

The Langmuir Properties of a Mixed Copolysiloxane Monolayer

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Abstract

A family of linear copolysiloxanes [1-3] substituted with side chains containing carboxylic head groups has been synthesised. The Langmuir properties of the mixed monolayer at the water-air interface has been studied using a single layer Langmuir trough. The area per molecule for the mixed monolayer is calculated theoretically and experimentally. This study has not only shown that there is an excellent agreement between theoretical and experimental values, but has also shown that this mixed monolayer at the water-air interface can be transferred as a monolayer onto a solid substrate.

Key Words: Langmuir properties, polysiloxane.

1. Introduction

The surface pressure [4-5] of a Langmuir monolayer is an important parameter to understand how organic molecules can be formed at the air-water interface and to investigate the characteristic surface behaviour of an organic molecule on the water surface. A surface pressure/area isotherm (Π -A) graph [6] shows a plot of surface pressure as a function of the area of the water surface available to each molecule and is recorded at constant temperature. An ideal Π -A isotherm graph is shown in Figure 1. Gas phase shows there is a little interaction between molecules. In the liquid phase molecules are forced closer together and some interactions occur between them. Molecules are relatively

well oriented and closely packed in the solid phase. Monolayer order is destroyed when molecules reach a critical pressure that is called collapse.

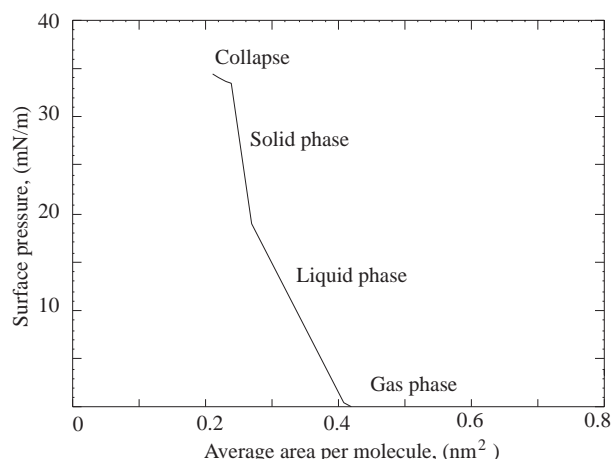


Figure 1. An ideal isotherm graph for a monolayer at the air-water interface.

The area per molecule for this monolayer can be calculated using Eq. (1):

$$a_m = \frac{AM_w}{cN_A V}. \quad (1)$$

A is the area of the water surface enclosed by the trough barriers, M_w is the molecular weight, c is the concentration of the spreading solution, N_A is the Avagadro's number and V is the volume of solution spread.

2. Experimental Work

Figure 2 shows the molecular structure of a linear copolysiloxane. The parameters x and y depend on the degree of substitution along the backbone and the ratio of (R)SiO(CH₃) units (x) to the (CH₃)₂SiO(y) units would give the fraction of backbone substituted with aromatic side chains. Material (A) has x = 7 and y = 6; material (B) has x = 10 and y = 17. Two materials are used to form a mixed monolayer system. In this work an A/B (60:40) mixed system is prepared using 60 % of A and 40 % of B copolysiloxane. Each material (A, B and A/B (60:40)) is dissolved in a 1:1 ratio of chloroform and 2-ethoxyethylacetate and is used to investigate the Langmuir properties of their monolayers using a single layer Langmuir trough [7-8]. All solutions are spread with each drop applied in a different position on the water surface. A time period of 15 minutes is allowed for the solvent to evaporate before the area enclosed by the barriers is reduced. The Π -A isotherm graph of A, B and A/B (60:40) with total concentration of 0.2 mg ml⁻¹ is recorded at pH \sim 6.0 and is shown in Figure 3a, b and c.

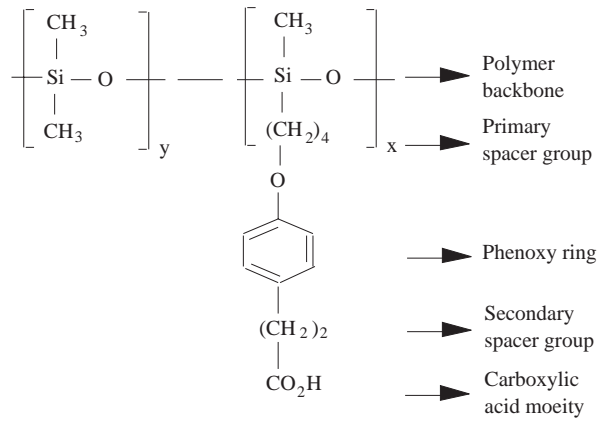


Figure 2. The molecular structure of linear copolysiloxane.

The isotherm characteristics of materials are summarised in Table 1. The values of a_m , b_m and c_m are the area per molecule of A, B and A/B (60:40), respectively as obtained from Eq. (1) and Figure 3a, b and c, respectively. They are experimental results.

Table 1. The characteristics of isotherms of A, B and A/B(60:40) at room temperature.

