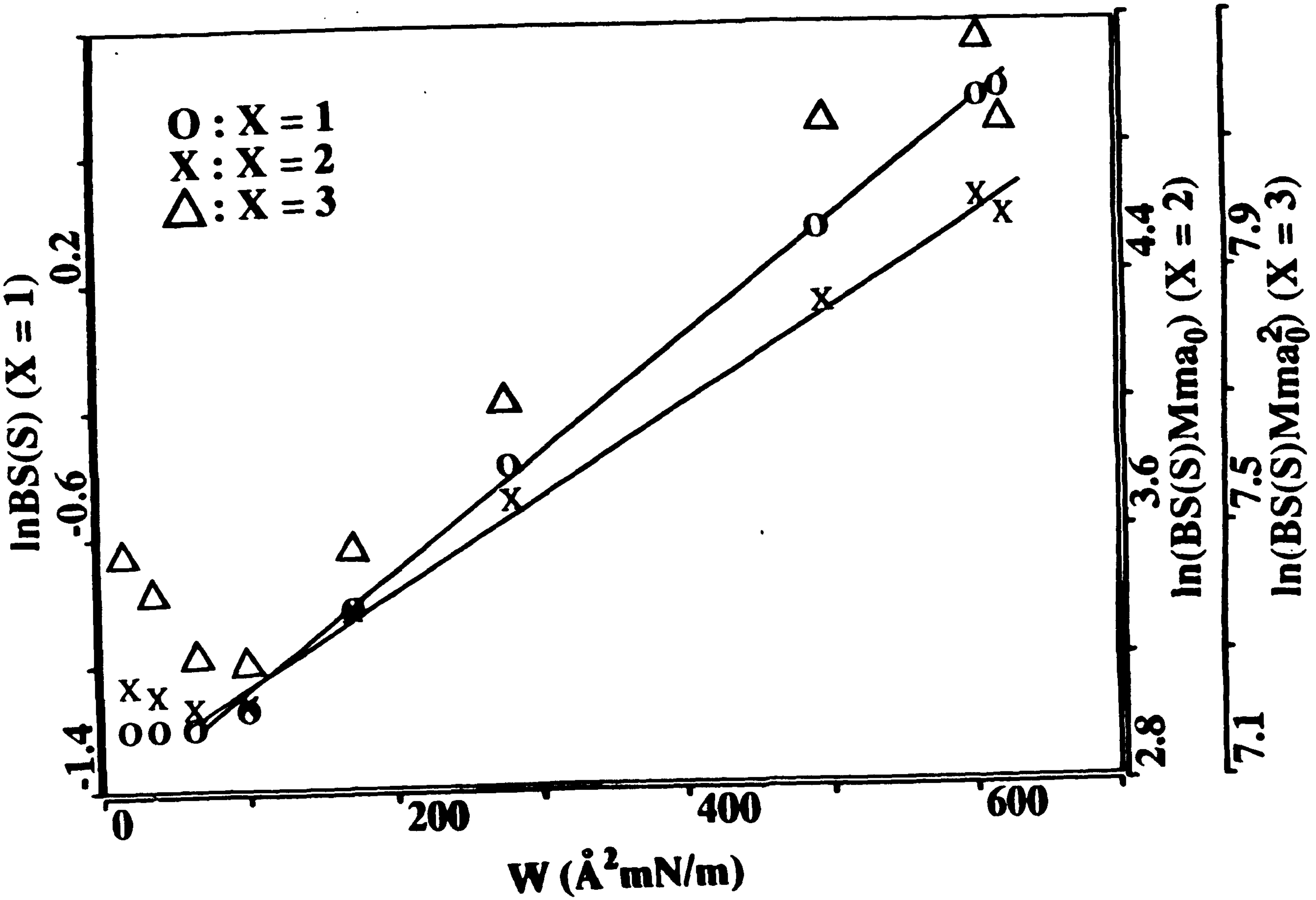

O : X = 1
X : X = 2
Δ : X = 3
lnBS(S) (X = 1)
0.2
-0.6
-1.4
0
200
400
600
W (Å^{2}mN/m)
ln(BS(S)Mma$_0$) (X = 2)
2.8
3.6
4.4
ln(BS(S)Mma$_0^2$) (X = 3)
7.1
7.5
7.9

Figure 12.