# Surfactant Interactions in Poly(vinyl Acetate) and Poly(vinyl Acetate–butyl Acrylate) Latexes

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## Synopsis

Saturation adsorption and penetration adsorption of several anionic surfactants at model poly(vinyl acetate–acrylate) latex/water interfaces are described. The effects of molecular weight and structure of anionic surfactants, latex composition, and the presence of adsorbed layers on latex particles on penetration type surfactant interactions leading to the formation of solubilized polymer–surfactant complex and latex thickening are considered. In the case of saturation-type adsorption of nonionic surfactants, surfactant adsorption at a vinyl acrylic latex/water interface is correlated satisfactorily with the polarity of polymer surface, in agreement with earlier surfactant adsorption studies.

## INTRODUCTION

Recent investigations have shown that the behavior and interactions of surfactants in a poly(vinyl acetate) latex are quite different and complex compared to that in a polystyrene latex.[1,2] Surfactant adsorption at the fairly polar vinyl acetate latex surface is generally weak[3,4] and at times shows a complex adsorption isotherm.[2] Earlier work[5,6] has also shown that anionic surfactants adsorb on poly(vinyl acetate), then slowly penetrate into the particle leading to the formation of a polyelectrolyte-type solubilized polymer–surfactant complex. Such a solubilization process is generally accompanied by an increase in viscosity. The first objective of this work is to better understand the effects of type and structure of surfactants on the solubilization phenomena in vinyl acetate and vinyl acetate–butyl acrylate copolymer latexes.

It was reported earlier[1] that surfactant adsorption at a polymer/water interface can be related to the polarity of the polymer surface. The model used in that study was tested satisfactorily by using the available literature data on polymer polarity and sodium lauryl sulfate adsorption on latex surfaces. The second objective is to verify experimentally the predicted relationship between polymer polarity and surfactant adsorption by studying the adsorption of a nonionic surfactant that shows a saturation type isotherm behavior on vinyl acrylic latexes of varying polarity.

In order to achieve the above objectives, three vinyl acrylic latexes of varying butyl acrylate content have been prepared and "cleaned" for use in the study. Several anionic and nonionic surfactants commonly used in emulsion polymerization have been used to investigate the effects of surfactant structure and polymer composition on the solubilization process. Polarity of latex surface estimated from contact angle measurements have been used to study the effect of polymer polarity on surfactant adsorption.

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## EXPERIMENTAL

### Materials

Commercial-grade vinyl acetate (VA) and butyl acrylate (BA) from Celanese Chemical Co. were used. Reagent-grade potassium persulfate was used as the initiator. Sodium lauryl sulfate (NaLS) from BDH Chemicals after purification[7] was used as the emulsifier in the polymerization. Surfactants used in the adsorption studies were the following: Igepal CO-630 (10 moles ethylene oxide adduct of nonylphenol) and Alipal EP-110 and EP-120 from GAF Corp.; Aerosol A-102 from American Cyanamid and BDH Chemicals sodium lauryl sulfate. According to the manufacturer's literature, Alipal EP-110 and EP-120 are ammonium salts of a sulfated nonylphenoxy poly(ethyleneoxy)ethanol of molecular weights 708 and 1640, respectively. Aerosol A-102 is an anionic/nonionic-type surfactant alcohol ($C_{10}$–$C_{12}$) half-ester of sulfosuccinic acid of molecular weight of about 1800.

### Emulsion Polymerization

A typical recipe is given in Table I. Emulsion polymerization was carried out at 60°C under a nitrogen atmosphere using a batch process. Theoretical solids content in all the formulations was 25%, and generally the conversions were better than 98%. A poly(vinyl acetate) homopolymer and two poly(vinyl acetate–butyl acrylate) copolymers having VA/BA composition of 85/15 and 70/30 were prepared according to the above procedure.

### Ion Exchange and Dialysis of Latexes

The above three latexes were "cleaned" by the ion exchange method of Vanderhoff[8] and dialysis. In general, the latexes were stable after the cleaning process. In some cases, the ion exchange resin was found to discolor after the treatment indicating some interaction, perhaps hydrolysis of the latex, between latex and ion exchange resin.

### Particle-Size Determination

Particle sizes of the "cleaned" latexes were determined using transmission electron microscopy after freeze-drying the samples and counting the particles with a Quantimet image analyzer. The number-average particle diameters ($d_n$) of the homopolymer, the 85/15 VA/BA and 70/30 VA/BA latexes were found to be 0.057, 0.062, and 0.073 $\mu$m, respectively. The polydispersity $dw/dn$ of the three samples were 1.09, 1.05, and 1.06, respectively.

TABLE I
Emulsion Polymerization Recipe

| | |
|---|---|
| Monomers | 500 g |
| Surfactant NaLS | 17.4 g |
| $K_2S_2O_8$ | 2.48 g |
| Distilled water | 1575 g |
| Solids | 25% |

## Adsorption Studies

Appropriate amounts of cleaned latex and surfactants were mixed, equilibrated for 24 hr, and the excess surfactant in serum analyzed after separation by centrifugation. Igepal CO-630 and Alipal surfactants were analyzed by UV adsorption at 275 m$\mu$. NaLS and Aerosol A-102 were analyzed by colorimetric titration with cetyltrimethylammonium chloride in the presence of methylene blue and a chloroform layer similar to the method of Epton.[9] Some nonionic surfactants and solubilized serum components were found to have a positive interference in the colorimetric analysis of ionic surfactants.

## Contact Angle Measurements and Polarity of Latex Films

Advancing contact angle measurements were made at 25°C using a Ramé Hart contact angle goniometer. Latexes "cleaned" by the above procedure were drawn on a glass plate and dried at 40°C. An average of eight measurements was taken as the contact angle. Water and methylene iodide were used as test liquids. Polarity of the dried latex films were estimated according to the method of Kaelble.[10]

## RESULTS AND DISCUSSION

### Saturation and Penetration Adsorption and Latex Thickening

Adsorption isotherms of NaLS and Aerosol A-102 surfactants on a "clean" 85/15 VA/BA copolymer latex are shown in Figure 1. It is seen that the shapes of the two isotherms are quite different. A-102 seems to exhibit a Langmuir-type saturation adsorption behavior typical of surfactant adsorption at a polystyrene/water interface. NaLS seems to have a more complex adsorption isotherm, perhaps a multiple step process as discussed by Giles et al.[11] The initial region of the isotherm up to B appears to be normal, and beyond that the isotherm become linear. Giles et al. have explained such a linear isotherm (classified as
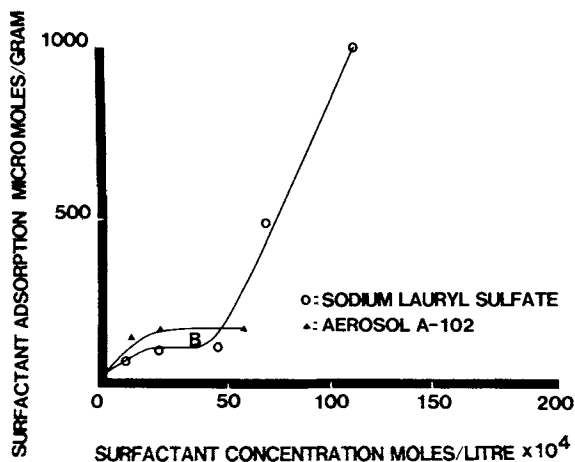


Fig. 1. Adsorption isotherms of NaLS and Aerosol A-102 surfactants on 85/15 VA/BA latex.

Type C) by penetration of substrate by solute, leading to new adsorption sites. Compared to NaLS, the size of Aerosol A-102 molecule is much larger and bulkier and thus perhaps hindered in being able to penetrate into the latex particle.

Figure 2 shows the adsorption isotherms of two sulfated ethoxylate-type anionics—Alipal EP-110 and Alipal EP-120—on the 85/15 VA/BA latex surface. Again it is seen that the lower molecular weight EP-110 shows a C-type isotherm similar to the NaLS while the higher molecular weight EP-120 exhibits a normal saturation-type isotherm.

It is well known[3,5,6] that sodium lauryl sulfate interacts with some polymers such as poly(vinyl acetate) causing solubilization of the insoluble polymer leading to an increase in viscosity. In Figure 3, viscosities of the homopolymer and 70/30 VA/BA at various NaLS/polymer ratio are shown. It is seen that the viscosity of the 2% latex dispersion increases with increase in NaLS/polymer ratio. Similar viscosity data for the 85/15 VA/BA were intermediate between the homopolymer and 70/30 VA/BA latexes. Surfactants that showed a normal saturation-type adsorption behavior did not show any significant viscosity increase of the latex.
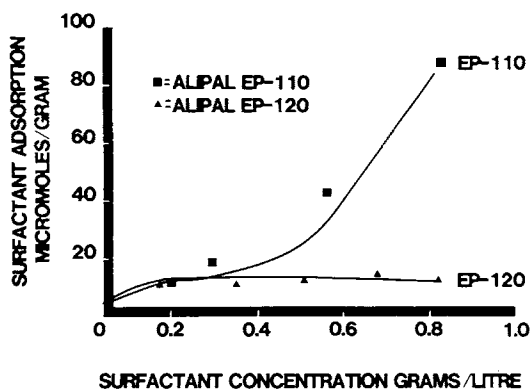


Fig. 2. Adsorption isotherms of Alipal EP-110 and Alipal EP-120 surfactants on 85/15 VA/BA latex.
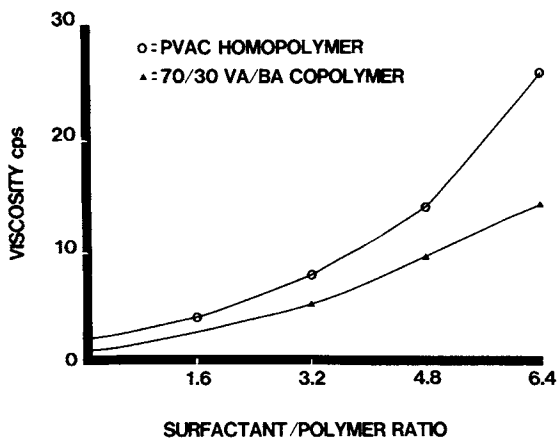


Fig. 3. Thickening of vinylacrylic latexes in the presence of NaLS.

Edelhauser[3] has explained his results on the interaction of anionic surfactants (sodium lauryl sulfate and sodium dodecylbenzene sulfonate) with a PVAC latex as a two-step mechanism involving surface adsorption followed by surfactant penetration into the interior of PVAC particles taking water with it and causing swelling and gradual dissolution of the disintegrated polymer chains. Based on this model, it is convenient to classify the adsorption behavior of anionic surfactants at vinylacrylic latex surface into penetrating and nonpenetrating types as shown in Table II. The smaller surfactant molecules seem to be capable of penetrating into the latex, causing disintegration and solubilization of the otherwise insoluble polymer. The larger and bulkier surfactants studied seem to adsorb only at the latex surface unable to penetrate into the particle. It appears that there exists a critical size and perhaps shape of anionic surfactant molecule for the surfactant to be able to penetrate into the particle. It is also likely that the nature of hydroprobe adsorbing at the latex/water interface and the charge density of the polymer–surfactant complex may influence surfactant penetration and latex solubilization. More extensive work with other anionic surfactants of varying chain length and shape would be needed to better define molecular parameters that influence the penetration of surfactants into a vinyl acrylic latex.

Latex thickening in the presence of penetrating-type anionic surfactants such as NaLS appears to depend on polymer composition as seen in Table III. The

TABLE II
Anionic Surfactants Studied in Vinyl Acrylic Latexes

| Penetrating type | Nonpenetrating type |
| --- | --- |
| (a) Sodium lauryl sulfate $C_{12}H_{25}SO_4Na$ MW = 228.4 | (a) Aerosol A-102 MW = 1800 disodium ethoxylated alcohol ($C_{10}$–$C_{12}$) half-ester of sulfosuccinic acid |
| (b) Sodium dodecylbenzene sulfonate $C_{12}H_{25}$⬡·$SO_3Na$ MW = 348.5 | $CH_2\cdot COO\ (H_2C\cdot CH_2\ O)_{30}C_{11}H_{23}$ \| $CH\ COONa$ \| $SO_3Na$ |
| (c) Alipal EP-110 MW = 708 $C_9H_{19}$⬡$-(OCH_2CH_2)_{8-9}O\cdot SO_3NH_4$ | (b) Alipal EP-120 MW = 1640 $C_9H_{19}$⬡$-(OCH_2\cdot CH_2)_{29-30}O\cdot SO_3NH_4$ |

TABLE III
Effect of Latex Composition on Thickening by Sodium Lauryl Sulfate

| Latex composition | Latex thickening |
| --- | --- |
| Poly(vinyl acetate) | 19.3 |
| Poly(vinyl acetate–butyl acrylate) (70/30) | 10.0 |
| Polystyrene | 1.1 |
| Poly(methyl methacrylate–ethyl acrylate) | 1.1 |

$$\text{Thickening}\ \frac{\eta}{\eta_0} = \frac{\text{Brookfield viscosity of 2\% latex in presence of NaLS}}{\text{Brookfield viscosity of 2\% control latex}}$$

extent of latex thickening in the presence of excess NaLS decreases with decrease in the VA content of a vinyl acetate–butyl acrylate copolymer. Polystyrene and polyacrylate copolymer latexes do not show any thickening.

Presence of nonionic surfactants such as Igepal CO-630 seems to prevent the thickening of PVAC latex by NaLS, as shown in Table IV. This can be interpreted as to show that the presence of nonionic surfactant at the PVAC latex surface prevents the penetration of NaLS into the particle.

Formation of solubilized complex in the presence of NaLS can influence the properties and performance of vinylacrylic latexes prepared with NaLS and other penetrating-type anionic surfactants. They seem to affect the glass transition temperature and film coalescence process.[12]

Our results on the interactions of anionic surfactants in vinylacrylic latexes can be summarized as follows:

Lower molecular weight (300–800) anionic surfactants such as NaLS and Alipal EP-110 adsorb at a vinylacrylic latex in a complex C-type adsorption isotherm, leading to penetration and solubilization of latex.

Relatively higher molecular weight (1600) anionic surfactants such as Alipal EP-120 and Aerosol A-102 adsorb in a normal manner, suggesting that there exist a critical size, specific charge density, and perhaps shape for the surfactant to be able to penetrate into the latex.

Latex thickening, a result of surfactant penetration and solubilization of the polymer, decreases with decrease in vinyl acetate content of the vinyl acetate–butyl acrylate content.

Presence of nonionic surfactants at the latex/water interface seem to interfere with the penetration of low molecular weight penetrating-type anionic surfactants.

## Polarity of Vinylacrylic Latex and Surfactant Adsorption

Contact angle measurements, dispersion and polar contribution to latex film surface tension, and polarity of polymer calculated according to the method of Kaelble[10] of the three latex films are shown in Table V. It is seen that the polarity of the latex film decreases with increase in butyl acrylate content of the vinylacrylic copolymer. The polarity of the 70/30 (VA/BA) latex is very similar to that of the poly(butyl acrylate) homopolymer estimated to be about 0.21.[1]

Polarity of 0.54 for the PVAC homopolymer is considerably higher than the 0.33 value determined for the homopolymer from interfacial tension measurements on polymer melts.[13] The higher polarity value found in the PVAC film strongly suggests that there was a significant amount of hydrolysis of PVAC,

TABLE IV
Effect of Nonionic Surfactant on Thickening of Poly(vinyl Acetate)–Sodium Lauryl Sulfate (NaLS)

| Latex | Latex thickening |
|---|---|
| Poly(vinyl acetate) + NaLS | 19.3 |
| Poly(vinyl acetate) + Igepal CO-630 | 1.0 |
| Postaddition of Igepal CO-630 to poly(vinyl acetate) + NaLS | 17.4 |
| Postaddition of NaLS to poly(vinyl acetate) + Igepal CO-630 | 1.3 |
| Poly(vinyl acetate) + mixed Igepal CO-630 and NaLS | 1.4 |

TABLE V
Polarity of Latex Surface by Contact Angle Measurements[a]

| Latex | Contact angle $\theta$, degrees | | Dispersion contributions, dyn/cm | Polar contributions, dyn/cm | Polarity $X^P$ |
|-------|---------------------------------|-----------|---------------------------------|-----------------------------|----------------|
|       | $H_2O$ | $CH_2I_2$ | | | |
| VA/BA 70/30 | 72 | 41 | 30.5 | 9.3 | 0.23 |
| VA/BA 85/15 | 67 | 38 | 30.0 | 12.2 | 0.29 |
| VA/BA 100/0 | 44 | 29 | 25.4 | 29.8 | 0.54 |

[a] VA = vinyl acetate; BA = butyl acrlate; $\theta$ = average of eight measurements.

either during polymerization and/or cleaning of the latex resulting in a more hydrophilic PVAC surface.

Table VI shows the adsorption data of Igepal CO-630 surfactant at the three latex/water interfaces. The isotherms were of the normal type, and no thickening of the latex in the presence of surfactant was observed. Area per molecule was calculated according to

$$A = \frac{9.961 \times 10^{-3}}{\Gamma \cdot \rho \cdot d} \tag{1}$$

where $A$ is the area per molecule in nm$^2$; $d$ the diameter of latex in nm; $\rho$ the density of polymer latex taken as 1.17 and 1.14 for the homopolymer and copolymer, respectively; and $\Gamma$, moles surfactant per gram polymer latex. Interaction parameter $(I)$ defined as $A_0/A$, where $A_0$ is the limiting area per molecule of surfactant, is given in the last column of Table VI.

It is seen that the adsorption of Igepal CO-630 decreases with increase in polarity of the vinylacrylic latex. Also the interaction parameter, as expected, decreases with increase in polarity of the latex surface.[12] It shows that at saturation adsorption, the extent of interaction of Igepal CO-630 with the PVAC homopolymer and VA/BA copolymer latexes under investigation is about 30 and 50%, respectively, of the theoretical limit corresponding to a close packed monolayer adsorption.

Figure 4 shows a plot of log $A$ versus polarity $(X^P)$ of latex surface. It is readily seen that the plot is quite linear and fits the following equation:

$$\log A = \text{const} + k(X^P) \tag{2}$$

Attempts to correlate the adsorption data of other surfactants such as Alipal EP-110 and NaLS on the three latex surfaces in a similar manner failed because of the more complex and specific interactions observed in these systems. Equation (2) can adequately describe the adsorption data of surfactants at polymer/water interfaces, provided that the free energy of the interface is related

TABLE VI
Adsorption of Igepal CO-630 on Vinyl Acrylic Latex of Different Polarity[a]

| Latex | Polarity $X^P$ | Particle size $d$, nm | Adsorption, moles/cm$^2$ polymer | Area, $A$ per molecule, nm$^2$ | Interaction parameter $I$ |
|-------|----------------|----------------------|----------------------------------|-------------------------------|---------------------------|
| VA | 0.54 | 0.057 | $8.89 \times 10^{-11}$ | 1.87 | 0.29 |
| VA/BA 85/15 | 0.29 | 0.062 | $14.7 \times 10^{-11}$ | 1.13 | 0.49 |
| VA/BA 70/30 | 0.23 | 0.073 | $17.3 \times 10^{-11}$ | 0.96 | 0.57 |

[a] $I$ = interaction parameter = $A_0/A$; $A_0$ = 0.55 nm$^2$ for Igepal CO-630.
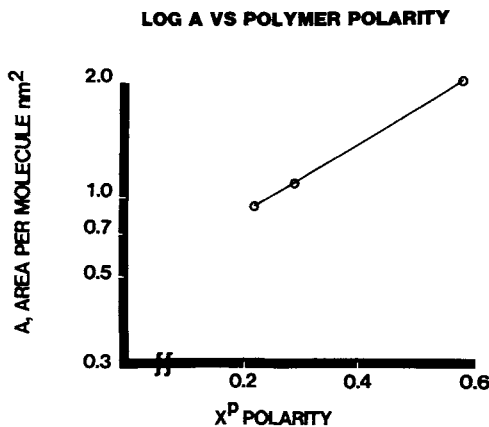
**LOG A VS POLYMER POLARITY**



Fig. 4. Effect of polymer polarity on the adsorption of Igepal CO-630 surfactant at vinylacrylic latex

to the free energy of adsorption and there are no specific interactions between surfactant and interface.[14]

## Implications on Latex Surface Chemistry

The polarity and adsorption data discussed above reveal some interesting aspects of the surface chemistry of vinylacrylic latex surfaces. It is quite likely that the polarity of the latex films, especially of the two copolymers, determined by contact angle measurements, may not correspond exactly with their respective latex surfaces in the dispersed state because of reorientation of polymer chains during film formation. But the surfactant adsorption data shows clearly that the three latex surfaces in their dispersed state do exhibit varying polarity paralleling the trend found from contact angle measurements. The result also shows that the surface of the copolymer latex surface is a mixture of vinyl acetate and acrylate units. This result is somewhat unexpected in a vinylacrylic latex prepared by a batch process, since one would expect the more reactive butyl acrylate to predominate the core structure leaving the less reactive vinyl acetate near the latex surface. Based on the electron micrographs of a batch and semicontinuous polymerized 63/37 VA/BA latex particles, Misra et al.[15] concluded that the batch sample has a heterogeneous structure comprising a relatively large butyl acrylate-rich core surrounded by a vinyl acetate-rich shell. In comparison, the semicontinuous polymerized particles were found to have a homogenous structure comprising a much smaller butyl acrylate-rich core surrounded by a shell of vinyl acetate–butyl acrylate copolymer. It would be interesting to study the two VA/BA latex samples of Misra et al. by the above methods to ascertain the differences in the surface composition of the two latexes.

In agreement with our earlier studies,[1,14] the adsorption results of Igepal CO-630 on the three vinyl acrylic latexes show that the area per molecule of surfactant can be related to the polarity of polymer surface. Further, the results show that one can employ the technique discussed above to characterize the polarity of copolymer latex surfaces.

# References

1. B. R. Vijayendran, *J. Appl. Polym. Sci.*, **23,** 733 (1979).

2. S. M. Ahmed, M. S. El-Aasser, G. W. Poehlein, and J. W. Vanderhoff, *Emulsion Polymers Institute Research Reports*, 1979.

3. H. A. Edelhauser, *J. Polym. Sci. Part C*, **27,** 291 (1969).

4. B. R. Vijayendran, Division of Colloid Abstracts, ACS spring meeting, Honolulu, 1979.

5. T. Isemura and A. Imanishi, *J. Polym. Sci.*, **33,** 337 (1950).

6. H. Arai and S. Harin, *J. Colloid Interface Sci.*, **30,** 372 (1969).

7. B. R. Vijayendran, *J. Colloid Interface Sci.*, **60,** 418 (1977).

8. H. J. Van den Hull, and J. W. Vanderhoff, *Br. Polym. J.*, **2,** 121 (1970).

9. J. R. Epton, *Trans. Faraday Soc.*, **44,** 226 (1948).

10. D. H. Kaelble, *Physical Chemistry of Adhesion*, Wiley–Interscience, New York, 1971, Chap. 4.

11. C. H. Giles, D. Smith, and A. Huitson, *J. Colloid Interface Sci.*, **47,** 755 (1974).

12. B. R. Vijayendran, T. Bone, and C. Gajria, *Vinyl Acetate Symposium Proceedings*, Lehigh University, April 1980.

13. S. Wu, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C-10,** 1 (1974).

14. B. R. Vijayendran, *J. Colloid Interface Sci.*, **68,** 383 (1979).

15. S. C. Misra, C. Pichot, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Lett.*, **17,** 567 (1979).