Material	Gas phase (mN/m)	Liquid phase (mN/m)	Solid phase (mN/m)	Collapse (mN/m)	Area/molecule at 22.5mN/m
A	~ 0 - 2	~ 2 - 20	~ 20 - 42	~ 42	3.83 nm ²
B	~ 0 - 2	~ 2 - 20	~ 20 - 40	~ 40	4.94 nm ²
A/B(60:40)	~ 0 - 2	~ 2 - 20	~ 20 - 42	~ 42	4.25 nm ²

The A/B(60:40) system contained 60% of A and 40% of B and the average area per molecule of A/B(60:40) is expected to be d_m (theoretically), where

$$d_m = a_m(60/100) + b_m(40/100). \quad (2)$$

A comparison can be made between c_m (experimental result) and d_m (theoretical expected result) as follows:

- i) If $c_m > d_m$, this signifies that there are some voids between molecules suggesting that the molecules remain perhaps in the liquid phase.
- ii) If $c_m = d_m$, this signifies that the molecules within the mixed layer are close-packed and very well ordered.
- iii) If $c_m < d_m$, the mixed system could behave as a new material or it is also possible that the molecules at air-water interface could start to collapse. However, the collapse point for A/B(60:40) system is around 42 mN/m in the isotherm graph.

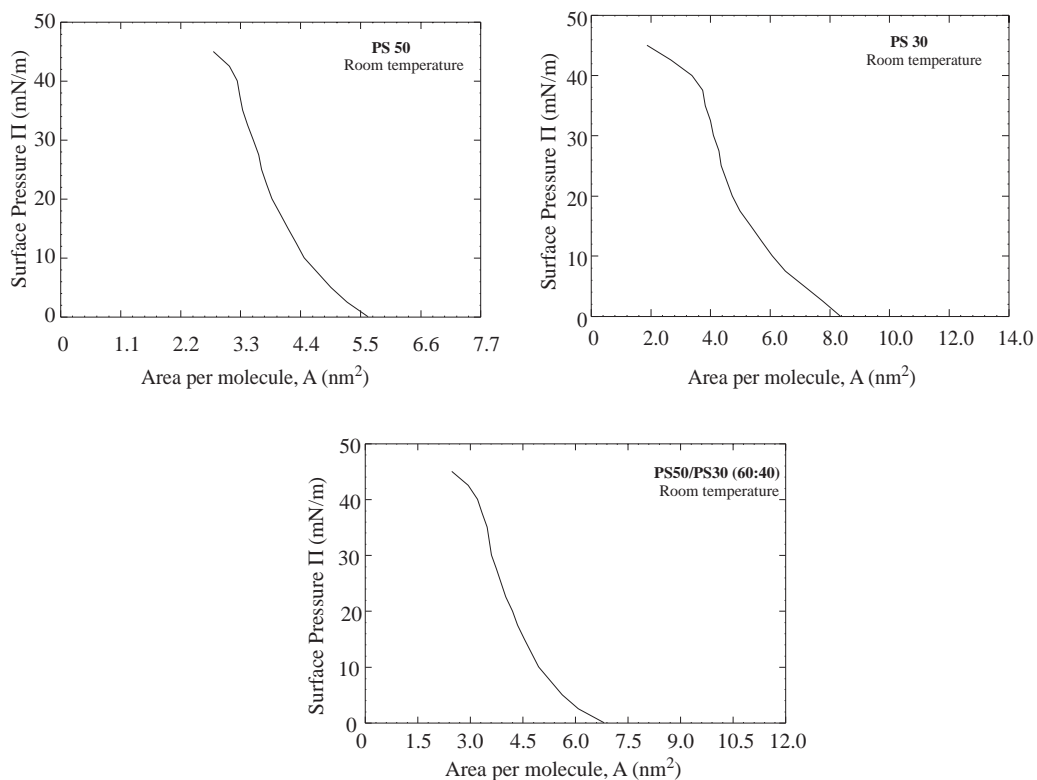


Figure 3. Surface pressure-area (Π - A) isotherm graphs of a) material A, b) material B and c) material A/B(60:40).

The values of c_m and d_m for A/B(60:40) are calculated using Eq. (1) and Eq. (2) at several surface pressure values and results are given in Table 2.

3. Summary

The Langmuir properties of a A/B(60:40) mixed monolayer system containing A and B copolysiloxane is investigated at the water surface. The isotherm results shown in Table 2 indicate that this mixed monolayer are close packed and are ordered very well at the air-water interface. The comparison of the area per molecule for A/B(60:40) mixed system at several different surface pressure values shows that the difference between experimental values of c_m and theoretical values of d_m is around $0.04 \sim 0.02 \text{ nm}^2$. This result indicates that there is an excellent agreement between c_m and d_m so that a closed packed monolayer can be assumed to exist for the mixed monolayer. There are two

possibilities for interpreting this result. First, and most probable, is that the mixed Langmuir film is composed of domains of material A and domains of material B; these domains themselves pack closely together. Secondly, and least probable, is that molecules of the two materials A and B mix together highly efficiently and form mixed domains. This latter explanation is less likely since the packing efficiency of two different components is usually less than that for one single component. Our future work will concentrate on the inclusion of a dye molecule inside the polysiloxane monolayer as a probe to facilitate the study of the polysiloxane domain structure via optical uv-visible spectroscopy.

Table 2. The values of c_m and d_m for the mixed system at several surface pressure.

Surface pressure	c_m (Experimental)	d_m (Theoretical)	$(d_m - c_m)$
20 mN/m	4.40 ± 0.01	4.44 ± 0.01	0.04 ± 0.01
22.5 mN/m	4.25 ± 0.01	4.27 ± 0.01	0.02 ± 0.01
25 mN/m	4.10 ± 0.01	4.14 ± 0.01	0.04 ± 0.01
27.5 mN/m	3.94 ± 0.01	3.90 ± 0.01	$- 0.04 \pm 0.01$
30 mN/m	3.84 ± 0.01	3.86 ± 0.01	0.02 ± 0.01

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