

Adsorption of Surfactant on Polystyrene-Styrene Interfaces*

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Synopsis

The adsorption of sodium dodecyl sulfate on polystyrene-styrene interfaces has been studied. Polystyrene interfaces of 20 and 60% were considered. Initial surfactant concentrations used in the study were 0.0004, 0.0008, and 0.004 mole/l. Two temperature levels, 25 and 75°C., were studied. Results showed no effect of initial surfactant concentration for a 20% interface at 25°C. However, the data for the 60% interface at 25°C. showed an effect of initial surfactant concentration. The apparent anomaly in the results regarding effect of initial surfactant concentration was explained in terms of the behavior of polystyrene-styrene as a mixed adsorbent and the work of Harkins and co-workers, which showed that surfactant adsorption was a function of initial surfactant concentration over certain concentration ranges. Rate of surfactant adsorption appeared to be a function of surfactant adsorption raised to a power. The order of the adsorption appeared to be first-order for the 20% interface and second-order for the 60% interface.

Emulsion and suspension polymerizations are important industrial processes. An important factor in these processes is the adsorption of surfactant by droplets of globules. A literature search showed that several studies had been directed to micelle structure and loci of emulsion polymerization. These included the investigations of Hughes et al.,¹ Harkins and Stearns,²⁻⁴ and Frick et al.⁵ The only work found relating directly to adsorption of surfactant was that of Harkins et al.⁶ who studied adsorption of surfactants on solid polystyrene.

The present work was therefore undertaken to study adsorption of surfactant at polymer-monomer interfaces. Polystyrene-styrene syrups were selected as a system for two reasons. First, most previous emulsion polymerization studies had dealt with such systems. Second, the adsorption studies of Harkins and co-workers had dealt with solid polystyrene.

The experimental procedure used basically involved preparation of polystyrene-styrene syrups, coating metal plates with these syrups, and then immersing these plates in radioactively tagged detergent solutions. Adsorption of detergent was determined by checking the count of detergent

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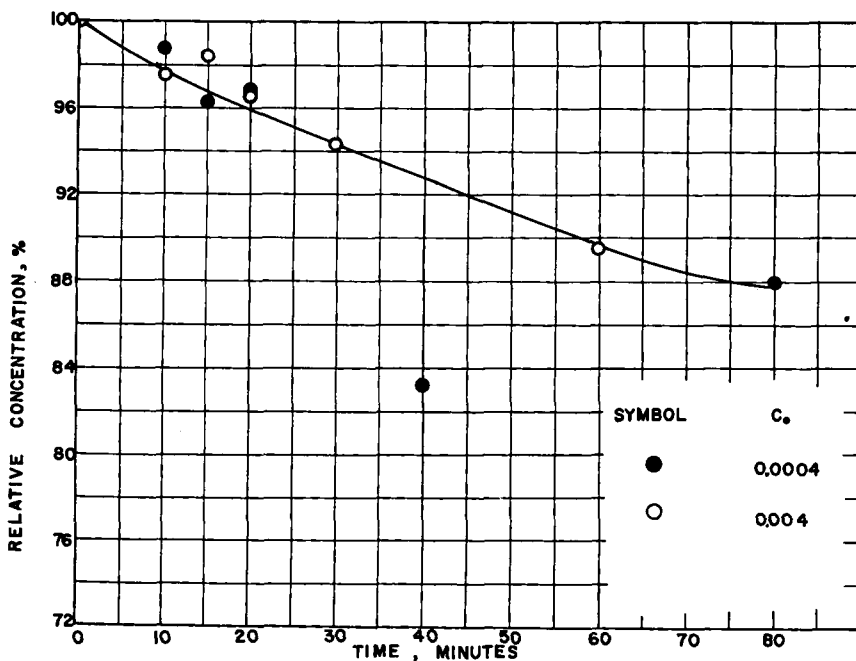


Fig. 1. Surfactant adsorption with time for a 20% polystyrene interface at 25°C.: (●) $C_0 = 0.0004$ mole/l.; (○) $C_0 = 0.004$ mole/l.

solution samples taken at various times. More specifically, detergent samples were withdrawn at various time intervals, dried with a heating lamp, placed in an iron pig and then counted with a number 104 Geiger-Mueller tube. Polystyrene-styrene syrups were prepared by thermal polymerization. The radioactively tagged detergent used was sodium dodecyl sulfate. This was prepared by first sulfating with radioactively tagged ^{35}S sulfuric acid and then saponifying.

Two polystyrene-styrene syrups were studied (20 and 60% polystyrene). Detergent concentration ranged from 0.0004 to 0.004 mole/l. Two temperature levels, 25 and 70°C., were considered.

Experimental results are shown in Figures 1-3. Figure 1 shows data taken with the 20% polystyrene interface at 25°C. As can be seen, the data for both 0.0004 and 0.004 mole/l. appear to yield the same change in relative detergent concentration with time.

However, Figure 2 appears to be anomalous, since different behavior appears to result at different initial detergent concentrations with a 60% polystyrene interface at 25°C.

At first glance the preceding results seem somewhat contradictory. However, upon further reflection possible explanation became apparent.

