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Abstract

The adsorption of sodium dodecyl sulfate (SDS) and sodium dodecyl benzenesulfonate (SDBS) on poly(vinyl chloride) (PVC) latex particles was investigated. Conductometric titrations were performed to determine the area per surfactant molecule at various temperatures (20-50ºC) and the adsorption isotherms of both emulsifiers were determined at 20ºC from surface tension titration curves. The adsorption data show some deviation with respect to the Langmuir isotherm due to their slight S-shape. The data can nevertheless be fitted very well with a limiting form of the general adsorption equation proposed by Zhu and Gu (Adv. Colloid Interface Sci. 37 (1991) 1).

1. Introduction

The adsorption of surfactants on polymer surfaces is an important issue in various industrial processes, namely because of its direct bearing on the colloidal stability and rheological behavior of polymer latexes [1,2]. Emulsion polymerization is one of the best examples of such processes. Indeed, surfactant partition plays a key role in emulsion polymerization, since it controls to a great extent particle nucleation, secondary nucleation, particle size distribution, etc. For this reason, it is essential to have reliable correlations and parameters for predicting surfactant adsorption when developing models of these systems.

Under equilibrium conditions, the surfactant concentrations in the aqueous phase and at the polymer-water interface are uniquely related by the adsorption isotherm [3]. A number of authors have determined adsorption isotherms of (ionic and non-ionic) surfactants on polymer latexes, but the large majority of these studies have been done for polystyrene (PS) [4-12], given its widespread use as model colloid. Consequently, there is a clear need for data on other important systems, of which PVC is an example.

Various methods have been proposed to obtain adsorption isotherms of surfactants on polymer particles. Usually, such methods rely on the monitoring of the equilibrium concentration of free surfactant in the aqueous phase. For the particular case of ionic emulsifiers, we can mention a few alternatives. Paxton [4] measured the adsorption of SDBS on PS and poly(methyl methacrylate) latexes from surface tension titration curves. Brown and Zhao [5] determined adsorption isotherms of the SDS-PS system, at different ionic strengths, by measuring the surface tension of the aqueous phase, after centrifugation of the latex. Zwetsloot and Leyte [6] determined the adsorption isotherm of SDBS on PS from measurements of the latex conductivity (without phase separation). The validity of this approach has nevertheless been

questioned by Stubbs et al. [13], who claim that the small effect of the partitioning of the anion upon the latex conductivity is hidden by the presence of higher concentrations of more conductive sodium ions in the aqueous phase. Turner et al. [9] investigated the adsorption of SDS on flat PS surfaces by neutron reflection and attenuated total reflection infrared spectroscopy. Colombié et al. [10] determined the adsorption of SDS on PS latexes by making use of the serum replacement technique in conjunction with conductivity measurements of the exit stream of the replacement cell. The same system was studied by Lin et al. [11], but using measurements of the latex surface tension. Sefcik et al. [12] investigated the SDS-PS system by analyzing a small amount of filtrate, obtained through utrafiltration, via ion chromatography.

The objective of the current work is to study the adsorption of the two surfactants (SDS and SDBS) most used in the production of PVC latexes by emulsion polymerization. Hopefully, this will provide useful data for the modeling of such process. The technique put forward by Paxton [4] is employed to determine the adsorption isotherms.

2. Experimental

2.1 Materials

Vinyl chloride monomer was supplied by Arkema, with a purity of 99.97%, as indicated by gas chromatography. Ammonium persulfate, APS, (ACS, Acros Organics) was used as initiator. The anionic surfactants, sodium dodecyl sulfate (99%, Acros Organics) and sodium dodecyl benzenesulfonate (88%, Acros Organics), were used as received. No attempt to purify the emulsifiers was made, since our purpose was to study the adsorption of SDS and SDBS as they are used in typical emulsion polymerization runs. Deionized water was used throughout the work.

2.2 Latex Preparation and Characterization

The PVC latex particles were produced via batch emulsion polymerization [14], carried out at 50ºC in a 1.5 L stainless steal reactor. The following recipe was used: 920 g of water, 106 g of monomer, 0.63 g of SDS and 0.23 g of APS. The polymerization was conducted for 6 h (92% conversion), after which the latex was stripped under vacuum for complete removal of the remaining monomer.

Surfactant and residual initiator were removed from the latex by repeatedly passing it over a mixture of anionic and cationic ion-exchange resins (Dowex MR-3, Aldrich). The withdrawal of the ionic species was monitored by measuring the latex conductivity, and it was assumed that the washing step was complete when the conductivity no longer decreased with successive passes over the resin.

At the end of this procedure the polymer content of the latex was 9.1 wt%, as determined by thermogravimetry. By dilution, four other latex solutions were prepared, with polymer contents of 7.0, 5.0, 3.0 and 1.0 wt%.

