Acid Distribution in Carboxylated Vinyl-Acrylic Latexes

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Synopsis

Distribution of acid groups in carboxylated vinyl-acrylic latexes has been determined by a combination of aqueous conductometric and nonaqueous potentiometric titrations. Titrations analysis of vinyl acrylic latexes, in comparison to earlier reported studies with carboxylated polystyrene and all acrylic latexes, is complicated by the presence of acetic acid which originates from the hydrolysis of polyvinyl acetate. Most of the copolymerized carboxylic acid is located at the latex particle surface with some of it being buried within the particle. No serum phase polymeric carboxylic acid is detected. Polymerization conditions and the choice of the carboxylic monomer affect acid distribution. Effect of acid distribution on some latex properties is also discussed.

INTRODUCTION

The distribution of acid groups in carboxylated styrene and acrylic latexes has been described in a number of recent publications.[1-6] The acid groups have been located, depending upon the polymerization conditions, at the particle surface, in the serum phase or buried within the interior of the latex particle. Carboxylic groups located at the particle surface or in the serum phase have generally been determined by potentiometric or conductometric titrations and the difference of their sum from the theoretical acid level ascribed to buried acid groups. A nonaqueous potentiometric titration procedure has been reported for the determination of buried acid groups for methacrylic acid-containing styrene–butadiene latexes.[7] Another reported procedure for determination of buried acid groups involves the stepwise dissolution of the latex and subsequent measurement of the carboxyl content in the dissolved polymer separated by centrifugation.[8]

In contrast to the above studies with styrene and acrylic latexes, little published material exists on another class of commercially important latexes, namely those based on vinyl acetate and its copolymers with acrylic monomers. We wish to report here the determination of the distribution of acid groups in carboxylated vinyl-acrylic latexes and point out the differences in the conductometric titration analysis of vinyl-acetate-based latexes. For the determination of buried acid groups, we describe a new nonaqueous titration procedure by which we are able quantitatively to account for the total theoretical acid level in a carboxylated vinly acrylic latex.

The copolymerized acid group location is seen dramatically to affect the final properties of the latex as shown, for example, by the pH–viscosity response of the latex, in good agreement with published results on carboxylic acrylic latexes.[9]

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EXPERIMENTAL

The vinyl acrylic latexes were prepared by a semicontinuous emulsion polymerization procedure using redox initiators. Latexes with 55% polymer solids were prepared using a monomer weight ratio of 85% vinyl acetate and 15% butyl acrylate. The carboxylic acid (acrylic or methacrylic acid) content was introduced by replacing an equal weight of vinyl acetate from the copolymer composition. Conductometric and potentiometric titrations of the latex were performed using a Metrohm Potentiograph E536 and a Metrohm Conductometer E518 with Dosimat E535 (Brinkman Instruments, Long Island, N.Y.).

The aqueous conductometric titrations were performed using the Hen procedure,[2] which is as follows: to about 100 mL of a 1–2% latex solids dispersion, obtained by dilution of the 55% solids latex with deionized water, $0.5M$ sodium hydroxide was added to raise the pH above 10. The sample was titrated using $0.1M$ hydrochloric acid solution (prepared from standardized concentrates supplied by Fisher Scientific). Latex serum titrations were performed similarly on visually clear serum samples obtained by centrifugation of the 55% solids latex in a Beckman Model L5-75B Ultracentrifuge.

Dialysis of the carboxylated latexes was performed on a 10% solids latex sample placed in "Spectrapor" (Spectrum Medical Industries, available from Fisher Scientific) cellulose dialysis tubing with a stated molecular weight cutoff of 12,000. A dialysate to sample volume ratio of at least 20:1 was used with daily changes of the deionized water over a period of 3–4 weeks. Serum replacement[10] was performed by placing a 3–5% solids latex sample in a Nucleopore Ultrafiltration Cell (Nucleopore Corporation, Pleasanton, Calif.) with a $0.1\text{-}\mu m$ filter and pumping deionized water through the cell by gravity feed. A time period of a few days was deemed sufficient for serum replacement, after which the conductivity of the water exiting the cell remained the same as the water fed in.

The nonaqueous titration procedure for determination of buried acid groups was developed for this investigation and was performed as follows: a weighed amount of the 55% solids aqueous latex was dissolved in pyridine and enough perchloric acid added to protonate all weak acid groups present in the sample. Potentiometric titration of the sample was performed using $0.1M$ tetrabutyl ammonium hydroxide in methanol as the titrant (Eastman Chemical). The "apparent" pH and its first derivative with respect to volume of titrant (Δ pH/Δ volume of titrant) were simultaneously recorded on a Metrohm Potentiograph E536 and an auxiliary chart recorder. End points for the titration curve were determined from the first derivative curve recorded on the Metrohm Potentiograph.

RESULTS AND DISCUSSION

For this study, a series of vinyl acetate (VA)–butyl acrylate (BA) latexes with acrylic (AA) or methacrylic (MAA) acid as the carboxylic acid comonomer were prepared and titrated following the conductometric titration procedure described above.

The conductometric titration curves for a control vinyl acrylic latex and a typical carboxylated vinyl acrylic latex are shown in Figures 1 and 2 respectively.
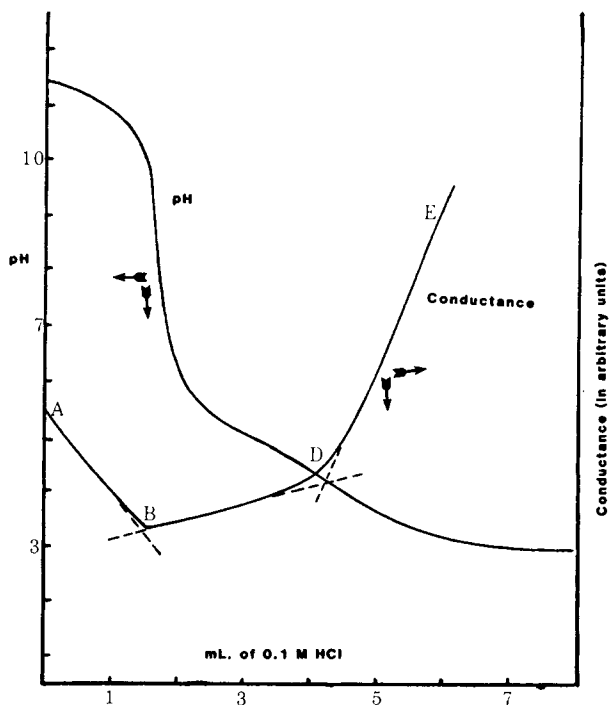
Fig. 1. Conductometric and potentiometric titration of a typical vinyl acrylic latex with no acid comonomer. Similar titration curve observed for all serum samples also.
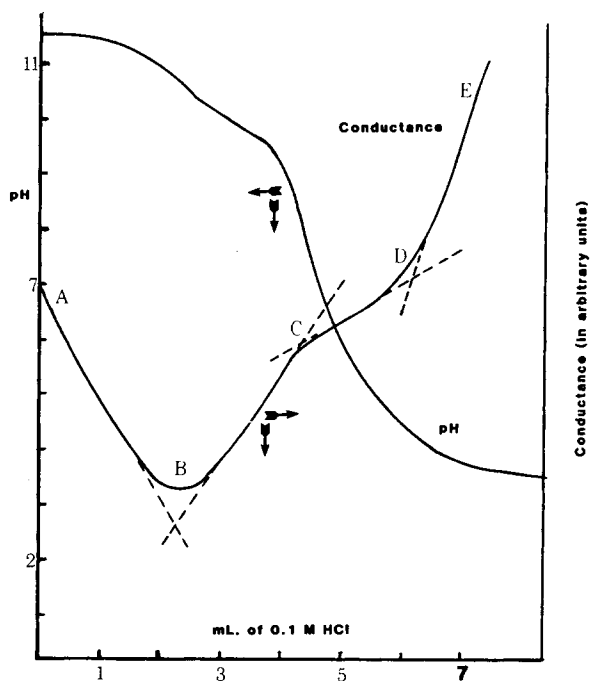

Fig. 2. Conductometric and potentiometric titration curve for a typical carboxylated vinyl acrylic latex.

TABLE I
VA/BA Latexes Prepared and Their Titration Analysis[a]

Latex	% Acid and type[b]	Placement of acid	Latex pH	Acid level[c]			
				Type I	Latex type II	Serum type II	Theoretical acid level[c]
A	0	—	4.3	—	92	46	—
B	0.5 AA	water	4.4	34	117	51	62
C	1.0 AA	water	4.2	72	139	47	133
D	1.0 AA	monomer	3.9	101	125	51	133
E-1	0.5 MAA	water	4.2	35	115	55	56
E-2	0.5 MAA	water	4.3	38	92	54	56
F	1.0 MAA	water	3.9	64	121	52	112
G	1.0 MAA	monomer	4.0	115	87	51	112

[a] The carboxylic acid level is a weight percentage based on total monomer concentration.
[b] AA = acrylic acid; MAA = methacrylic acid.
[c] All acid values are μeq/g latex solids.

In this procedure, basic groups (excess hydroxide, conjugate base of weak acid anions such as acrylate, acetate, etc.) are titrated in order of their decreasing strength. Following the analysis by Hen, the initial decrease in conductance (AB in Figs. 1 and 2) is attributed to the neutralization of excess base and the final increase (DE) due to the addition of excess titrant acid. The change in conductance values in between the initial decrease and the final increase, regions BD in Figure 1 and BC and CD in Figure 2, is attributable to the neutralization of conjugate bases of weak acids present in the system.

Thus, at least one kind of weak acid (region BD) is distinguishable in the titration of latexes of the type in Figure 1 and at least two kinds of weak acids (regions BC and CD) in latexes with a titration curve of the type in Figure 2. For all latex serums of this study, the titrations are represented by a curve of the type shown in Figure 1 with at least one type of weak acid distinguishable.

Table I lists the results of our conductometric titrations of VA/BA latexes with AA or MAA prepared for this study. A process variation with the acid being placed in the monomer feed or an auxiliary aqueous feed was also examined during this study. The two kinds of latex weak acids distinguishable by the titration, regions BC and CD in Figure 2, are labeled as type I and type II acid in Table I. Also included in Table I are the serum titration results and the latex pH after preparation. All acid values in Table I are given in units of microequivalents of acid per gram of latex solids (μeq/g).

The precision of our titration analysis was determined by five consecutive titrations of a latex for which the mean weak acid values for type I and type II acids were 112 μeq/g and 226 μeq/g, respectively. The standard deviation of type I value was 7.1 and that of type II was 6.1.

Several interesting observations can be made of the results in Table I. Sample A, with no acid comonomer and representing the control composition for this study, exhibited one kind of weak acid in the latex; and its serum titration revealed orly a fraction of that weak acid content. For all AA- or MAA-containing latexes, samples B–G in Table I, at least two types of weak acids were distinguishable in their latex titrations (titration curve of the type in Fig. 2). The serums for samples B–G, however, as mentioned earlier, exhibited only one type

TABLE II
Titration of Latexes with Externally Added Acetic Acid[a]

Latex	Latex (as is)		Acetic acid added	Latex acid after addition of acetic acid		Expected[b]	
	Type I acid	Type II acid		Type I	Type II	Type I	Type II
A	—	92	47	—	147	—	139
B	34	117	45	36	166	34	162
C	72	139	47	76	183	72	186

[a] All acid values are in μeq/g latex solids.

[b] For expected level the externally added acetic acid is assumed to add to Type II acid of the latex.

of weak acid (titration curve of the type in Fig. 1). The serum weak acid content surprisingly does not correspond to either type I or type II latex weak acid values.

In the analysis of the carboxylated polystyrene latexes,[2,4] type I acid has been shown to represent surface carboxylic acid and type II, serum phase oligomeric acid. For vinyl acrylic latexes, however, serum phase acid is detectable for sample A with no carboxylic acid comonomer. The type II acid in carboxylated vinyl acrylic latexes (samples B–G) is often larger than the theoretical carboxylic acid content (Table I), and thus the conductometric titration of carboxylated vinyl acrylic latexes cannot be explained on the basis of earlier literature work.[2,4]

We have established from our acid distribution analysis that type II acid (region BD in Fig. 1 and CD in Fig. 2) in vinyl acrylic latexes represents acetic acid present in the system. Acetic acid possibly can arise from the hydrolysis of monomeric vinyl acetate to acetaldehyde and acetic acid. Our results, however, show that a more likely explanation is that the acetic acid arises from the hydrolysis of poly(vinyl acetate) units in the latex to poly(vinyl alcohol) and acetic acid. The hydrolysis of polymeric ester groups can be catalyzed by the sulfonate and sulfonic acid end groups derived from initiator fragments.[11]

The assignment of type II acid as acetic acid in vinyl acrylic latexes is supported by the results of Table II which shows that externally added acetic acid is quantitatively accounted for, within experimental error, as latex type II acid. Gas chromatographic (GC) analysis of the latex for acetic acid was not successful due to experimental difficulties. GC analysis of the serum, however, showed that the serum type II acid was acetic acid. Quantitative agreement between serum type II titration values and GC was also observed. Thus, for example, latexes A and B had 46 and 51 μeq/g of type II acid by titration in good accord with GC analysis of 45 and 55 μeq/g of acetic acid for the two samples. This also shows that serums of carboxylated vinyl acrylic latexes of this study contain only acetic acid and no other detectable polymeric acids.

Dialysis and serum replacement results in Table III lend further evidence to the assignment of acetic acid as type II acid. Table III shows that the amount of acetic acid was reduced substantially by both treatments; however, the type I acid value remained unchanged within experimental error.

The difference between serum replacement and dialysis on the acetic acid values can be explained on the basis of the former technique being more effi-

TABLE III
Latex Analysis after Dialysis and Serum Replacement[a]

Latex	Sample treatment	Type I acid	Type II acid (Acetic Acid)
C	As prepared	72	139
	After dialysis	64	37
	After serum replacement	65	18
D	As prepared	101	125
	After dialysis	93	55
	After serum replacement	100	0

[a] All acid values are in μeq/g latex solids.

cient[10] in removing low molecular weight species. Also, over the longer time period for dialysis (3–4 weeks) as compared to serum replacement (less than 1 week), continued hydrolysis of polymeric vinyl acetate units to acetic acid results in a higher level of acetic acid after dialysis.

The presence of acetic acid in vinyl acrylic latexes is further supported by titration results on aged latex samples of this study. Table IV shows that acetic acid level of latexes stored for 6 months increased dramatically. As in the case of the dialyzed and serum replacement samples mentioned earlier, type I weak acid values remain unchanged on aging. The significance of this finding in the interpretation of acid distribution in vinyl acrylic latexes is discussed later.

The difference in the acetic acid levels between the latex and serum (type II acid values in Table I) suggests partitioning of the low molecular weight species. To investigate this and the possible adsorption/desorption of oligomeric acid species, the serum acetic acid value was determined as a function of the latex pH at centrifugation. Table V shows the results of such an analysis. The serum acetic acid value increased as the pH of the latex at centrifugation was raised. Even externally added acetic acid appeared to partition between latex and serum as a function of latex pH.

Partitioning of a low molecular weight species between a poly(vinyl acetate) latex and its serum is not surprising since the latex polymer is known to be permeable to monomers, low molecular weight glycols,[12] and surfactants.[13,14]

The increased acetic acid level in the serum phase at higher latex pH values is probably due to ionic repulsion forcing out acetate anions from inside the permeable and negatively charged latex particle. Swelling of the carboxylated latex particle (see discussion on the viscosity increase of latex) also causes increased solvation by water and leads to more acetate ion in the serum phase.

TABLE IV
Titration of Aged Latex Samples (6 Months at Room Temperature)[a]

Latex	After preparation		After 6 months	
	Type I acid	Acetic acid	Type I acid	Acetic acid
A	—	92	—	139
B	34	117	31	194
E-2	38	92	45	172

[a] All acid values are in μeq/g latex solids.

TABLE V
Serum Acid as a Function of Latex pH at Centrifugation[a]

Latex	pH at centrifugation	Latex acid Type I	Type II	Serum acid	Serum level as a % of Latex type II
A	3.6	—	97	52	54
	4.2	—	94	53	56
	4.9	—	93	66	71
	6.0	—	103	79	77
C	4.2	72	139	47	34
	6.5	78	147	109	74
	7.7	78	147	130	88
A + 100 μeq/g of acetic acid	3.1	—	193	121	63
	5.0	—	198	153	77
	7.1	—	195	169	87

[a] All acid values are in μeq/g latex solids.

The constancy of type I acid values after dialysis, serum replacement, and aging shows that this, in similarity to carboxylated polystyrene latexes,[2,4] must represent copolymerized surface carboxylic acid groups. For our purposes, surface acid groups represent those groups at or close to the latex particle surface accessible by aqueous titration. Attempts to confirm that type I acid is copolymerized surface carboxylic acid by ion exchange [similar to reported work on polystyrene[2,9,10]] were not successful. Discoloration of the ion-exchange resins after contact with the carboxylated vinyl-acrylic latexes, the reasons for which are not known, and a substantial reduction in latex solids after ion-exchange limits our confidence in the results obtained on ion-exchanged vinyl-acrylic latexes.

Summarizing our results of Tables I–V, latex type I weak acid is permanently bound surface carboxylic acid and latex type II is totally accounted for by acetic acid derived from the hydrolysis of polymeric vinyl acetate groups. No significant level of polymeric acid is found in serum. The acetic acid partitions between the permeable latex and the serum phase, dependent upon pH. The surface carboxylic acid, type I, is generally less than the theoretical carboxylic acid level (Table I), and this indicates that some acid must remain "buried" and is not accessible by aqueous titration. Determination of buried acid groups by nonaqueous titration is discussed next.

Attempts at nonaqueous titration by earlier reported procedures[7] were unsuccessful, and after considerable effort the procedure described in the experimental section was arrived at. The titrant, tetrabutyl ammonium hydroxide in methanol is often recommended for nonaqueous titration.[15] The potentiometric titration and its first derivative curve for a sample of this study titrated by our procedure is shown in Figure 3. Two end points are obtained from the first derivative curve with the first corresponding to the neutralization of excess perchloric acid and the second to the neutralization of all weak acids present in the system. Table VI gives the results for two MAA-containing samples of this study. The difference between the nonaqueous weak acid value and the total aqueous weak acid content is assigned to buried groups. The sum of type I surface acid groups (from aqueous titration) and buried acid groups as obtained
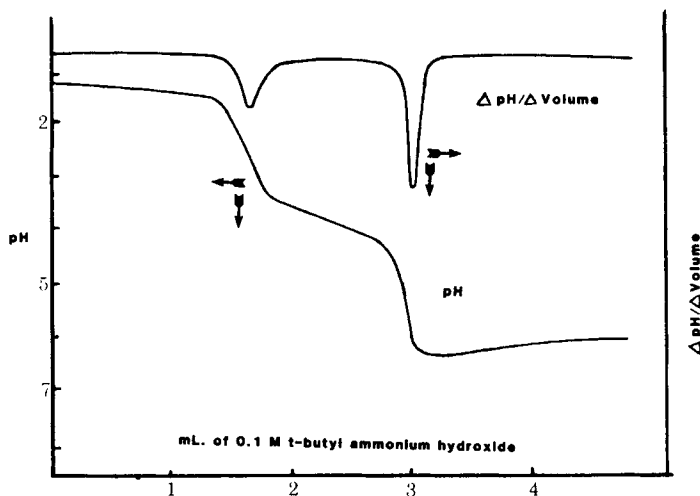
Fig. 3. Potentiometric and first derivative curve for the nonaqueous titration of a carboxylated vinyl acrylic latex dissolved in pyridine and titrated with tetrabutyl ammonium hydroxide in methanol as titrant.

above using the nonaqueous titration corresponds, within experimental error, to the theoretical acid level of the latex. This would confirm GC analysis of serum that there is no detectable free polymeric acid in the serum of the latexes, a result in contrast to those reported for carboxylated polystyrene and all acrylic latexes.[2,4,5]

The utility of the nonaqueous titration is limited by the precision of the aqueous titration. Since the total error in aqueous titrations is of the order of 10–12 μeq/g weak acid, the nonaqueous titration, is found useful for latexes possessing at least 15 μeq/g of buried acid groups.

Returning again to the results of Table I, we have now established, that for the carboxylated vinyl acrylic latexes, type I acid represents surface carboxylic acid and its difference from the theoretical level is due to buried groups. Some other points of note are:

—the surface acid level increases as the copolymer acid concentration increases.

—at 1% acid level, feeding the acid with the VA/BA monomer feed instead of an auxiliary aqueous feed results in more surface acid with the effect being more pronounced with MAA compared to AA.

TABLE VI
Nonaqueous Titration of Buried Acid[a]

Latex	Aqueous surface a	Aqueous acetic acid b	Total aqueous acid $(a + b)$	Total nonaqueous acid C	Buried acid $d = c - (a + b)$	Total carboxyl polyacid $(a + d)$	Theoretical carboxyl polyacid
E-1	35	115	150	170	20	55	56
F	64	121	185	238	53	117	112

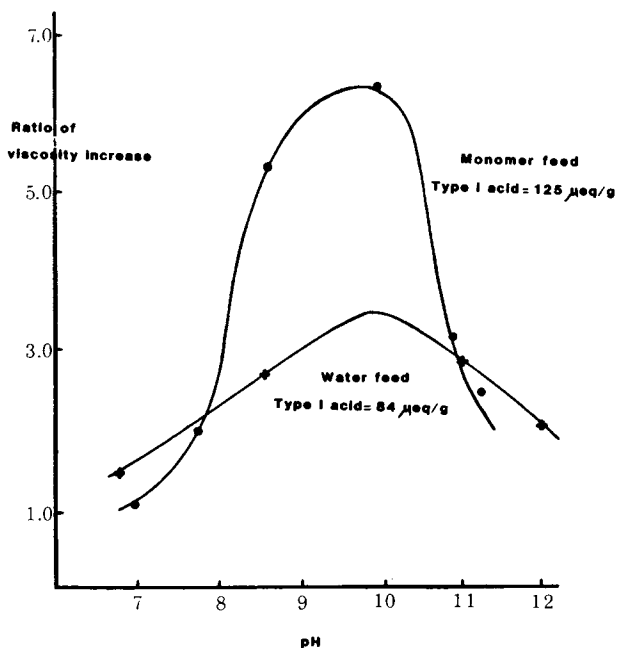[a] All acid values are in μeq/g latex solids.

Fig. 4. Viscosity increase relative to viscosity at pH = 5 for a carboxylated vinyl acrylic latex with the acid being introduced in the monomer or an auxiliary aqueous feed.

Thus, it can be seen that it is possible to change the location of acid groups in carboxylated vinyl acrylic latexes by process and compositional variations.

It is well recognized[5,9] that acid distribution controls many useful end-use properties of carboxylated latexes. One such effect for carboxylated vinyl acrylic latexes is in the rheological properties as shown in Figure 4. The viscosity increase, and thus the swelling of the latex, is dependent on surface acid level. This result is in good agreement with the work of Bassett and Hoy.[9] Other investigations in our laboratory[16] have shown that type II acid in vinyl-acrylic latexes dramatically affects the high shear rheology of pigmented systems formulated with such latexes.

CONCLUSION

In conclusion, we have developed a convenient method to determine the acid distribution in carboxylated vinyl-acrylic latexes. The presence of acetic acid, formed as a result of polymer hydrolysis, and its distribution between the latex particle and the serum phase is found to complicate the titration behavior of the vinyl acrylic latex in comparison with polystyrene latexes. In contrast to published results on carboxylated polystyrene and all acrylic latexes, it is shown that very little, if any, oligomeric/polymeric acid exists in the serum of vinyl acrylic latexes at 1% carboxylic acid level. Factors such as acid level, acid type, and mode of acid addition during polymerization control the acid distribution. Finally, acid distribution affects rheology and other physical properties of carboxylated vinyl acrylic latexes.

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