Surface Effects with Natural Rubber Latex

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ABSTRACT

Measurements of zeta potential (microelectrophoresis) and surface charge (polyelectrolyte titration) were performed on natural rubber latex with the addition of anion-active tensides of the fatty acid type. The negative zeta potential showed a monotonous rise with increasing tenside concentration for decanate, while a maximum was observed for laurate, myristate, and palmitate. The surface charge increased monotonously. A comparison with direct adsorption measurements showed that zeta potential measurements allow a simple determination of optimal tenside concentration, and that the mentioned maximum is related to the saturation concentration of the tenside.

INTRODUCTION

Natural rubber consists of isotactic *cis*-1,4-1,4-polyisoprene. Latex represents a two-phase system, consisting of more or less spherical latex particles of about 0.5 μm diameter in an aqueous serum. The latex particle consists of a rubber core surrounded by layers of lipids and proteins. Most important is a phospholipid of the lecithin type, which is connected to the protein layer, consisting mainly of

α-globuline. This outer layer determines the surface charge and therefore both the electrokinetic properties and the coagulation behavior (Fig. 1). Natural rubber is obtained by tapping the *Hevea brasiliensis* as a 25–40% dispersion with an average molecular weight ranging between 0.25 and 2.7 $\times$ 10^6, depending on the clone and on the season [1]. Latex particles have a wide range of diameters ranging between 0.1 and 2 μm and have a bimodal distribution with peaks at approximately 300 and 700 μm [2]. The lipids in fresh *Hevea brasiliensis* latex are classified into neutral lipids (mainly triglycerides, diglycerides, and free fatty acids), glycolipids (free and esterified sterylglucosides), and phospholipids (phosphatidyl ethanolamine, phosphatidyl choline, and phosphatidyl inositol). The amount of neutral lipids varies with the clones and is between 0.5 and 2,3%, of glycolipids between 0.2 and 0.5%, and of phospholipids between 0.3 and 0.6% rubber. The lipid layer is connected with a protein layer (about 0.3% of rubber) mainly consisting of α-globuline (14 and 24 kDa protein) [3].

The mechanical and chemical stability of freshly tapped latex is low (MST < 100 s). The mechanical stability time (MST) is considerably increased by treating latex with ammonia. This effect depends on the storage time. The mechanical stability time can be more than 1500 after a 3 months of storage. The addition of ammonia results in the hydrolysis of the phospholipids and in the formation of higher fatty acids (HFA). The HFA soap is adsorbed on the rubber particle, thus increasing the surface charge and the stability. The fatty acids set free by hydrolysis mainly consist of linoleic acid, oleic acid, stearic acid, and palmitic acid.

In order to increase stability during transportation and processing, the mechanical stability time is regulated by the addition of potassium laurate. For compounding the latex, the concentrate is mixed with curing chemicals. Water-soluble compounds are added in the form of a dispersion. Because salts are also being added, the stability must be further increased to avoid too early gelling. Thin-walled dipped products, such as medical gloves, are made by the coagulant dipping method. For this purpose porcelain or glass formers are coated with a thin layer of a salt of polyvalent ions, e.g., $Ca(NO_3)_2$. The rubber film is obtained by destabilization of the electrical double layer of the latex particles by means of polyvalent metal
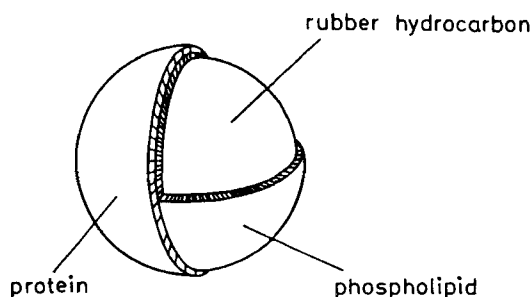
Latex - particle

FIG. 1.   Schematic of a latex particle.

ions. With fatty acids, insoluble salts are formed. The high ionic concentration on the surface of the former assists in coacervation of the latex and results in a dense film. The stability of the latex and the velocity with which the film develops are largely determined by the kind of surface-active materials. Alkali salts of higher fatty acids give high mechanical stability and lead to rapid coacervation, producing a dense film. The stability of the latex and the effect of coacervation depend on the length of the paraffinic chain.

This work was intended to determine the influence of various fatty acids on the mechanical and chemical stability of natural rubber latex.

ADSORPTION AND ZETA POTENTIAL

The general features and properties of the electric double layer at the solid/liquid boundary in an aqueous medium are well known. We distinguish three kinds of ions.

1. Potential determining ions (pdi), which exert a fundamental control on surface charge and surface potential.
2. Specifically adsorbed ions (here forces other than electrostatic come into play). These ions enter the inner part of the double layer and undergo a specific interaction with the surface.
3. Indifferent ions, which control the extension of the double layer out into the solution but are not involved in any specific interaction with the surface.