The particle size distribution of the latex was determined by static light scattering (Coulter LS230). The latex was found to be nearly monodisperse (PI=0.04), with number average diameter $d_{1,0}$=95 nm and volume-to-surface average diameter $d_{3,2}$=104 nm. The surface charge density of the latex was measured by titrating the washed latex with NaOH until the isoelectric point was reached. A value of 7 mC/m^2 was found.

2.3 Conductivity Measurements

Conductometric titrations were done to determine the critical micellar concentration (CMC) and the surface concentration of emulsifier at saturation. Usually, 60 g of cleaned latex (9.1 wt%) or deionized water were placed in a stirred thermostated cell and the emulsifier solution was added using a motor-driven syringe at a rate of 0.5 mL/min. The conductivity of the solution was monitored with a Copenhagen CDM 83 conductivity meter, equipped with a platinum cell. Titrations were conducted at 20.0, 40.0 and 50.0±0.5ºC.

2.4 Surface Tension Measurements

The surface tension measurements were performed with a Krüss K12 automatic tensiometer, equipped with a Du Noüy ring and a Metrohm 665 Dosimat. Normally, 20 g of latex with a given polymer content were added to a small glass vessel and after 10-min wait for thermal equilibrium the series of measurements started. Emulsifier was automatically added as a solution in water, and each increment of emulsifier was followed by 3 min stirring, after which 3 surface tension readings were made. This procedure was repeated up to the end-point, beyond which more surfactant produced

only a slight decrease of the surface tension. All surface tension measurements were made at 20±2ºC. Cleaning the ring during titration was found to be unnecessary.

3. Results and discussion

Table 1 summarizes the data obtained from the conductometric titrations, namely the CMC, the surface concentration at saturation (Γ_{sat}) and the area per surfactant molecule ($a_s = (\Gamma_{sat} N_A)^{-1}$). Note that no Γ_{sat} or a_s values are reported for SDBS. This is because the change of slope at the saturation point is rather faint with this surfactant, making it very hard to determine the breakpoint in an objective manner, particularly when titrating the latex. In addition, the presence of impurities (homologs with different alkyl chain lengths) is likely to exacerbate the situation.

The a_s values found for the SDS-PVC system are somewhat beyond the range (37-42 Å^2) reported by Palmgren [15]. However, as shown subsequently, our results have been confirmed by surface tension measurements, which reinforces their validity. With respect to the CMC of SDBS, the values obtained lie between the value for pure SDBS (1.2 mM) [16] and the value reported for a commercially available product (3.0 mM) [6]. Since the CMC decreases with increasing hydrophobic chain lengths [17], this probably indicates that the SDBS grade used in this work contains a certain amount of homologs with shorter alkyl chains. Concerning the effect of the temperature, we see that it is small, but definite: the CMC increases and Γ_{sat} decreases with increasing temperature.

The adsorption isotherms were determined from a series of surface tension titration curves performed at different polymer contents, according to Paxton's method [4]. The latter is based on the assumption that equal surface tensions indicate equal equilibrium emulsifier concentrations in the aqueous phase ($[S]_w$) and hence equal values of adsorbed emulsifier (Γ). The surface tension titration curves of the PVC latexes with SDS and SDBS are shown in Fig. 1. Surface tension measurements were only performed at room temperature, because of the experimental difficulties of

controlling water evaporation at higher temperatures. Note that the initial value of the latex surface tension is independent of the polymer content and very close to the value for pure water at the temperature of the measurements, as expected.

From the curves in Fig. 1, we can obtain the value of the total surfactant concentration [S], at a given surface tension, for each polymer content. In addition, we have the surfactant material balance equation,

$$[S] = [S]_w + \Gamma \frac{A_p}{V_w} \tag{1}$$

where $A_p = (6m_p)/(r_p d_{3,2})$ is the area of the polymer particles and V_w is the volume of the aqueous phase. Note that A_p/V_w is directly related to the latex polymer content. Therefore, by plotting [S] as a function of A_p/V_w, for a given surface tension, one can easily estimate the corresponding values of $[S]_w$ and Γ.

In Fig. 2, the total emulsifier concentrations determined from Fig. 1 are plotted as a function of A_p/V_w for the chosen values of surface tension (the spacing is 2 mN/m). In this figure, the lines represent linear regressions to the data, according to Eq. (1). The smallest values of the determination coefficient are $R^2=0.994$ (Fig. 2a) and $R^2=0.999$ (Fig. 2b), which quantitatively confirms the visible linearity of the data and supports the assumptions of Paxton's method. Finally, the adsorption isotherms, constructed from the intercept and slope of the aforementioned linear regressions, are depicted in Fig. 3.

