Colloid Science

Polymethylmethacrylate and stearic acid compatibility in monolayers*)

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Abstract: Mixed monolayers of polymethylmethacrylate (PMMA) and stearic acid (SA) on substrates with different pH are examined at 25°C.

The spreading isotherms of the pure components and their mixtures in different molar ratios indicate a critical pH value of the support, above which the components are miscible.

This limiting pH value, which is confirmed also by surface potential measurements, allows a sufficient ionization of the carboxylic acid.

Key words: Binary system, compatibility in monolayers, ionizable monolayers, degree of dissociation.

Introduction

It has been demonstrated in previous studies [1] that a substance of high molecular weight and a low molecular weight compound are surface compatible when at least one of them contains ionizable groups.

It has also been shown that when the substances are neither ionic nor ionizable, the surface compatibility can be attributed to attractive interactions between the hydrophobic chains [2]; in this case it is conditioned by a favourable (i.e. almost parallel) orientation of the hydrophobic chains of the two components.

When the compounds contain ionizable groups, the compatibility is possible even if the chains are not correctly oriented, this however is possible only if one of the two components is “sufficiently” ionized [3].

The aim of this work is to quantify the term “sufficiently” and to establish the degree of dissociation of the low molecular weight substance above and below which the surface compatibility could or could not occur.

Stearic acid (SA) and polymethylmethacrylate (PMMA) were chosen because we could demonstrate that compatibility depends on the degree of dissociation of the stearic acid [3].

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Experimental

Polymethylmethacrylate (PMMA) (Aldrich Chemical Company) had an average molecular weight of 490,000 (by viscosimetry). Stearic acid (SA) was supplied by Carlo Erba, Milan. High purity chloroform (Merck Company) was used as spreading solvent.

A pH of 8.3 of the substrate was obtained by a 0.1 M solution of Na2B4O7·10H2O (Merck Company) in bidistilled water purified of colloids with active charcoal. 0.1 M HCl was added to maintain pH = 8.3 (ionic strength σ = 0.06 M). For pH = 7.7, 0.1 M NaH2PO4·2H2O (Merck Company) and NaOH in twice distilled water were used (ionic strength σ = 0.093 M). The measurements of surface pressure, surface potential, MIR spectra, spreading and monolayer compression procedures have been described [3, 4, 8].

Isotherms and surface potentials were measured at 25°C ± 0.1°C at the water/air interphase.

The values of the surface pressure were accurate within ± 0.02 m²/mg and the values of the surface potential within ± 3 %. pH of the substrates was measured with a glass electrode with an accuracy of ± 0.1 units.

Results and discussion

PMMA – The spreading isotherms of PMMA on substrates buffered at pH = 8.3 and pH = 7.7 showed no appreciable variations from those previously determined at pH = 10.1 (solutions of 0.1 M NaHCO3 + 0.1 M NaOH) and in solutions containing only 0.01 M NaCl. Therefore, ionic strengths or the kind of ions in support are of minor influence.

The surface potential values of PMMA on the support at pH = 7.7 (Fig. 1) were slightly higher than those...
previously measured on 0.01 M NaCl at pH = 6.7 [3]. This can probably be attributed to the presence of the ions in the support, which increased the ionic strength by about one order of magnitude, \( \sigma = 0.093 \text{ M} \) whereas \( \sigma = 0.01 \text{ M} \) in the previous case [3] and has been verified by other authors [5].

Hence for PMMA monolayers the ionic strength appreciably influences only the value of the surface potential, not the trend of the spreading isotherms.

SA – The spreading isotherms of SA at pH = 8.3 and at pH = 7.7 were strictly comparable to those at pH = 6.7 and at pH = 10.1, previously determined, but the values of \( \Delta V \) as a function of the surface area were similar to those previously reported for pH = 6.7 [3]. The degree of dissociation \( \alpha \) was obtained by the Gouy equation from the surface potential [3]:

\[
\alpha = 21\% \text{ at pH = 8.3}
\]

\[
\alpha = 18\% \text{ at pH = 7.7}
\]

and

\[
\alpha = 3\% \text{ at pH = 6.7}
\]

\[
\alpha = 21\% \text{ at pH = 10.1,}
\]

as previously determined.

The surface ionization is negligible at pH \( \leq 6.7 \). As soon as the pH became slightly nonacidic (pH = 7.7), the surface ionization is considerable, about 18 %, and increased slightly up to pH = 10.1, without appreciable solubility in the support, as previously shown [3].

In order to verify that SA in the monolayer had remained unaltered by the alkaline pH of the support, the monolayers were investigated by MIR.

The MIR spectra obtained from monolayers transferred to germanium support [4, 8] by Langmuir-Blondgett technique, showed the bands of the SA in bulk phase, as reported by other authors [6]. These bands were unaltered; either the stearic acid is transferred from alkaline (pH = 10) or acidic support (pH = 2).

PMMA-SA mixtures. – The isotherms \( \pi - A \) of mixtures of PMMA and SA in different ratios between moles of PMMA monomeric unit and moles of SA (from now on simply molar ratios) were measured at pH = 8.3 and 7.7 at 25 °C. Figure 2 shows the areas as a function of the molar ratios for three surface pressures. At pH = 8.3 considerable negative deviations from additivity of areas occur and this, as widely reported by other authors [7] constitutes a first indication of surface miscibility.

At pH = 7.7 almost linear behaviour indicates ideal miscibility and insolubility in the substrate. To confirm these indications, the behaviour of the collapse pressure was examined as a function of molar ratios. At pH = 7.7 (Fig. 3) the collapse pressure was independent of the molar ratios PMMA/SA and corresponded to that of PMMA (which is lower than that of SA) indicating a lack of miscibility between the components. At pH =