Specifically adsorbed ions may change the sign of the zeta potential, while indifferent ions can only change its amount or reduce it asymptotically to zero. To characterize the electrokinetic situation, we have the point of zero charge (pzc), which informs us that there is no net charge on the solid surface. It is a characteristic of the solid and its determination is complicated. It may be changed by specifically adsorbed ions. Further, we have the isoelectric point (iep), where the zeta potential is zero. Its determination is straightforward. It is of practical importance, since here the mobility is zero, the mutual repulsion of particles minimal, and flocculation maximal. The net charge at the sliding plane is zero. Without specific adsorption, we find pzc = iep and ζ = 0. Selective adsorption will shift the iep contrary to the shift of pzc. Indifferent ions will not change the iep, which means that the latter is independent of ionic strength. However, they will, of course, change the ζ-values.

For our considerations we use the parameter zeta potential (ZP, symbol ζ). It can be measured with high accuracy and reproducibility, and although its theoretical foundation is still somewhat fuzzy, it has proved a very useful parameter for surface processes. In particular, two cases are of interest. If the potential determining ions are dissociable groups on the surface of the solid, the dependence of ζ on pH can be used to determine the pK-value of the dissociable groups. With this method, we could follow the change of pK at the latex surface in the course of ripening. On the other hand, if the ions are adsorbed, the dependence of ζ on the concentration of the adsorbate can be used to determine the free enthalpy of adsorption according to the equation [4]

$$\Delta G_{ads}^{o} = zF\zeta + \phi_{\pm}$$

where z = valency

F = Faraday's constant

$\phi_{\pm}$ = nonelectrostatic term of adsorption free energy

Since in our problem we deal with adsorption of surfactant ions on the latex surface, we shall concentrate on this case. However, we were not interested in the thermodynamics of adsorption, rather we wanted to find a simple method to determine the adsorption isotherm, and mainly the concentration where saturation takes place. This is indicated, for example, in the Langmuir isotherm by a flattening out to a horizontal line. However, direct adsorption measurements on the latex/tenside system are not easy, and therefore we were looking for a way to determine the saturation concentration by means of ζ-measurements. Some time ago we had published a method to express ζ-data in the form of a Langmuir isotherm by using the following plot [5]:

$$\zeta - \zeta_0 = \frac{Kc}{b + c}$$

where ζ_0 = without adsorption

c = equilibrium concentration

K, b = constants

In this paper we analyze our measurements by this method and investigate whether we can determine the saturation concentration in this way. The results are controlled by direct adsorption measurements.

Another question is the correlation between surface charge and ZP. The former generates the latter, but no simple relationship exists due to the presence of other types of ions. We measured the titrable surface charge by means of a streaming current detector and tried to correlate it with ζ-data. This proved to be complicated because the adsorption does not always follow a simple Langmuir curve, but rather shows deviations after reaching a first saturation. Some thoughts about the reason for this effect will be presented in the Discussion.

EXPERIMENTAL

Zeta potential was measured in a Repap-Electrophoresis instrument. The stationary layer was calculated according to the formula of Komagata, which was checked experimentally and found to be correct. Details can be found elsewhere [3]. A few experiments were made with a Laser Zee Meter 501; they were in full agreement with the Repap measurements. All measurements were made at room temperature and at neutral pH because the zeta potential showed a strong dependence on the latter. Under these conditions, latex without any additions had a zeta potential of -78 mV. The surface charge of the latex particles was determined by polyelectrolyte titration with a streaming current detector (SCD); N-cetylpyridiniumchloride (0.002 mol/L) served as the cationic electrolyte.

Direct adsorption measurements posed several problems. As the latex has a lower density than the serum, it will accumulate at the top (cream up). This makes

it difficult to obtain samples of the serum underneath. We used the following method. After adding the correct amount of tenside to the latex dispersion, the mixture was centrifuged at 7000 r/min for 2 hours in polystyrene tubes. Then the tubes were punctured below the latex layer by means of a hot needle, so then an aliquot portion of the latex could be removed by means of a syringe. In this way the serum could be obtained without contamination by the latex layer. The tenside content was determined by polyelectrolyte titration with a streaming current detector. The measuring temperature was 20°C.

The natural rubber latex was obtained from Semperit Co., came from Malaysia, and had a solid content of 61.2%. Its dispersion state was stable. The anion-active tensides used were commercially available as fatty acids. We used

Decanate	C10
Laurate	C12
Myristate	C14
Palmitate	C16

All fatty acids were added in ammonium solutions, so we worked with ammonium salts. The detailed experimental data are given elsewhere [6].