Several equations have been used to describe and interpret the adsorption of surfactants on colloids. In particular, Zhu and Gu [3] have proposed a general adsorption equation, based on a two-step adsorption model, capable of representing

Langmuir-type, S-type and two-plateau-type isotherms. A useful form of the general expression is the following limiting case,

$$\Gamma = \Gamma_{\infty} \frac{K[S]_w{}^n}{1 + K[S]_w{}^n} \qquad (2)$$

where Γ_{∞} is the limiting surface concentration, n is said to be the aggregation number of the hemimicelles (but is in fact an adjustable parameter), and K is the product of the equilibrium constants for the first and second adsorption steps. The Langmuir isotherm is recovered when $n=1$.

This 3-parameter equation was used to fit the experimental adsorption data. The curves thus obtained are plotted as solid lines in Fig. 3 and the corresponding parameters are summarized in Table 2. The calculated values of Γ_{sat} and a_s are also included in Table 2, from which we can see that the a_s value for SDS matches the result previously determined by conductimetry (cf. Table 1).

As we can notice in Fig. 3, the experimental data are very well described by Eq. (2). For both surfactants, the value of the parameter n is found to be above unity, indicating a certain degree of deviation with respect to the Langmuir equation. Indeed, although at first sight, one might think the data could also be described by a Langmuir isotherm, a plot of the residuals would clearly show an S-like pattern arising from the slight S-shape of the data not taken into account by the Langmuir equation. Nevertheless, the value obtained for the aggregation number of the hemimicelles ($n=1.33$) appears too small to be a sign of a two-step adsorption mechanism. It is also interesting to observe that an identical value of n is determined with the two emulsifiers, as if it were a property of the polymer and not of the surfactant. Zwetsloot and Leyte [6]

also found a low value of n (=1.5) when investigating the adsorption of SDBS on PS particles. These authors suggested that some process, possibly the charges in the polymer surface, could be responsible for the deviations with respect to what would be a Langmuir adsorption mechanism. However, our PVC latex has a very low surface charge density $\sigma=7$ mC/m^2 (about one order of magnitude less than the latex of Zwetsloot and Leyte) and despite that the deviations persist. Thus, it is not clear at present what might be mechanisms responsible for the observed shape of the isotherms.

4. Conclusions

In this work, we studied the adsorption of SDS and SDBS on PVC latex particles. In particular, we measured the adsorption isotherms of these two emulsifiers from surface tension titration curves performed at different polymer contents. The data thus obtained was fitted to the equation of Zhu and Gu, the agreement between the calculated curves and the experimental points being very good. Unfortunately, firm conclusions could not be drawn upon the nature of the phenomena concealed behind the actual shape of the isotherms. The correlations obtained can be used, particularly in emulsion polymerization, to estimate the surface coverage of the polymer particles, which is a key parameter to compute the coagulation rate coefficients between the particles.

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Tables

Table 1

Adsorption parameters of SDS and SDBS on PVC particles at different temperatures, as determined by conductimetry

T (ºC)	SDS			SDBS
	CMC (mM)	Γ_{sat} (μmol/m^2)	a_s (Å^2)	CMC (mM)
20	8.3	3.6	47	1.8
40	8.7	3.2	52	1.9
50	9.1	3.1	54	2.1

Table 2

Parameters obtained by fitting Eq. (2) to experimental data on the adsorption of SDS and SDBS on PVC particles at 20ºC

	Γ_{∞} (μmol/m^2)	K (M^{-n})	n	Γ_{sat} (μmol/m^2)	a_s (Å^2)
SDS	5.9	8.4×10^2	1.33	3.5	47
SDBS	4.3	1.8×10^4	1.33	3.3	50

Figure Captions

Fig. 1. Surface tension titration curves at various polymer contents, with SDS (a) and SDBS (b).

Fig. 2. Plots of the total surfactant concentration as a function of polymer surface per unit volume at constant surface tension, for SDS (a) and SDBS (b).