First, polystyrene-styrene interfaces actually constitute a mixed adsorbent. Therefore, as the percentage of polystyrene changes, the adsorbent itself is altered. Investigations on mixed adsorbents other than poly-

styrene-styrene have been carried out by Schilow et al.⁷ as well as Chowdhury and Pal.⁸ Their studies showed that the amount adsorbed increased as the percentage of one of the components in the mixed adsorbent increased until a maximum was reached. The amount adsorbed then decreased until only one pure component remained (i.e., 100% of the added component). Thus, the differences in adsorption behavior for the 20 and 60% interfaces can possibly be attributed to the increasing percentage of polystyrene in the mixed adsorbent system.

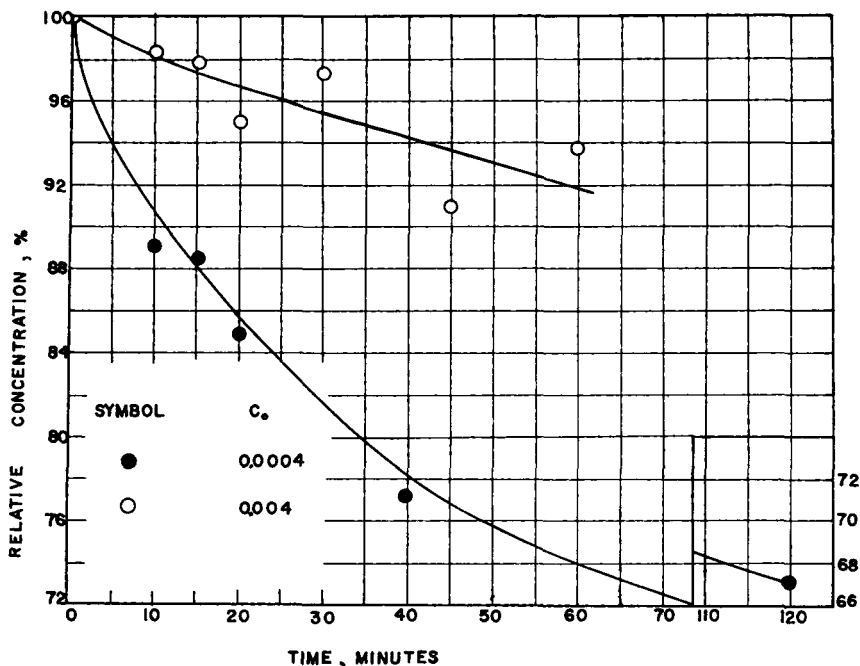


Fig. 2. Surfactant adsorption with time for a 60% polystyrene interface at 25°C.: (●) $C_0 = 0.0004$ mole/l.; (○) $C_0 = 0.004$ mole/l.

Another factor which helps to possibly account for the anomalous behavior of Figures 1, 2, and 3 can be found in the work of Harkins et al.⁶ These investigators found that the equilibrium amount of surfactant adsorbed by a surface increased with increasing initial surfactant concentration; reached a maximum, decreased, and then levelled off at a plateau for increasing surfactant concentration. All curves were of the same shape. However, data at different temperatures for the same surface or for different surfaces at the same temperature were shifted with respect to surfactant concentration. Harkins and co-workers cited the papers of Neff et al.⁹ and Wohl¹⁰ as furnishing theoretical explanations for this behavior.

The data of Figures 1 and 2 can be analyzed by using the results of Harkins and co-workers, even though equilibrium adsorption concentrations were not attained in the present work.

It is possible that the data of Figure 1 represent the plateau portion of the equilibrium amount adsorbed versus surfactant concentration curves, while the data of Figure 2 reflect the changing shape of such a curve. It can therefore be concluded that the apparent anomaly between the data of Figures 1 and 2 can possibly be explained by the results of Harkins and co-workers as well as by the occurrence of mixed adsorbents.

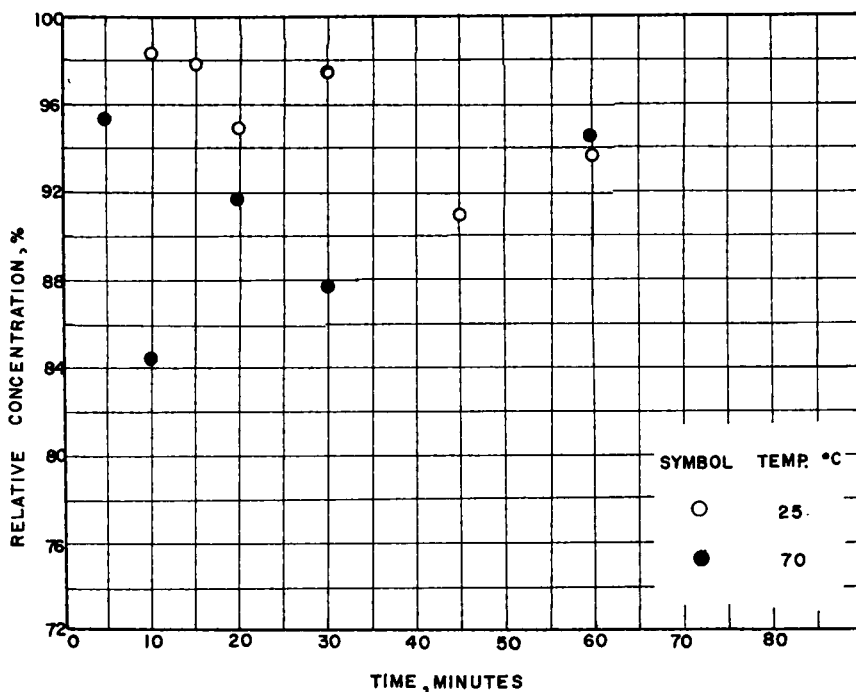


Fig. 3. Comparison of surfactant adsorptions with time for 60% polystyrene interface and initial surfactant concentration of 0.004 mole/l. at temperatures of 25°C. and 70°C.: (○) 25°C.; (●) 70°C.

Figure 3 shows data obtained for a 60% polystyrene interface and an initial detergent concentration of 0.004 mole/l. at two different temperatures, 25 and 70°C. As can be seen, the data show an increased adsorption rate at 70°C. This behavior can be readily explained by the usual temperature effect observed in rate processes, that is, an Arrhenius type relation between a rate constant and temperature.

The data of Figures 1 and 2 were tested with a series of possible rate equations. One form tested was

$$df/dt = -k_1 C_0^{n-1} f^n \quad (1)$$

where $f = C_t/C_0$, C_t is surfactant concentration at time t , C_0 is surfactant concentration at $t = 0$, k_1 is the rate constant, and n is the order of adsorption.

Another form was that proposed by Davies:¹¹

$$df/dt = k_2(1 - \theta)f \quad (2)$$

where f , C_i , C_0 , and t are as above, k_2 is the rate constant, and θ is the fraction of adsorbent surface covered.

It was found that the rate equation (2) proposed by Davies¹¹ could be used to fit the data of the present study. However, k_2 was found to vary with initial surfactant concentration C_0 , which should not have occurred. Hence, it was felt that Davies' equation was not suitable to describe the rate of adsorption in the present study.

Tests of the data with eq. (1) yielded mixed results. It was found that the data of Figure 1 appeared to follow a first-order mechanism while the data of the lower curve of Figure 2 appeared to be second-order. The mechanism for the upper curve of Figure 2 is uncertain.

The differences in rate order could possibly be due to the differences in the 20% and 60% interfaces.

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Résumé

L'adsorption de sulfate de dodécyl-sodium aux interfaces polystyrène-styrène a été étudiée. Des interfaces de 20 à 60% de polystyrène ont été considérées. Les concentrations initiales en agents tensio-actifs utilisés dans cette étude étaient 0.0004, 0.0008 et 0.004 moles/l. On a effectué les mesures à deux températures, 25°C et 75°C. Les résultats ne montraient aucun effet de la concentration initiale en tensio-actif pour une interface de 20% à 25°C. Toutefois, les résultats pour l'interface à 60% à 25°C montraient un effet de cette même concentration. L'anomalie apparente de ces résultats, en ce qui concerne la concentration initiale du tensio-actif était expliquée sur la base du comportement du polystyrène-styrène comme absorbant mixte et du travail de Harkins et collaborateurs qui ont montré que l'adsorption du tensio-actif était fonction de la concentration initiale de celui-ci dans un certain domaine des concentrations. La vitesse d'adsorption du tensio-actif apparaît être une fonction de l'adsorption du tensio-actif élevé à une certaine puissance. L'ordre de cette adsorption apparaît être unitaire pour l'interface à 20% et égal à deux pour l'interface à 60%.

Zusammenfassung

Die Adsorption von Natriumdozecylsulfat an Polystyrol-Styrolgrenzflächen wurde untersucht. Es wurden Grenzflächen mit 20 und 60% Polystyrol verwendet. Die verwendeten Surfactant-Ausgangskonzentrationen waren 0,0004, 0,0008 und 0,004 Mol/l. Die Messungen wurden bei zwei Temperaturen, 25 und 75°C ausgeführt. Die Ergebnisse liessen keinen Einfluss der Surfactant-Ausgangskonzentrationen bei einer 20%-Grenzfläche bei 25°C erkennen. Hingegen zeigten die Ergebnisse für die 60%-Grenzfläche bei 25°C einen solchen Einfluss. Die scheinbare Anomalie dieser Ergebnisse in bezug auf den Einfluss der Surfactant-Ausgangskonzentration wurde als Verhalten von Polystyrol-Styrol als gemischtes Adsorbens und anhand der Arbeiten von Harkine und Mitarbeitern, welche zeigten, dass die Surfactant-Adsorption in gewissen Konzentrationsbereichen eine Funktion der Surfactant-Ausgangskonzentration war, erklärt. Die Geschwindigkeit der Surfactant-Adsorption schien eine Funktion der zu einer Potenz erhobenen Surfactant-Adsorption zu sein. Die Adsorption scheint für die 20%-Grenzfläche von erster Ordnung und für die 60%-Grenzfläche von zweiter Ordnung zu sein.

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