The densities of the latex dispersions as a function of latex concentration were determined in a DMA 46 instrument. We obtained an excellent correlation according to:

$$d = 0.9977 - 8.6 \times 10^{-4}c$$

(where c is the latex concentration) with a correlation coefficient of 0.997. This yields a density of 0.9117 g/mL for the solid latex particles, in good agreement with literature data (Fig. 2).
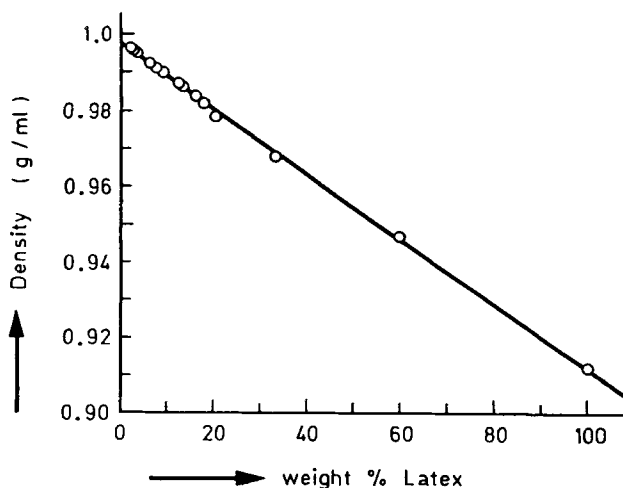

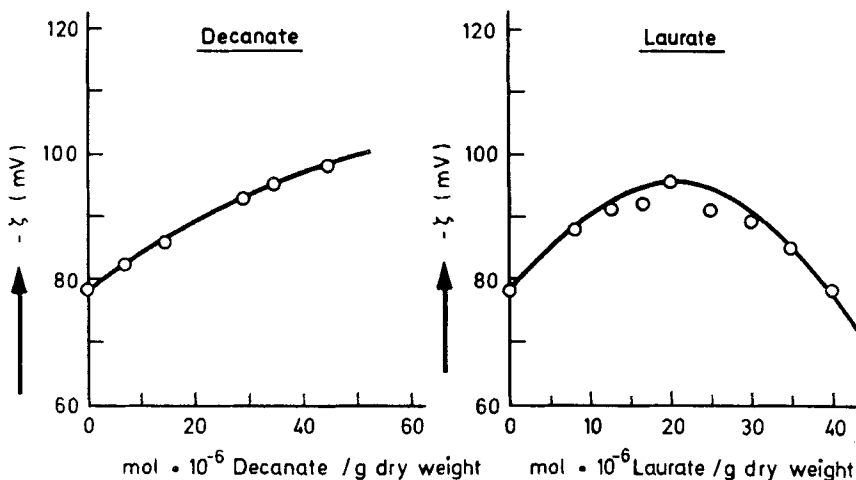FIG. 2.   Latex density as a function of concentration.

FIG. 3.   Zeta potential of latex as a function of tenside concentration for decanate and laurate.

RESULTS

In a first series of experiments we measured the zeta potential as a function of tenside addition. In all cases the negative ζ-values were enhanced. For decanate we found a continuous rise (Fig. 3), but all other tensides yielded curves with a maximum (Figs. 3 and 4). This maximum was correlated with the length of the carbon chain, as shown in Fig. 5. However, from this curve we would expect a maximum for decanate at about 30 μmol/g, but this was not found in our measurements. The
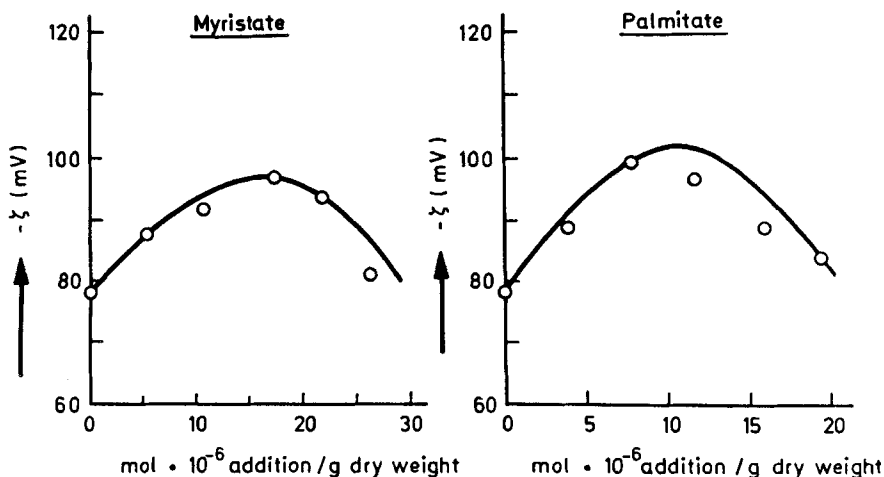

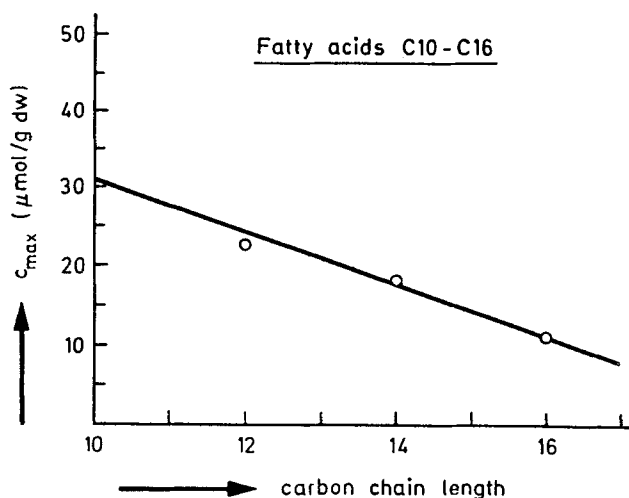FIG. 4.   Zeta potential of latex as a function of tenside concentration for myristate and palmitate.

FIG. 5.   Maximum concentration c_{max} as a function of chain length.

reason for this maximum is not clear. It is most probably not related with the CMC (critical micelle concentration). We compared our concentrations at the maximum (c_{max}) with CMC values from the literature [7]. To accomplish this, the concentrations given in our data (mol tenside/g dry weight) were recalculated. The results are given in Table 1.

Our concentrations at the maximum are smaller than the CMC values by 3–4 orders of magnitude. Thus we are in a concentration range far lower than the CMC. Therefore, we conclude that the maximum must be related to the adsorption process.

Next we plotted our data according to the method we had developed to obtain a straight line in the case of pure Langmuir adsorption. We shall call these "ζ-Langmuir plots" in the following. The results are shown in Figs. 6–9. While for decanate we obtained the expected response, strong deviations were found for the other tensides at concentrations higher than c_{max}. This is an indication that beyond c_{max} we no longer have regular one layer Langmuir adsorption, but other effects must come into play.

Now our results with direct adsorption shall be presented. As the experiments proved rather tricky, the results are not very precise and should be regarded as

TABLE 1.   Comparison of c_{max} and CMC for Different Tensides

Fatty acid	c_{max} (NH$_4$-salt), mol/L	CMC (Na-salt), mol/L
C10	—	1.0×10^{-1}
C12	4.4×10^{-6}	1.5×10^{-2}
C14	3.9×10^{-6}	6.5×10^{-3}
C16	1.7×10^{-6}	1.7×10^{-3}
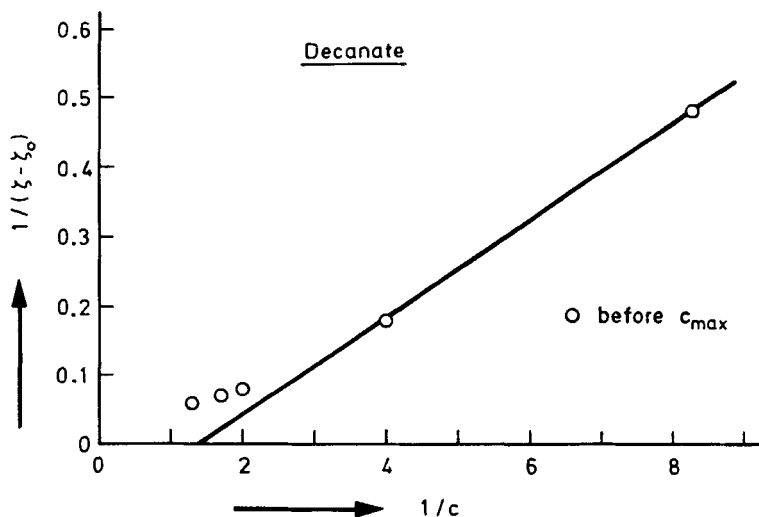
FIG. 6. ζ-Langmuir plot for decanate.

preliminary. However, the essential features show up in a significant way. Figure 10 shows an adsorption isotherm (for 20°C) for decanate. We note a regular adsorption curve; the saturation concentration can be easily observed. Langmuir plots are shown in Figs. 11–13 for the tensides used. We note the expected straight line for all the tensides measured. Palmitate is not included because the experiments with this tenside failed for unknown reasons. The saturation concentration can easily be deermined from the intersection with the abscissa. From these results we draw the
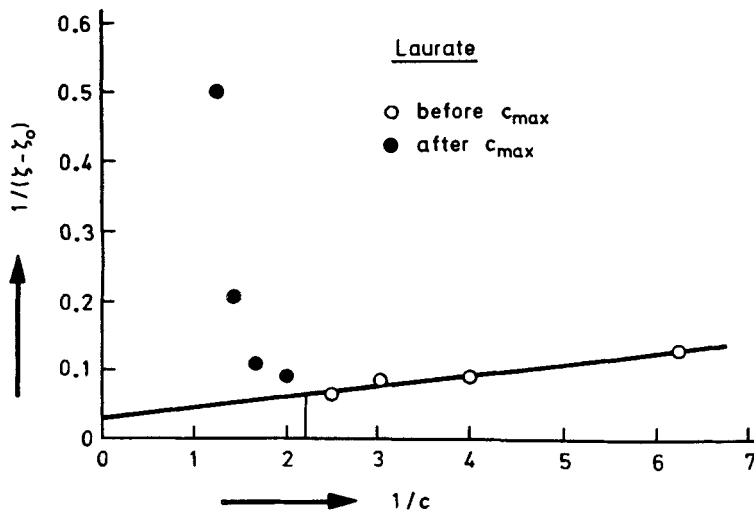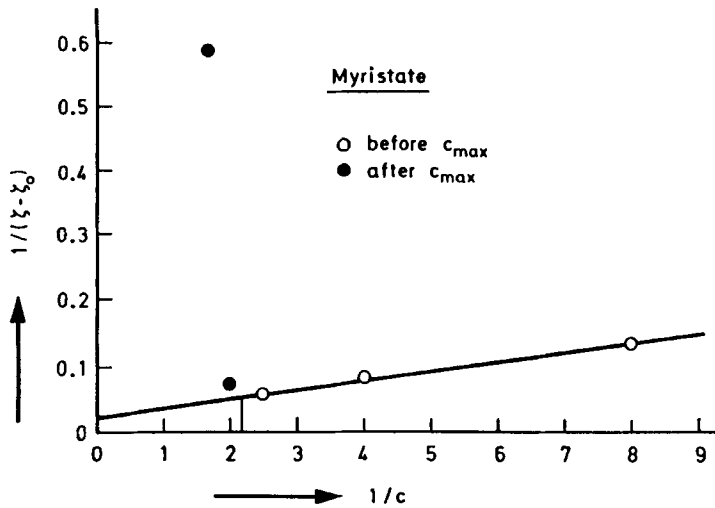

FIG. 7. ζ-Langmuir plot for laurate.

FIG. 8. ζ-Langmuir plot for myristate.

conclusion that the adsorption of tensides on latex particles follows a regular Langmuir mechanism and does not explain the maximum in the zeta potential curves.

We have also tried to correlate surface charge measurements by SCD titration and zeta potential. Figure 14 shows the surface charge as a function of tenside concentration for decanate. Note the plain linear response. Similar curves were found with all other tensides. This means that the titratable charge rises with tenside addition in a linear fashion, even beyond the maximum in the ζ-curves (c_{max}).
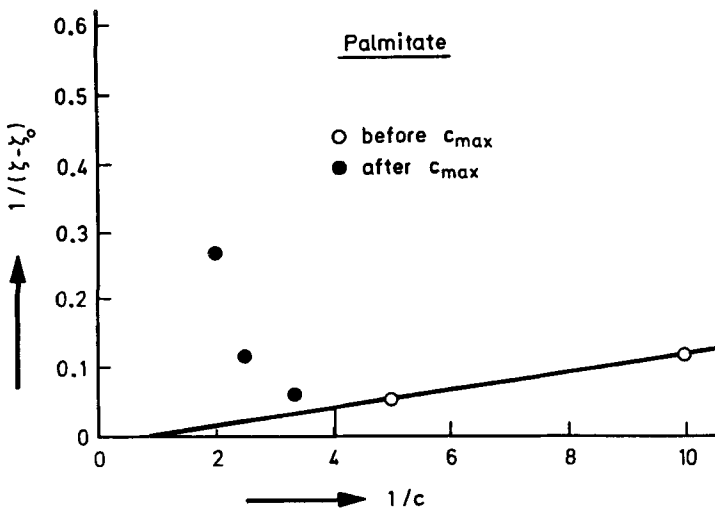
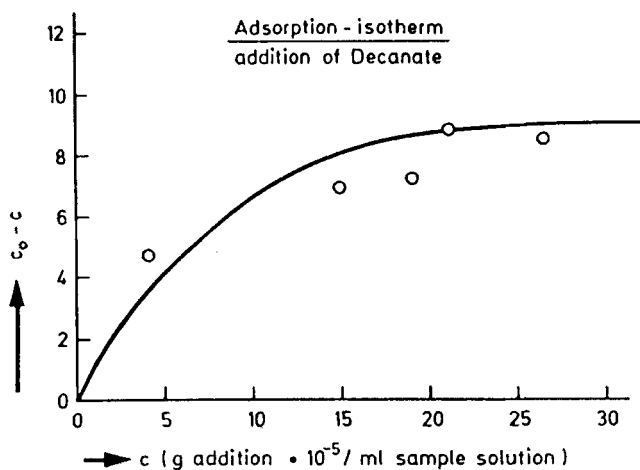FIG. 9. ζ-Langmuir plot for palmitate.

FIG. 10.   Adsorption isotherm for decanate.

However, c_{max} shows up in plots of the charge vs zeta potential. In Fig. 15 this plot is shown for decanate. The plot is a straight line, so in this case no c_{max} is found. In Fig. 16 the same plot is shown for palmitate. Here things are different: we find a rising straight line before c_{max} and a falling one after c_{max}. This behavior was, of course, to be expected. It proves that a simple and unequivocal correlation between surface charge and zeta potential cannot be expected.
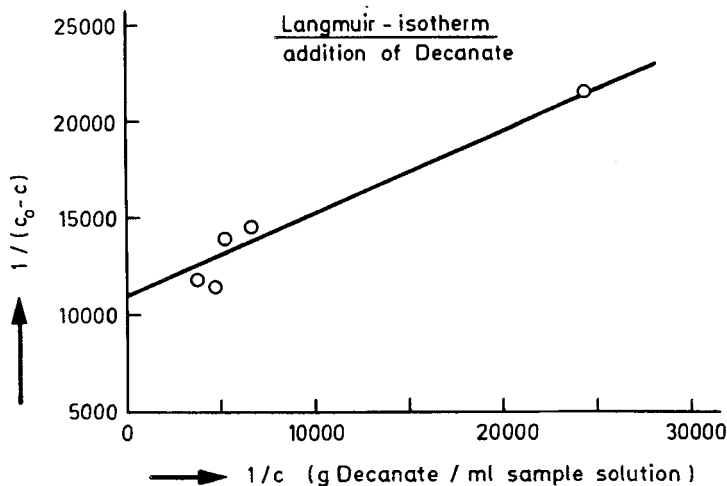
FIG. 11.   Langmuir plot for decanate.
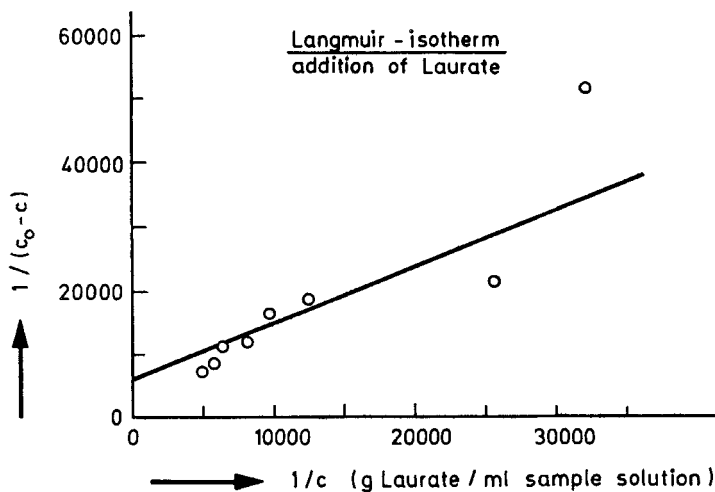
FIG. 12.   Langmuir plot for laurate.

DISCUSSION

We have confirmed the fact that an addition of tensides will improve the stability of latices. An unequivocal correlation with the length of the carbon chain could not be detected, but it appears that decanate, with the shortest C-chain, shows a deviating behavior in several regards. For both the adsorption measurements and the electrokinetic experiments we found indications for a first saturation. In particular, the zeta potential showed maxima at a certain tenside concentration

FIG. 13.   Langmuir plot for myristate.

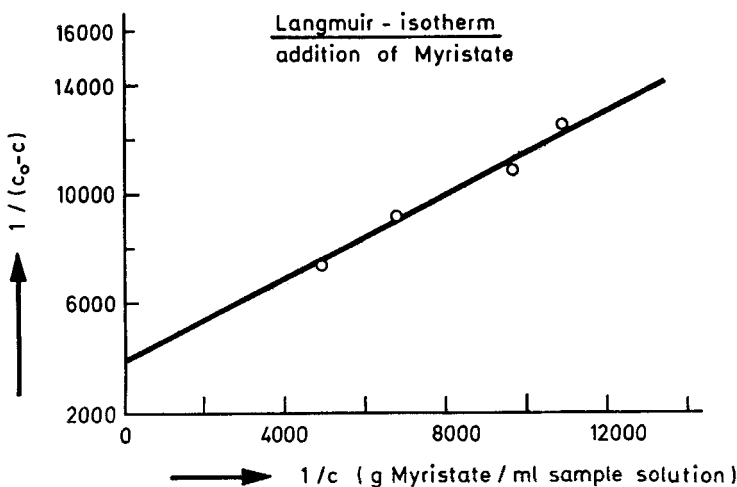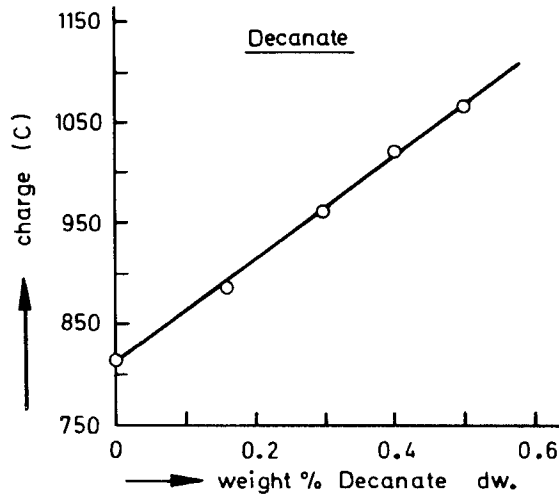FIG. 14.   Surface charge as a function of tenside concentration for decanate.

(with the exception of decanate). Such maxima could not be detected in electric charge titrations by the SCD method. This leads to the conclusion that zeta potential is a much more sensitive indicator for colloid stability than is the electric charge. This appears reasonable because the charge is a surface property while the zeta potential depends on the electric double layer and will therefore reflect the interaction of the particle and the dispersing medium to a high degree.

FIG. 15.   Zeta potential as a function of surface charge for decanate.

FIG. 16.   Zeta potential as a function of surface charge for palmitate.

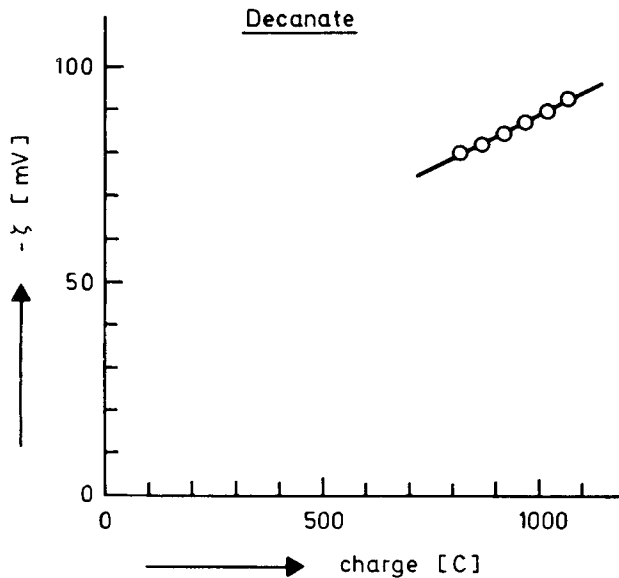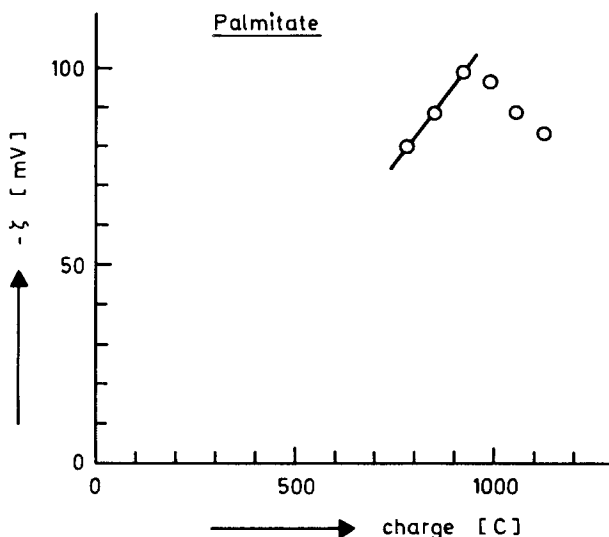In particular, we have found the following. The electric charge obtained with the SCD method shows a 15% increase up to about 0.25 wt% tenside, independent on chain length. Beyond 0.25 wt% the charge increase is steeper for laureate C12 to palmitate C16. The increase is smaller and less steep for decanate. Zeta potential measurements showed a maximum for laurate to palmitate at a lower tenside concentration the longer the C-chain. Decanate shows no such maximum.

The most important feature of this investigation was a comparison of the adsorption experiments with the zeta potential measurements and the interpretation of the latter as adsorption phenomena. In Fig. 17 we have listed the relevant plots schematically. From the adsorption isotherms (Fig. 17a) we obtained the saturation increment Δc_{sat} which is the maximum amount of tenside attached to the latex in the first step of adsorption. The same value can be obtained from a Langmuir plot (Fig. 17b). Furthermore, we obtained from the adsorption isotherm the value for c_{sat}, the concentration where saturation occurs. All these values correspond to the adsorption equilibrium. These figures were compared with the concentration maximum (c_{max}) as observed in the plot of zeta potential vs tenside concentration (Fig. 17c). Finally, from the ζ-Langmuir plots we have determined c_{lim}, where deviations from the straight line occur (Fig. 17d).

In Table 2 we have compiled the data for these figures as obtained from our measurements. First, we note good agreement between c_{max} and c_{lim}. This is to be expected, since both figures are, basically, identical. All measuring points before the maximum can be represented as a straight line, while strong deviations are observed after the maximum. This corroborates the assumption that in the ζ vs $c_{tenside}$ curves the points before the maximum describe regular adsorption while after the maximum other effects come into play. Presumably the electric double layer is modified so that the zeta potential will no longer depend solely on the adsorption

a : Adsorption - isotherm   b : Langmuir - plot

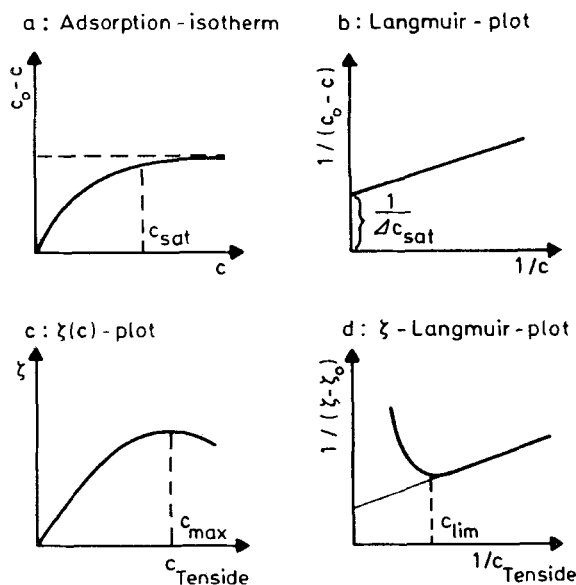c : $\zeta(c)$ - plot   d : ζ - Langmuir - plot

FIG. 17.   Different adsorption plots shown schematically.

process. Perhaps the adsorption process itself is modified. Since such phenomena, which are related to the double layer, will only show up in the zeta potential, it is understandable that no such effects are observed in the surface charge where we have a monotonous rise with tenside concentration.

The decisive comparison, however, is between the results of adsorption measurements and the electrokinetic data. From Table 2 we note that c_{sat} as obtained from isotherms directly or from Langmuir plots is enhanced with increasing length of the carbon chain. However, in agreement with our assumption, the concentration c_{sat} where saturation occurs agrees within the accuracy of our measurements with the concentration of the zeta potential maximum c_{max}. This can be regarded as a proof of our thesis that the zeta potential will indeed reflect the adsorption process taking place before the maximum. Therefore, c_{max} can be used to control the adsorp-

TABLE 2.   Comparison of Zeta Potential and Adsorption Measurements (c in g addition/g dry weight)

Adsorbent	Δc_{sat}		c_{sat}, isotherm	c_{max} in $\zeta(c)$	c_{lim}
	Isotherm	Langmuir plot			
Decanate	2.1×10^{-3}	2.0×10^{-3}	5.1×10^{-3}	—	3.4×10^{-3}
Laurate	3.7×10^{-3}	4.7×10^{-3}	2.3×10^{-3}	4.5×10^{-3}	4.5×10^{-3}
Myristate	3.5×10^{-3}	5.9×10^{-3}	6.1×10^{-3}	4.1×10^{-3}	4.4×10^{-3}
Palmitate	—	—	—	2.1×10^{-3}	2.5×10^{-3}

tion of tensides. Obviously, c_{max} indicates saturation adsorption. A further enhancement of tenside concentration will therefore lead to a changed adsorption process modified by other effects on the one hand and bring about no additional advantage for the stability of the latex dispersion on the other hand.

At present we have no convincing explanation for the maximum in the zeta potential vs tenside concentration curves for fatty acid salts with carbon chains of C12 to C16. We assume that some change in the adsorption mechanism must occur at this point. It is possible that the adsorbed fatty acid chains lie flat at the surface of the latex particle before the maximum, so that the charge will also be close to the surface. Beyond c_{max} the chains might be adsorbed perpendicularly to the surface and therefore extend into the surrounding medium because of steric reasons. Therefore, the charges will reach out into the double layer and so influence it. But this does not explain why we obtained distinct saturation in the direct adsorption experiments, so this question must remain undecided.

Finally, we arrive at the following conclusions from our experiments:

1. The addition of tensides will enhance the stability of latex dispersions.
2. Stabilization takes place over adsorption processes, whereby the electrokinetic properties are changed.
3. These adsorption processes can be controlled by measuring the zeta potential. In particular, such measurements allow the tenside concentration where saturation takes place to be determined.
4. Thus, zeta potential measurements can be used to obtain quick information on the stabilizing action of various tensides and on the optimal concentration.

ACKNOWLEDGMENT

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