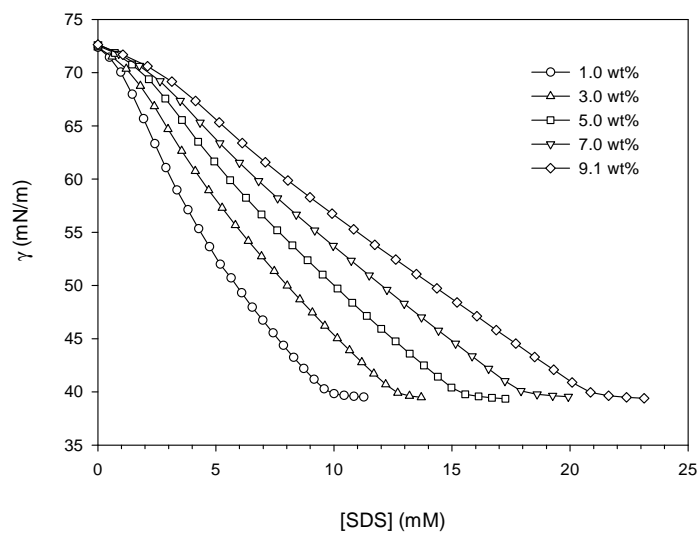Fig. 3. Adsorption isotherms of SDS (a) and SDBS (b) on PVC particles, at 20ºC. The lines represent the fitted isotherms.
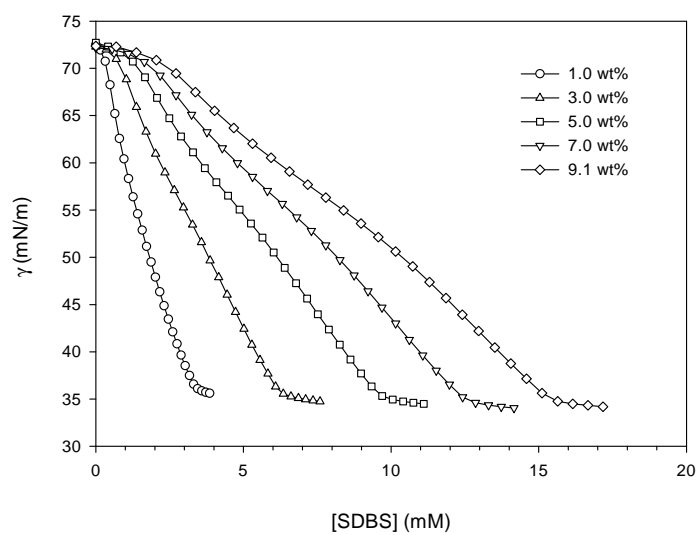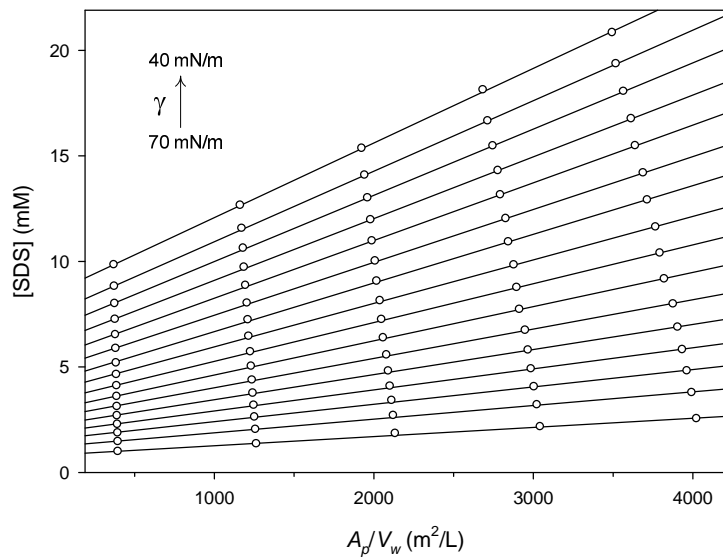
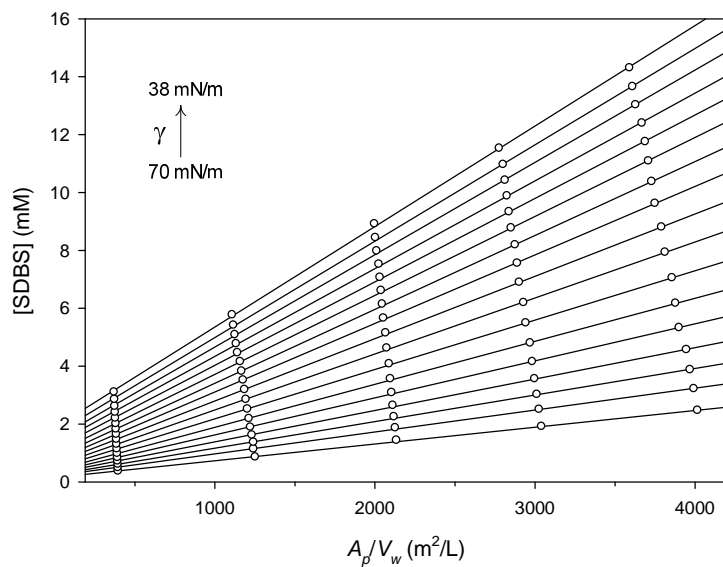**Figures**

Figure 1a:

Figure 1b:

Figure 2a:

Figure 2b:

Figure 3a:

Figure 3b: