

## Influence of Polymer Solubilization on Latex Behavior

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### Synopsis

The effect of solubilization of latex polymers was investigated in various anionic surfactant solutions. The process of solubilization was studied by measuring the increase in light transmission and viscosity of the latexes. It was found that anionic surfactants differ widely in their ability to solubilize a given polymer, and susceptibility to solubilization is significantly affected by comonomer content of the polymer. If, for example, a poly(vinyl acetate) latex is stabilized exclusively by a strongly solubilizing sodium dodecyl benzene sulfonate, it is less stable and hydrolyzes faster than a similar latex made with a polyoxyethylene derivative, which has only a slight solubilizing action. Dibutyl maleate copolymers of vinyl acetate are less susceptible to solubilization than homopolymers of vinyl acetate.

### INTRODUCTION

There are a number of reports concerning the solubilization of polymers in aqueous solutions of surfactants. To our knowledge, only one paper has mentioned<sup>1</sup> the possibility of partial solubilization of polymer in a latex and its influence on polymerization mechanism. Sata and Saito<sup>2</sup> first observed the solubilization of poly(vinyl acetate) in solutions of sodium dodecyl sulfate (SDS). They suggested two alternative explanations: either the anions of the soap were being selectively adsorbed on sites in the polymer, or a cosolvent action of soap and water. Subsequent investigations by Saito<sup>3</sup> and Isemura<sup>4</sup> appear to prove the former hypothesis. In a 0.2M SDS solution the solubilized poly(vinyl acetate) carries one adsorbed soap molecule for five monomer units and behaves like a polyelectrolyte. Poly(vinyl alcohol), although water-soluble to begin with, also complexes with soaps (ratio: one soap molecule to seven monomer units in the same SDS solution) to give a higher viscosity. Poly(vinyl formal), insoluble in most organic and inorganic solvents, also dissolves in 0.2M SDS solution and adsorbs one soap molecule for six monomer units. It was noted that the bulk polymers will dissolve only in fairly concentrated solutions of soaps, but will not precipitate on dilution. In general, the solubilization is limited to anionic surfactants, with nonionic materials showing no effect and cationic ones having only a very small effect. No

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water-insoluble polymers other than poly(vinyl acetate), poly(vinyl acetals) and poly(methyl acrylate) are reported to have been solubilized. It is important to note that due to its polyelectrolyte nature the solubilized polymer often has a higher specific viscosity in water than in a true solvent.

The role of solubilization in emulsion polymerization has long been recognized. Harkins<sup>5</sup> postulated that monomer is solubilized in soap micelles which are entered by initiator radicals and thus form the initial locus of polymerization. We are suggesting that a partial solubilization of the polymer may have an influence on the emulsion polymerization process and definitely affects the properties of the resulting latex.

## EXPERIMENTAL

### Polymerizations

The vinyl acetate homo- and copolymers were made by a continuous monomer addition process, with the use of a three-necked flask equipped with condenser, thermometer, and stirrer. No attempt was made to exclude air. The monomer was dripped through the condenser at such a rate as to require 4 hr. for complete addition. Batch temperature was maintained between 70 and 75°C. Stirring was with a Teflon paddle at 400 rpm. After all the monomer was added, the reaction was continued until the total solids content agreed within 1% with the theoretical value for 100% conversion. A similar procedure was used for the acrylic polymerizations reported here, except that the reactions were run under a nitrogen atmosphere after purging.

### Materials

Vinyl acetate monomer was used as received from Union Carbide Chemicals. It was inhibited with hydroquinone. Dibutyl maleate was obtained from the Dewey and Almy Division of W. R. Grace and contained about 25% fumarate. Fisher reagent grade potassium persulfate and sodium bicarbonate were employed as initiator and buffer. The Santomerse D94 emulsifier is a relatively salt-free sodium dodecylbenzene sulfonate supplied as a 50% paste by the Monsanto Chemical Co. Ultrawet M is a similar product supplied as a clear gel at 66% solids by the Atlantic Refining Co. Benax 2A1 is disodium dodecyl diphenyl ether disulfonate from Dow. It was purified by extraction with ethanol and evaporation of the extract before use to remove the 6% salt impurity. Abex VA40 is a blend of anionic and nonionic emulsifier from Alcolac Chemical Co. containing only about 1% ethanol-insoluble salt and was used as such. Acrylic monomers were used as supplied by Monomer-Polymer Laboratories and Rohm and Haas. The styrene type latexes were supplied by the Dewey and Almy Division of W. R. Grace. The polyethylene dispersions were prepared by the Research Division of W. R. Grace.

### Hydrolysis Measurements

The degree of hydrolysis of the vinyl acetate latexes was determined by titration of free acid in diluted latex with 0.57*N* ammonium hydroxide, or alternatively in a methanol solution of the latex with 0.1*N* NaOH.

### Particle Size and Light Transmission

The particle size of the vinyl acetate polymers was estimated from the turbidity data on a series of dilutions according to the procedure of Hlousek<sup>6</sup> by using a Bausch & Lomb Spectronic 20 spectrophotometer at 409 and 532  $m\mu$  wavelength. Values were checked for representative samples by electron microscopy and with a Spinco Model E ultracentrifuge according to the procedure of McCormick.<sup>7</sup>

The change in light transmission during and after solubilization was determined with the Bausch & Lomb spectrophotometer at 532  $m\mu$ . Pure surfactant solutions were used to zero the instrument for surfactant-diluted dispersions.

### Viscosity Measurements

Viscosity was used as the chief measurement of degree of solubilization.<sup>4</sup> Measurements of the 1% latex dilutions and surfactant solutions were made in a No. 100 Ostwald-Cannon-Fenske viscosity pipet in a water bath at  $30.0 \pm 0.1^\circ\text{C}$ . Efflux times of hydroxyethyl cellulose solutions were measured in a No. 400 pipet. Relative viscosities were calculated relative to the surfactant solutions alone, and reduced specific viscosities were further corrected for the theoretical viscosity of a dispersion as in the work of Gillespie.<sup>8</sup>

### Latex Stability

**Mechanical Stability.** Mechanical stability of the latexes and mixtures was estimated by using a simple rubbing device shown in Figure 1.

The drive motor is set to give 1 cycle/sec. with a travel distance of 4 cm. Since the clearance under working conditions is about 20 $\mu$ , this corresponds to an average shear rate of about 4000  $\text{sec.}^{-1}$ . Besides, there is, of course, the small vertical pressure of the 300 g. weight to be taken into account.

To perform the test, a single drop of latex (which must be >20% total solids for reproducible results) is put on the plate glass base and immediately the microscope slide is placed over the drop. The Plexiglas holder is then fitted over the slide and the 300-g. weight applied. The microscope light is focused to show the leading edge of the flattened drop of latex against the black background. The motor is then turned on and the leading edge of latex is observed carefully until it suddenly begins to become opaque. On most latexes this occurs after 3–20 cycles of 1 sec. each. Some latexes, especially those with large amounts of protective colloids, do not become opaque but begin to form streaks throughout the film. In any case, the endpoint is taken as the beginning of opacity or streakiness. A new slide

is used for each test, because any scratch or speck of coagulum causes erratic results. The integer nearest the average of five measurements is taken as the rub stability.

This test correlates well with mechanical stability of paint and coating latexes in actual industrial uses.

**Storage Stability.** Storage stability was followed by measuring the light transmission of the diluted latex.

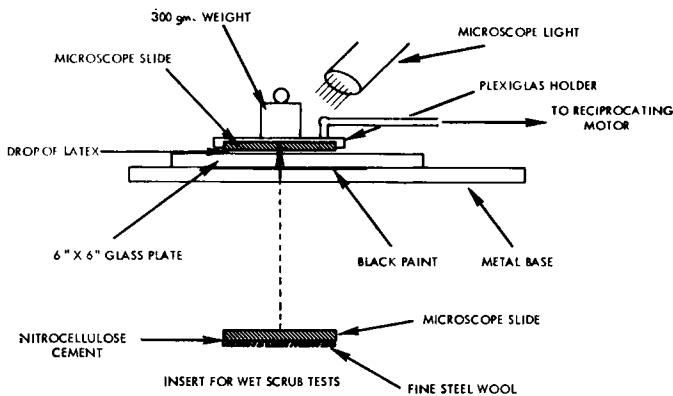


Fig. 1. Device for mechanical stability and wet scrub tests.

**Heat Stability.** Heat stability was measured by immersing a sample of the latex in a water bath of 100°C. for a certain length of time and observing its light transmission afterwards.

## RESULTS AND DISCUSSION

### Polymers Showing Solubilization Effects

The degree of solubilization of various polymers was estimated by the increase in reduced specific viscosity at 1% latex polymer in 3% Santomerse D94 solution. In this way we hoped to get an idea of which polymers other than poly(vinyl acetate) might show solubilization effects in their behavior. Table I gives some of the data.

The data indicates that poly(vinyl acetate) homopolymer is by far the most completely solubilized, followed by poly(methyl acrylate), where the process of solubilization is slower and which is completely solubilized (to give a clear solution) only in 10% sodium dodecylbenzene sulfonate (SDBS) at the 1% polymer level.

Of the materials tested, only the vinyl acetate homopolymers gave optically clear solutions very rapidly already in 3% SDBS. Figure 2 shows the change in optical density and approximate particle size (from tables of Hlousek<sup>6</sup>) with time for a typical anionically stabilized PVA latex in surfactant solution. The asymptote varies with the surfactant.

TABLE I  
Reduced Specific Viscosity (RSV) of 1% Latex Solids in 3% SDBS (2 hr. after Mixing)

Latex designation	Chemical type	RSV at 30°C.
PVA 1	Vinyl acetate homopolymer, MW 80,000	3.34
PVA 2	Vinyl acetate homopolymer, MW 250,000	4.5
PVA 3	Vinyl acetate-dibutyl maleate copolymer (VA-DBM), 77:23	0.40
PVA 4	Vinyl acetate-dibutyl maleate copolymer, 67:33	0.23
MMA 1	Methyl methacrylate homopolymer, MW 80,000	0.05
MA 1	Methyl acrylate homopolymer	1.10 <sup>b</sup>
MA 2	Methyl acrylate-hydroxymethyl methacrylate copolymer, 90:10	0.07
SBR 1	Styrene-butadiene copolymer, 60:40	0.00
SBR 2	Styrene-butadiene-acrylic acid terpolymer, 60:39:1	0.02
PS 1	Styrene homopolymer	0.00
PS 2	Styrene-acrylic acid copolymer, 98:2	0.07
PE 1	Emulsion-polymerized polyethylene	0.00
PE 2	Post-emulsified carboxylated polyethylene	0.16

<sup>a</sup> Corrected for RSV = 0.02 of ideal 1% suspension of spheres in water.

<sup>b</sup> 24 hr. after mixing.

### Surfactants Giving Polymer Solubilization

Saito<sup>2</sup> stated that anionic surfactants in general are effective solubilizing agents for poly(vinyl acetate). Table II shows the results obtained with various surfactants and several concentrations for the PVA latex 1.

TABLE II  
Reduced Specific Viscosity (RSV) of 1% Solids in 3% Emulsifier

Emulsifier	Chemical nature	RSV at 30°C.
Santomerse D94	Sodium dodecylbenzene sulfonate	3.3
Ultrawet M	Sodium dodecylbenzene sulfonate	5.0
Abex VA40	Nonionic blend with an alkyl polyoxyethylenesulfate	0.02
Benax 2Al	Dodecyl diphenyl ether disulfonate	1.4
Poly(vinyl alcohol)	...	0.0

It is clear that not all anionic surfactants have the same solubilizing ability; in fact, there appears to be some difference even between two brands of SDBS with the same nominal composition. In all cases the amount of soap used was known to be greater than that required by the ratio one soap molecule to five monomer units. Abex, of undisclosed exact composition, had an anion-active surfactant content that did not appre-

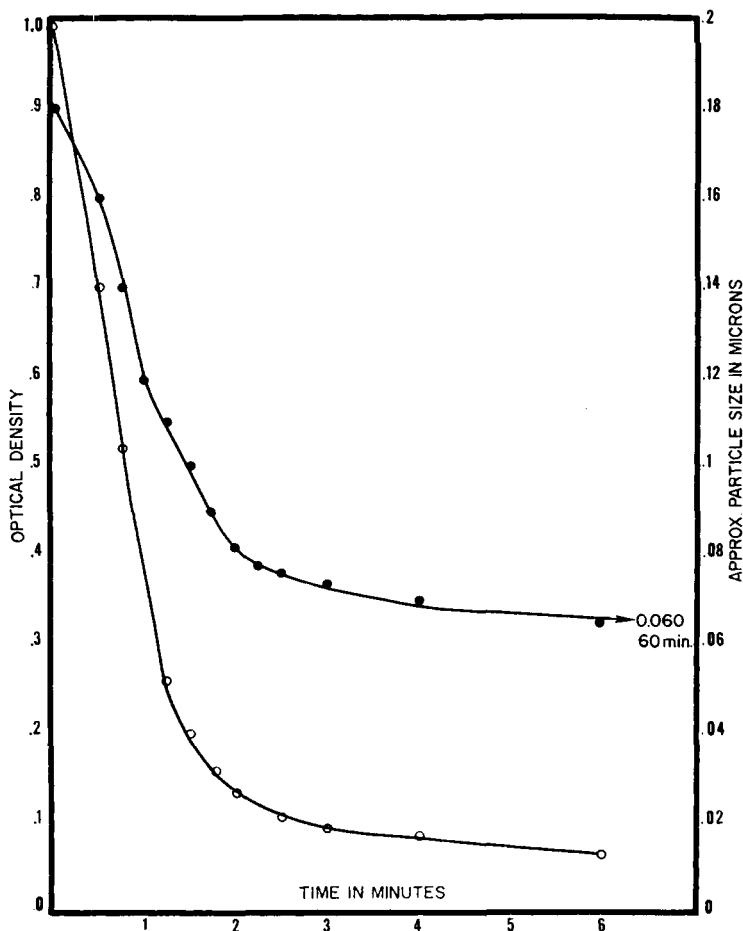


Fig. 2. Optical density vs. partical size of PVA in SDBS solution: (O) optical density; (●) particle size.

ciably solubilize PVA. In fact, Saito<sup>3</sup> mentioned already that no complex formation took place between polyvinylpyrrolidone and sodium dodecyl polyoxyethylene sulfate, if more than 4 oxyethylene units were situated between the paraffin chain and the sulfate group.

### Influence of Solubilization on Poly(Vinyl Acetate) Hydrolysis

**Unbuffered Systems.** The hydrolysis of poly(vinyl acetate) in water suspension is accelerated markedly below about pH 3 and above pH 7. However, we have observed that the rate of hydrolysis is greatly influenced by the emulsifiers that are present. Figure 3 shows the extent of hydrolysis of unbuffered poly(vinyl acetate) emulsions immediately after polymerization and after 6 hr. heating at 90°C. The values are plotted against the RSV of data given in Table I for the emulsifiers used in the respective la-

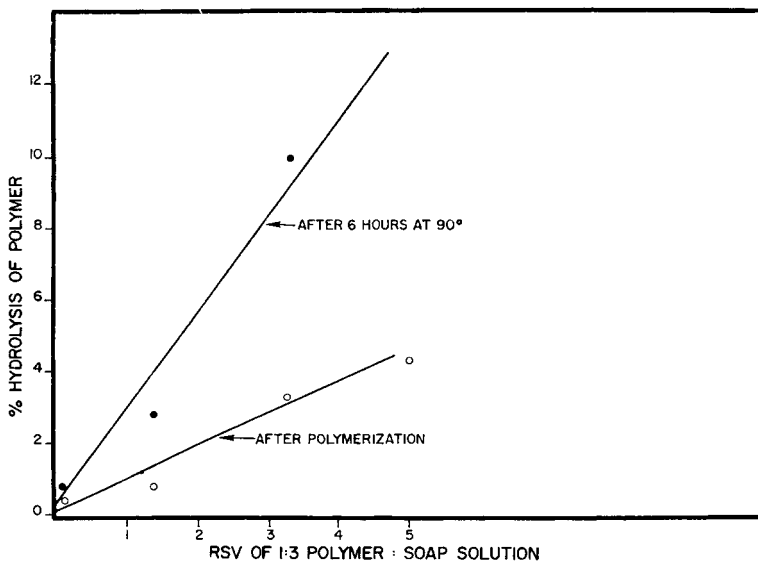


Fig. 3. Hydrolysis of vinyl acetate homopolymer latexes with various emulsifiers.

texes. It is evident that the extent of hydrolysis is proportional to the apparent degree of solubilization for each surfactant. This relationship seems to suggest that the rate of hydrolysis is increased by the presence of an agent that can bring polymer and water into the same phase.

The most plausible picture of acceleration of hydrolysis by surfactant is one in which the soap capable of interacting with the polymer penetrates into the particle interior bringing water with it. The increasing water concentration inside the particle increases the number of ester bonds accessible to saponification. Due to hydrolysis the polymer becomes more hydrophilic and, therefore, even more capable of imbibing additional water and soap which again accelerates hydrolysis, and so forth.

A further proof of the hypothesis of soap penetrating into the increasingly hydrophilic polymer particle interior is the increase in surface tension of about 5 dyne/cm. as the hydrolysis proceeds.

Soap titration also shows a decrease in saturation at the particle surface with increasing degree of hydrolysis. A buffered SDBS-stabilized latex revealed, by soap titration, that only about 15% of the surface of its particles were occupied by soap anions. Heating this latex to 100°C. for 16 hr. resulted in a sixfold increase in particle diameter and about 5% hydrolysis. This increase in particle size means a reduction of the total particle surface to  $\frac{1}{6}$  its original value. The original amount of SDBS (achieving 15% saturation in the latex prior to heating) should, therefore, now be sufficient to saturate the whole surface of these larger particles. Soap titration, however, showed that the heat-treated latex could still adsorb an amount of soap about equal to the one originally present, meaning that this original soap must have disappeared from the surface.

**Buffered Poly(Vinyl Acetate) and Vinyl Acetate-Dibutyl Maleate Copolymer Latexes.** Figure 4 shows the progression of hydrolysis for different PVA and VA-DBM copolymer latexes during storage for several months at room temperature; in addition to PVA 1 (homopolymer) and PVA 3 (co-

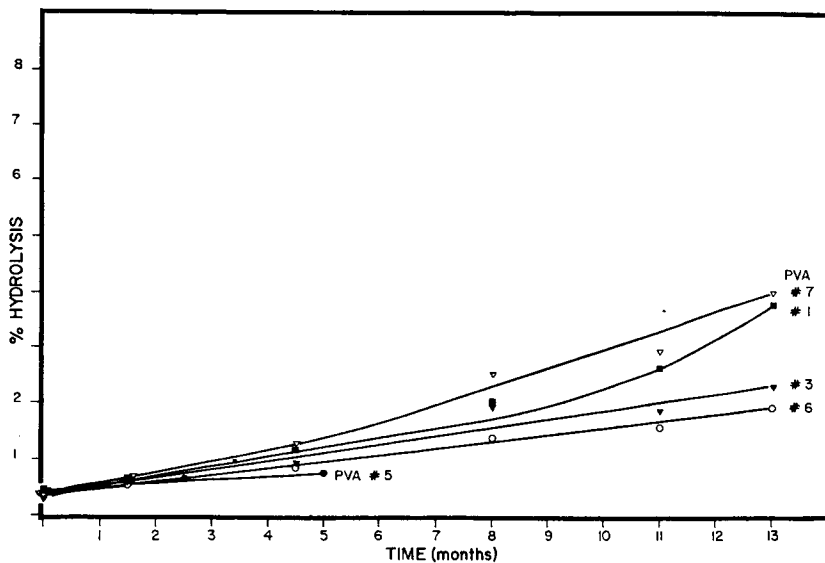


Fig. 4. Hydrolysis of vinyl acetate homopolymer and copolymer latexes during storage at room temperature.

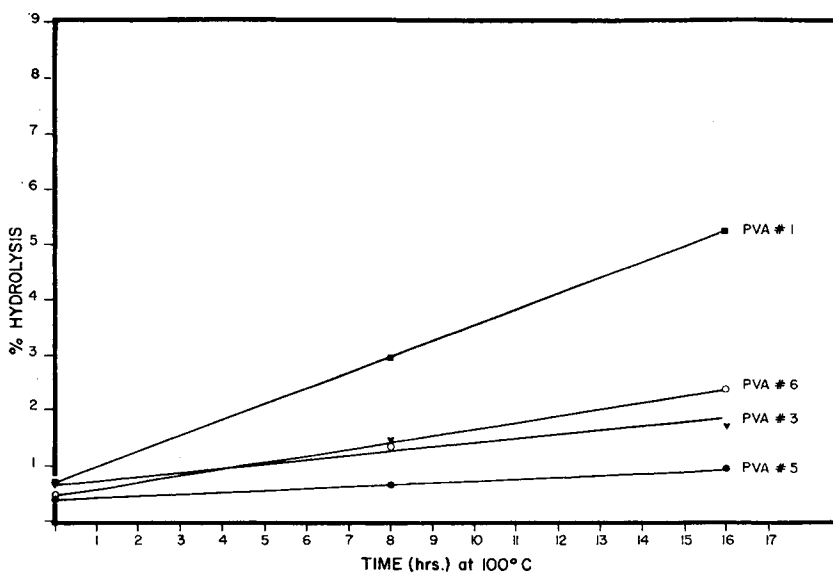


Fig. 5. Hydrolysis of vinyl acetate homopolymer and copolymer latexes during heating at 100°C.



polymer) already described in Table I the following latex polymers have been kept under observation: PVA 5, a large particle size homopolymer latex stabilized by poly(vinyl alcohol); PVA 6, a very small particle size homopolymer latex stabilized like PVA 1 by SDBS, and additionally by a small amount of a vinyl sulfonate-vinyl acetate copolymer; PVA 7, a VA-DBM copolymer latex similar to PVA 3, only stabilized by twice the concentration of SDBS.

All these latexes had been buffered during polymerization by a small amount of sodium bicarbonate, and consequently, exhibited a pH of 4-5 immediately after polymerization.

Figure 5 shows the hydrolysis of the freshly prepared above latexes after artificial aging by heating the samples for several hours to 100°C.

In line with our earlier argument, both figures indicate that hydrolysis is practically negligible under the conditions investigated if the particle stabilizer does not solubilize the polymer (PVA 5). Hydrolysis is equally retarded by a vinyl sulfonate-vinyl acetate copolymer at the particle surface (PVA 6 in comparison to PVA 1) which possibly retards the auto-accelerated penetration of SDBS and water into the particle interior.

On the other hand, the rate of hydrolysis will also be significantly lower, if instead of the homopolymer, the DBM copolymer, which is much less susceptible to solubilization (compare Table I) is stabilized by the same amount of SDBS (PVA 3 versus PVA 1). However, solubilization must also play some role with the DBM copolymer, because at twice the concentration of SDBS hydrolysis is markedly accelerated (PVA 7 versus PVA 3).

### Effect of Solubilization on Latex Stability

**Shear Stability.** The factors involved in latex shear stability have been discussed by several authors.<sup>9,10</sup> There is general agreement that if particle-particle interaction is prevented, good shear stability should result.

TABLE III  
Rub Stability of Latex Compositions in the Presence and Absence of Hydroxyethyl Cellulose (HEC) (Latex Solids = 45% in All Cases)

Latex designation (Table I)	Approx. particle size, $\mu$	Emulsifier used in polymerization	Emulsifier in latex solids, %	No. of rubs to incipient coagulation	
				Unmodified	0.4% HEC added
PVA 1	0.18	Santomerse D94	0.7	2	0-1
			5.0	2	0-1
PVA 1	0.18	Abex VA 40	0.7	2	5
			5	16	
PVA 3	0.18	Santomerse D94	0.7	4	0-1
		Benax 2Al	0.7	2	1
		Abex VA 40	0.7	5	20
PVA 2	0.50	Polyvinyl alcohol	5	10	30

We have noted that both shear and storage stability of many latexes are profoundly affected by the nature of the emulsifier and the presence of water-soluble polymers, in a way that suggests a primary role of solubilization phenomena.

Table III shows the rub stability values obtained for various latex compositions, using the device described in the section on methods.

The emulsifiers which show interactions with polymers in water give somewhat poorer rub stability than those which show little or no interaction. Note also that the rub stability of solubilizing systems is not improved by adding more emulsifier, but that of nonsolubilizing systems is improved. More striking is the effect of added Cellosize, where in the case of Santomerse-stabilized PVA, coagulation often ensued without any shear. The same protective colloid used in Abex-stabilized systems, however, increased their stability considerably.

The explanation of these results seems to lie in the different tendency of the surfactants to be removed from the globule surface and penetrate into the interior of the globule or, on addition of a water-soluble polymer additive, to be removed from the globule surface and be bound instead by the water-soluble macromolecule.\* Consequently, a water-soluble polymer can increase the mechanical stability by becoming adsorbed onto the particle surface, provided it does not interfere with the stabilizing action of the original emulsifier anion. Thus, the Abex VA40 gives a better stability with PVA than Santomerse or Benax, and since it does not interact with Cellosize it allows a considerable increase in stability when that water-soluble polymer is added.

The effects here are not limited to hydroxyethyl cellulose because the same type of results were obtained with alginates, poly(vinyl alcohol), high molecular weight polyethylene oxides, sodium polyacrylates, and methyl cellulose. The thickening effect of these latex additives is undoubtedly influenced by their interactions with the soaps. A high interaction with a strongly solubilizing soap could increase thickening efficiency but may also decrease mechanical stability.

**Storage and Heat Stability of Buffered PVA and VA-DBM Copolymer Latexes.** Figure 6 shows particle agglomeration during storage at room temperature for the same latexes that were used in the rate of hydrolysis experiments.

Figure 7 illustrates the same process during artificial aging of the freshly prepared latexes by heating to 100°C. for several hours.

The effects of solubilizing and nonsolubilizing systems seem to be particularly clear cut. The nonsolubilizing poly(vinyl alcohol) not only represses polymer hydrolysis, it also practically prevents particle agglomeration (PVA 5). The only slightly solubilizable VA-DBM copolymer, although softer, gives much higher stability at the same SDBS level than

\* The effect of a water-soluble polymer depends on a balance between water-polymer and particle-polymer interaction on the one side, and polymer-surfactant and particle-surfactant interaction on the other side.

the PVA homopolymer (PVA 3 versus PVA 1). At twice this SDBS concentration even the DBM copolymer is much less stable (PVA 7) but still noticeably superior to the homopolymer, which after about 5 months is already coagulated (not described in Fig. 5).

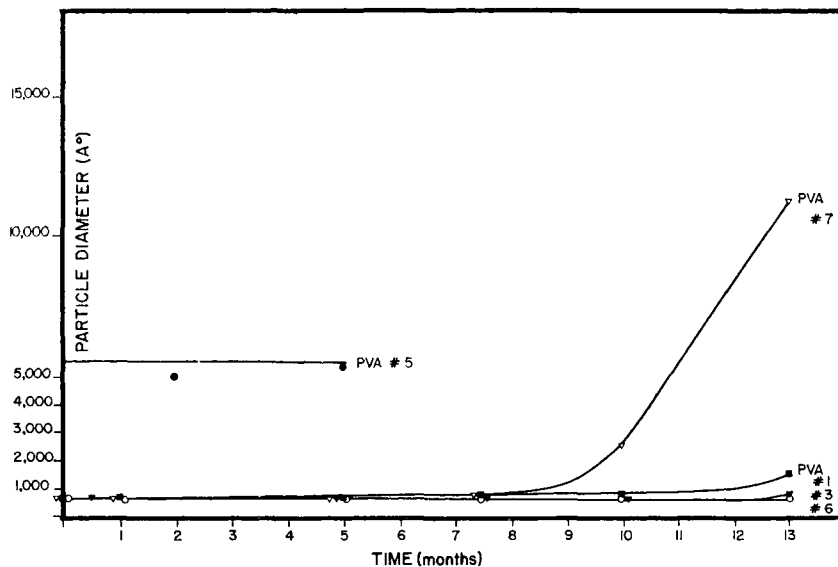


Fig. 6. Particle agglomeration in vinyl acetate homopolymer and copolymer latexes during storage at room temperature.

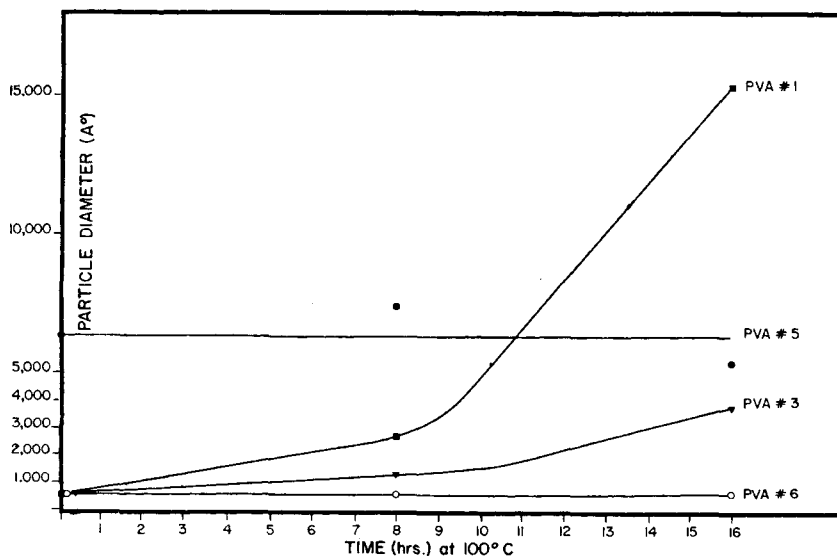


Fig. 7. Particle agglomeration in vinyl acetate homopolymer and copolymer latexes during heating at 100°C.

The vinyl sulfonate-vinyl acetate copolymer retards hydrolysis and definitely increases the stability of the latex particles (PVA 6).

Using similar arguments as in the previous section, we would interpret these data on the assumption that in nonsolubilizing systems the surfactant stays at the particle surface and thereby stabilizes them, whereas in solubilizing systems the surfactant disappears from the particle surface with the resulting loss in stability.

The vinyl sulfonate-vinyl acetate copolymer cannot migrate into the particle interior, but instead due to its macromolecular nature forms a protective, colloidlike elastic skin around the particles, which prevents their agglomeration, even if the SDSB has left the surface.

### CONCLUSION

The difficulty in obtaining high solids anionic vinyl acetate latexes is usually ascribed to the water solubility of the monomer and hence the need for protective colloids. Acrylates are often of equal or greater water solubility but will produce stable latexes with simple soaps alone. Here too, the high solubilizability of vinyl acetate polymers is probably the most important factor in determining the relative instability of its polymerizing latexes, compared to the lower solubilizability of acrylates.

Most anionic soaps tend to solubilize poly(vinyl acetate) which, as we have seen, leads to an unstable latex. Furthermore, the anionic PVA systems are very sensitive to electrolyte, which is probably due to the fact that the soap is either in the particle or bound up with dissolved polymer. One of us (HAE)<sup>11</sup> has noted that as little as 50 mmole/l. of monovalent cations, in addition to those originating from the emulsifier, always leads to coagulation in a system such as PVA 1. Such an addition of nonsurface-active electrolyte will decrease the electrical double layer thickness. Since there is little soap adsorbed on the surface to provide mechanical protection, this decrease in thickness is fatal. In an acrylic system, or in the case of a PVA with protective colloid, dependence of stability on double layer thickness is probably minimized by the presence of a distinct adsorbed emulsifier layer.

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### Résumé

On a étudié l'effet de la solubilisation de polymères du latex dans des solutions de tensio-actifs anioniques. Le procédé et le degré de solubilisation final ont été étudiés en mesurant l'accroissement de transmission lumineuse et l'accroissement de viscosité du latex. Les tensio-actifs anioniques diffèrent grandement du point de vue de la capacité à solubiliser un certain polymère; la susceptibilité d'un certain type de polymère à être solubilisé peut être affectée d'une façon significative suivant sa teneur en comonomère. Si par exemple un latex d'acétate de polyvinyle est stabilisé exclusivement par un tensio-actif anionique qui est fortement capable de solubiliser le polymère, ce dernier s'hydrolyse rapidement et la stabilité de la dispersion est diminuée si on la compare à celle d'un latex d'acétate de polyvinyle où peu ou pas d'interaction de cette nature ne se passe entre le tensio-actif et le polymère.

### Zusammenfassung

Der Einfluss der Solubilisierung in Lösungen anionenaktiver Emulgatoren auf das Verhalten einiger Polymerlatizes wurde untersucht. Der Vorgang und der schliesslich erreichte Solubilisierungsgrad wurde durch Messung der Zunahme der Lichtdurchlässigkeit und der Viskosität des Latex verfolgt. Verschiedene anionische Emulgatoren unterscheiden sich stark in ihrer Fähigkeit, ein bestimmtes Polymeres zu solubilisieren, die Solubilisierungsfähigkeit eines bestimmten Polymertyps kann in charakteristischer Weise durch seinen Comonomergehalt beeinflusst werden. Wennz. B. ein Polyvinylacetatlatex ausschliesslich durch einen anionischen Emulgator mit starker Solubilisierungsfähigkeit für das Polymere stabilisiert wird, hydrolysiert das Polymere rascher, und die Stabilität der Dispersion wird im Vergleich zu einem Polyvinylacetatlatex, bei welchem nur eine geringe oder keine derartige Wechselwirkung zwischen Emulgator und Polymeren stattfindet, herabgesetzt.

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