Some Physicochemical Properties of Poly(ethyl Acrylate) Emulsions Containing Carboxyl Groups

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Synopsis

Conductometric and potentiometric titration behavior of emulsions of ethyl acrylate copolymers with acrylic acid and methacrylic acid was investigated. On the conductometric titration curves of the emulsions of the copolymers with more than 5 mole-% of the acids, two equivalence points, based on the copolymerized acids, were observed, but only one equivalence point was observed on potentiometric titration. Almost all of the copolymerized acids could be detected by both titration methods. The change in optical density of the dilute emulsions with their pH was measured. The particles of these emulsions were studied under an electron microscope. These results showed that, when the pH of the emulsions was raised, the surface layers of the particles began to dissolve and their cores started to swell near the pH of their first equivalence points. When the pH was again lowered the dissolved polymers coagulated, tiny particles were formed, and the swollen cores were dehydrated. The surface layers thickened with increasing amount of the copolymerized acid. These behaviors were very similar in the emulsions of the copolymers with acrylic acid and methacrylic acid. The quantity of water-soluble polymers formed in the course of the emulsion copolymerization was approximately 3–4% or slightly more. This quantity depended only slightly upon the amount and type of the copolymerized acid. The acid contents of the water-soluble polymers were higher in cases of the copolymers with acrylic acid than in those with methacrylic acid. No relationship with the amount of copolymerized acid was established.

INTRODUCTION

Several investigations[1–3] have been made dealing with improvement of mechanical and freeze-thaw stability of emulsions by copolymerizing an unsaturated acid, which also imparts reactivity with metal oxides[4,5] or an ether of methylolated melamine[6] to the polymer.

As yet, very few fundamental studies have been made on the behavior of the unsaturated acids in emulsion copolymerization. It was shown by Fordyce and Ham[7] that a considerable portion of itaconic acid is polymerized in the aqueous phase on emulsion copolymerization with styrene. A recent electrophoretic study[8] on emulsions of methyl methacrylate copolymers with acrylic acid and methacrylic acid has shown that acrylic acid diffuses with difficulty into the emulsion particles and consequently it is liable to be polymerized in the aqueous phase, whereas methacrylic acid diffuses easily into the emulsion particles and therefore it can be copolymerized well with methyl methacrylate. It has been also shown that

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these acids tend to be concentrated at the surface of a particle; acrylic acid has this tendency much more than methacrylic acid.

In the present paper, conductometric and potentiometric titration studies of the emulsions of ethyl acrylate copolymers with acrylic acid and methacrylic acid were made in order to understand the distribution of the acid in the emulsions. Changes in optical density of the emulsions with pH were measured in order to study morphological changes of the emulsion particles with pH, and the emulsion particles were investigated under an electron microscope. Furthermore, amounts of water-soluble polymers formed in the course of emulsion copolymerizations and their acid contents were measured.

In this study, ethyl acrylate (EA), acrylic acid (AA), and methacrylic acid (MAA) were used as monomers because of their commercial importance.

EXPERIMENTAL

Materials

Monomers employed in the preparation of the copolymer emulsions were used after purification, by the usual method, of chemically pure grade reagents. Polyoxyethylene nonylphenyl ether (Emulgen 913) and sodium polyoxyethylene nonylphenyl sulfate (Levenol WZ) used as emulsifiers were supplied by the Kao Soap Co. in Japan. Sodium hydroxide used in the titrations was of analytical grade.

The emulsions were prepared in a 500-ml. four-necked flask equipped with a stirrer, a reflux condenser, a thermometer, and a dropping funnel. The following polymerization procedure was employed for all preparation of the samples: The ingredients listed in Table I were mixed in a 1-liter bottle. One-fifth of this monomer emulsion was transferred into the flask. The emulsion was heated to 70°C. on a water bath with stirring. After polymerization took place and the temperature reached 80°C. in a nitrogen atmosphere, the remaining monomer emulsion was then added slowly over 3 hr. After all the monomer had been added, the temperature was kept at 85°C. for 3 hr. At this point, conversion was almost 100%.

TABLE I
Formulation of the Emulsions

Ingredients		Amt., wt.-%
Monomers		38.28
Emulgen 913		1.23
Levenol WZ		0.31
Potassium persulfate		0.11
Dodecyl mercaptan[a]		0.08
Distilled water		59.99
	Total	100.00

[a] Used to dissolve the resulting polymers in a solvent.

Methods

Conductometric Titration. The titrations were carried out at 20°C. by placing a cell filled with 30 ml. of a dilute emulsion of 5–10% solid content suitable for the titration in a conductometric titrimeter. Aqueous $0.1N$ NaOH was added at the rate of one drop per minute (approximately 0.03 ml./min.) to the emulsion with stirring. The readings of the conductance of the emulsion in the titration were taken 1 min. after each addition of a NaOH solution drop.

Potentiometric Titration. The titrations were carried out with a pH meter for convenience to permit the pH of the emulsions simultaneously to be checked. The titration procedure was similar in manner to the conductometric titration.

Optical Density Measurement. The change in optical density of an emulsion with pH was measured at 20°C. as follows. An emulsion was diluted to 0.1% solid content. Its pH was changed by adding $0.1N$ aqueous NaOH or HCl at the rate of 1 ml./min. to 1000 ml. of the emulsion with stirring. The optical density of the emulsion samples at appropriate intervals was measured by placing a 10 mm. square quartz cell filled with the sample in a photometer. The wavelength of incident light in this measurement was 610 mμ.

Optical density readings were corrected by using Lambert-Beer's law, since the concentration of the emulsion was diluted by adding aqueous solutions of NaOH or HCl.

On the basis of Rayleigh's law of scattering, there is the following relationship among turbidity of a sol τ, the number of particles per unit volume of the sol N, and the particle volume V:

$$\tau = (24\pi^3 n_0^4/\lambda^4)[(n^2 - n_0^2)/(n^2 + 2n_0^2)]NV^2 \tag{1}$$

where n and n_0 are the refractive indices of the particle and dispersion medium, respectively, and λ is the wavelength of the incident light in vacuum. This relationship is valid only when selective absorption of light does not occur and the diameter of the particles is less than 0.1λ.

The turbidity is defined by Lambert as follows:

$$I = I_0 \exp\left\{-\tau l\right\} \tag{2}$$

where I_0 and I are the intensity of the incident and transmitted light, respectively, and l is the length of optical path. In this measurement l is 1 cm. and consequently the eq. (3) is obtained:

$$\tau = \ln (I_0/I) = 2.303 \log (I_0/I) \tag{3}$$

$$= 2.303D$$

where D is the optical density. On combining eqs. (1) and (3), eq. (4) is obtained:

$$D = A_R[(n^2 - n_0^2)/(n^2 + 2n_0^2)]^2 V^2 \tag{4}$$

where

$$A_R = 24\pi^3 N n_0^4/2.303\lambda^4$$

RESULTS AND DISCUSSION

Conductometric and Potentiometric Titration

The acid detectable by NaOH in the emulsions of EA copolymers with AA was measured by conductometric and potentiometric titration method. Results are shown only for two emulsions of the copolymers with 2 and 10 mole-% AA (Figs. 1 and 2). Other emulsions, having 5–15 mole-% AA in the copolymer showed very similar titration behavior. For a comparison, the conductometric titration curves of a dialyzed emulsion of copolymer (10 mole-% AA), which was dialyzed in a cellophane dialysis tube and washed for 7 days, is shown in Figure 2.

Two distinct equivalence points are shown on the conductometric titration curve for the emulsion of the copolymer with 2 mole-% AA. In reasonable agreement, two corresponding equivalence points are also observed for other emulsions; in addition to these, one vague equivalence
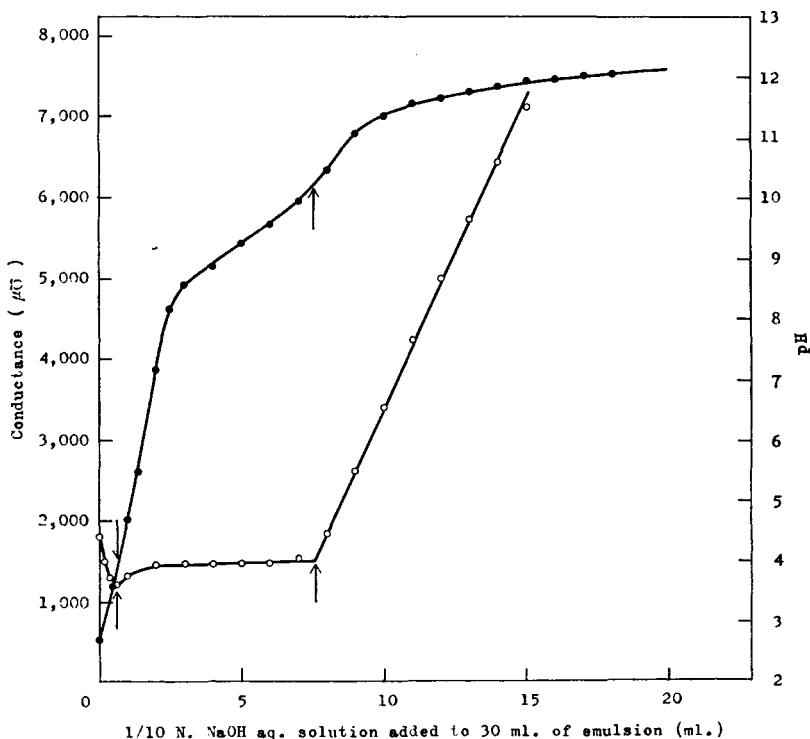

Fig. 1. Conductometric and potentiometric titration curves of EA copolymer (with 2 mole-% AA) emulsion of 10% solid: (O) conductometric titration curve, (●) potentiometric titration curve. Arrows indicate each equivalence point.

point appears between them, which could not be detected by potentiometric titration method.

As seen in Figures 1 and 2, the first equivalence points show characteristics of strong acid–base titration and the others are characteristics of weak acid–strong base titration curves.

From the fact that the first equivalence point disappeared after the dialysis of the emulsion, it is concluded that it is based on the decomposed initiator fragment. Consequently, the second and the third equivalence points are based on AA in the copolymer.

In the dialyzed poly(ethyl acrylate) emulsion, 0.24 mole-% of acid (based on the polymer) was detected. This may have been formed by hydrolysis of EA in the course of the emulsion polymerization.

The amounts of acid detected at each equivalence point, from which the amount of acid based on the decomposed initiator fragment is subtracted, are given in Table II.

Furthermore, the emulsions of the EA copolymers with MAA, which is said to show different copolymerization behavior from AA in emulsion
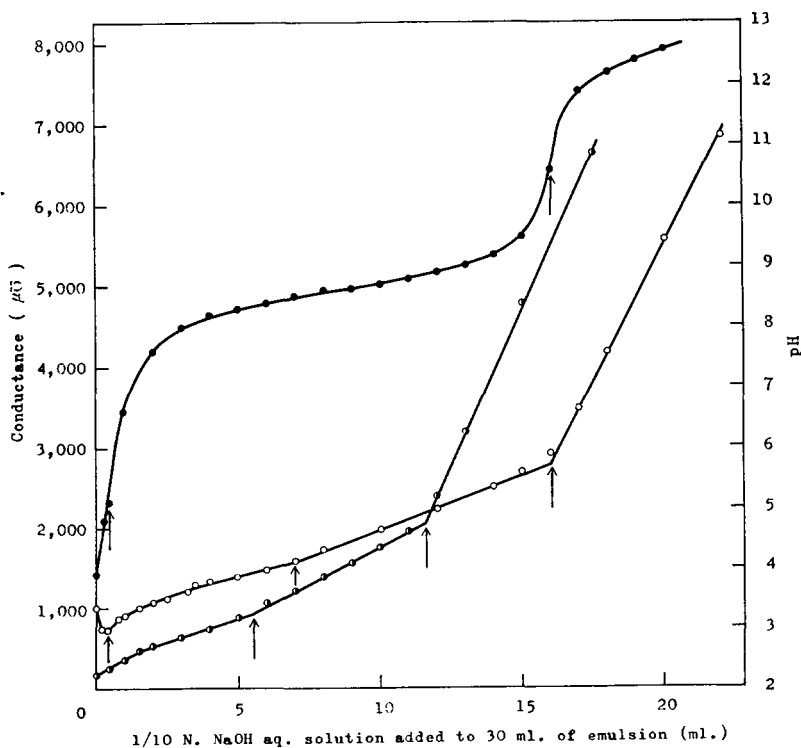

Fig. 2. Conductometric and potentiometric titration curves of EA copolymer (with 10 mole-%) emulsion of 5% solid: (○) conductometric titration curve, (◑) conductometric titration curve of dialyzed emulsion, (●) potentiometric titration curve. Arrows indicate each equivalence point.

TABLE II
Amounts of Acid Detected by Aqueous $0.1N$ NaOH
at Each Equivalence Point

Emulsion	Acid in monomers, mole-%	Acid in copolymer, mole-%[a]	Acid detected at second equivalence point, mole-%	Acid detected at third equivalence point, mole-%
EA–AA	0	0.23	—	0.24
	2	2.54	—	2.54
	2[b]	—	—	2.45
	5	5.32	2.75	5.24
	10	11.00	4.18	10.51
	10[b]	—	4.23	10.45
	15	15.38	6.06	15.09
EA–MAA	2	2.98	—	2.60
	5	6.26	2.58	5.04
	10	11.13	4.21	10.30

[a] Titrated with KOH methanol solution in acetone solution.
[b] Dialyzed emulsion.

copolymerization,[5,8] were conductometrically titrated. Contrary to expectation, however, the emulsions showed conductometric titration behavior very similar to that of the emulsion of the copolymer with AA, as shown in Figure 3, except for the difference that the equivalence points of the former are shifted to higher pH than those of the latter, as shown in Table III. The amounts of acid, based on copolymerized MAA, detected at each equivalence point are given in Table II.

Table II shows that the ratio of the amount of acid detected at the second equivalence point to the amount of copolymerized acid gradually decreases with increase of the latter.

The amount of acid detected at the third equivalence point is in good agreement with the amount determined in acetone solution by the titration with methanolic KOH as shown in Table II. This fact shows that the third equivalence point is a point where the whole copolymerized acid is neutralized. This is a quite surprising fact.

On the other hand, the second equivalence point seems to be a neutralization point at which the acid present in aqueous phase and at the surface of the emulsion particles has been neutralized. Beyond this point, further acid present inside the particles may be neutralized, accompanied with some morphological changes of the particles.

The second equivalence point seems to depend upon the rate of neutralization, but further experiments were not carried out, because it did not seem important in this case.

Change in Optical Density of Diluted Emulsions

The results of the conductometric titrations suggest that some morphological changes may take place inside the emulsion particles containing
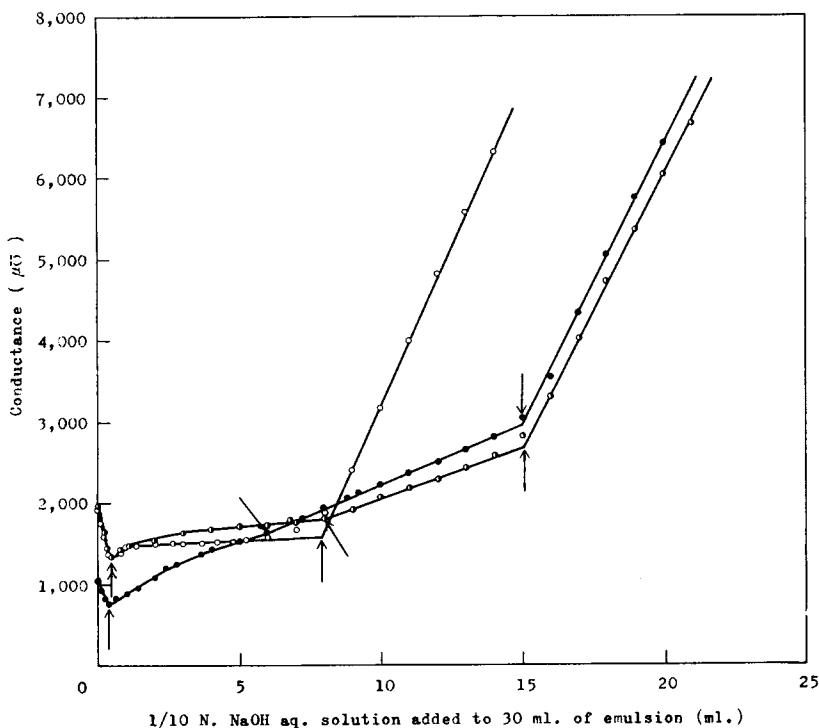
Fig. 3. Conductometric titration curves of emulsions of EA copolymers with different amounts of MAA: (O) with 2 mole-% (10% solid); (◑) with 5 mole-% (10% solid); (●) with 10 mole-% (5% solid). Arrows indicate each equivalence point.

carboxy groups with changes in pH, especially in the pH range between the second and third equivalence points. In order to verify this assumption, the change in optical density of the dilute emulsion with the pH was measured. The pH of the dilute emulsions with 0.1% solid content was raised by adding 0.1N aqueous NaOH. The results are shown in Figures 4 and 5.

Equation (4), which describes the relationship between optical density and volume of particles, is not strictly consistent in this experiment as already described, since the average particle diameters of the emulsions used are approximately 0.2 μ, as seen in the electron micrographs (Figs. 6 and 7). It seems to be possible, however, to discuss the volume change of particles in relation to optical density.

Figures 4 and 5 show that the optical densities of the emulsions containing carboxyl groups decrease sharply in the characteristic pH range approximately between the second and third equivalence points on the conductometric titration curves, whereas the poly(ethyl acrylate) emulsion used as a control shows scarcely any change in the optical density. These ranges are tabulated in Table III in comparison with the pH at the second and third equivalence points.
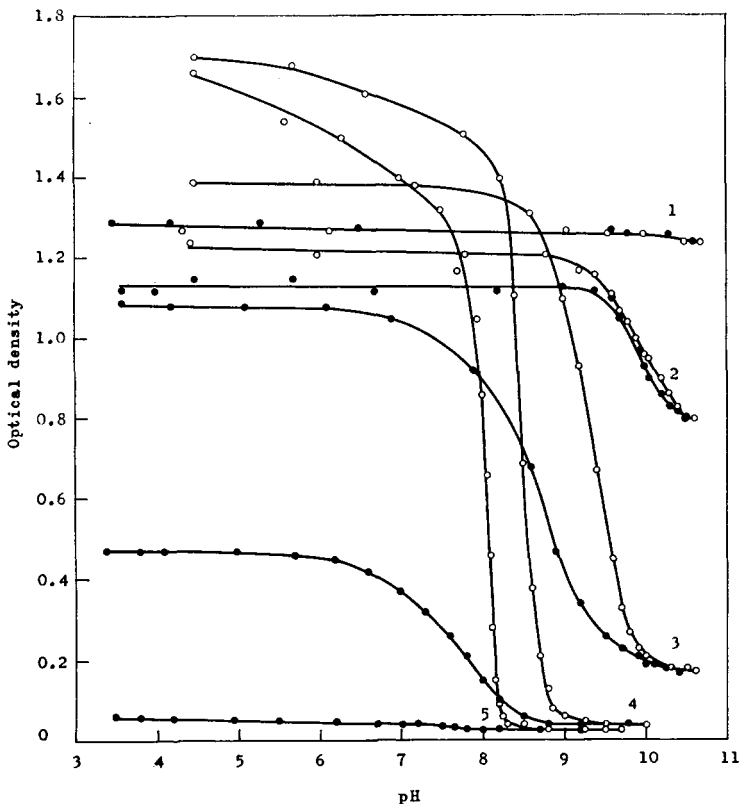
Fig. 4. Optical density vs. pH of emulsions of EA copolymers with different amounts of AA (0.1% solid):   (O) from low to high pH; (●) from high to low pH, (1) control, (2) with 2 mole-%, (3) with 5 mole-%, (4) with 10 mole-%, (5) with 15 mole-%.

The degree of decrease of optical density at high pH becomes more marked with increasing amounts of copolymerized acids.   The emulsions of the copolymers with 15 mole-% of the acids, especially, became transparent as they dissolved.   The pH where the optical density begins to decrease shifts to the acid side with increasing amount of the acids.

The change in the optical density of the emulsions of the copolymers with AA with their pH and that of the emulsions of the copolymers with MAA are very similar, but different in the pH ranges where the optical density suddenly changes.   This difference can obviously be attributed to the difference between the dissociation constants of AA and of MAA.

The pH of the same emulsions on the alkaline side were lowered by adding 0.1 N aqueous HCl, and the change in the optical density was measured.   The results are shown with solid plots in Figures 4 and 5.

In this case, the optical density increases with decreasing pH, but the curve obtained with decreasing the pH from a high to a low value is not superposed on the curve obtained by increasing pH.   Once the emulsion
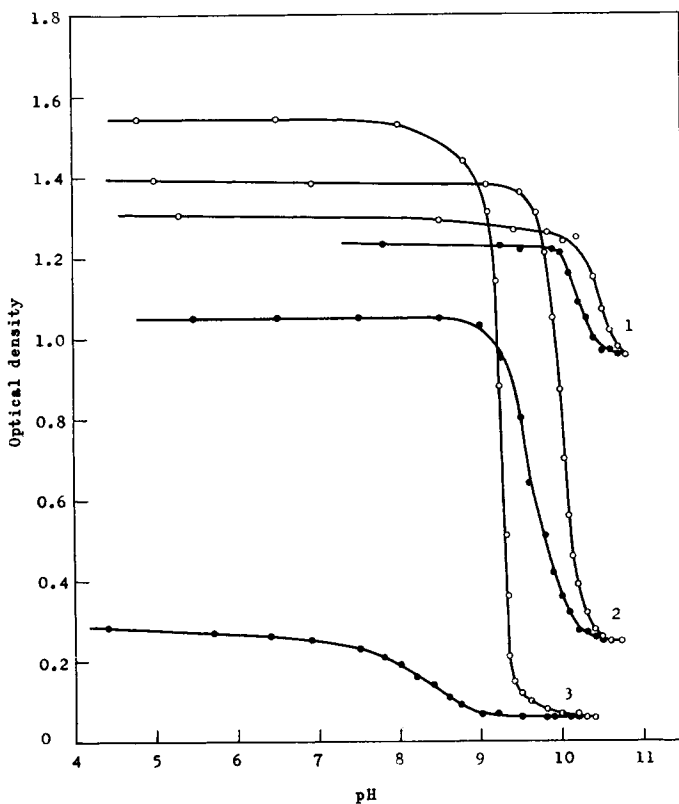
Fig. 5. Optical density vs. pH of emulsions of EA copolymers with different amounts of MAA (0.1% solid); (O) from low to high pH, (●) from high to low pH; (1) with 2 mole-%, (2) with 5 mole-%, (3) with 10 mole-%.

TABLE III
Relationship between pH at Each Equivalence Point and pH
Where Optical Density of Emulsion Suddenly Changes

| Emulsion	Acid in monomer, mole-%	pH at each equivalence point		pH where optical density suddenly changes
		Second	Third	
EA–AA	2	—	8.4	9.4–10.5
	5	8.5	9.2	8.6–10.0
	10	8.3	8.9	7.9– 9.0
	15	7.9	8.6	6.8– 8.4
EA–MAA	2	—	9.6	10.3–10.7
	5	9.4	9.8	9.5–10.5
	10	9.1	9.4	8.7– 9.6

has been treated with an alkali and then an acid, its optical density is different from that of the original untreated emulsion; the higher the acid content of the copolymer, the greater this deviation is. The optical

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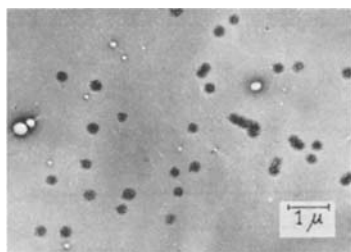
(original emulsion)
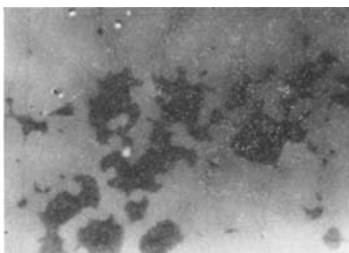
(emulsion adjusted to pH 10)
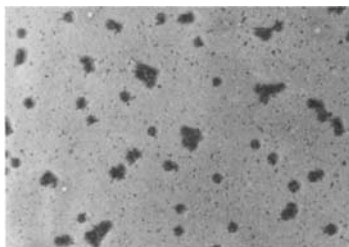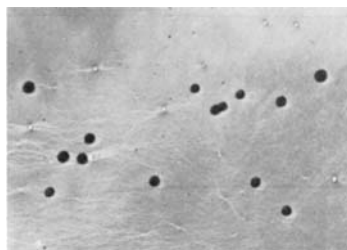

(emulsion subjected to a pH cycle)

Fig. 6. Electron micrographs of EA copolymer (with 2 mole-% AA) particles subjected to different pH treatments.

densities of the emulsions of the copolymers with 15 mole-% of the acids are especially affected by reacidification.

The emulsions of the copolymers with AA subjected to different pH treatments were studied under an electron microscope, in order to understand more exactly why the optical density of the emulsions changed with pH. The photographs of the emulsions of the copolymers with 2 and 10 mole-% AA are shown in Figures 6 and 7. Photographs of the other emulsions are not given, because they showed similar tendencies.

The emulsion particles of the copolymer containing less acid are flattened to some extent because they are too soft to maintain their original shape during drying.
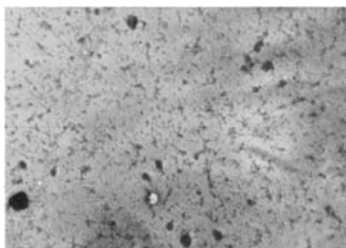
The electron microscopic observation shows marked changes in the particles with varying pH. First, in the emulsions adjusted to the alkaline side, no spherical particles are observed at all; only thin flakes are seen.

(original emulsion)
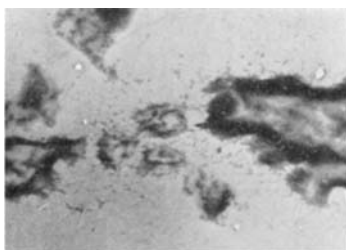
(emulsion adjusted to pH 10)

(emulsion subjected to a pH cycle)

Fig. 7. Electron micrographs of EA copolymer (with 10 mole-% AA) particles subjected to different pH treatments.

Secondly, when the pH of the same emulsions are readjusted to the acidic side, many extremely tiny particles beside the original particles are formed, and the diameters of the original particles are considerably decreased by the alkali–acid treatment. This tendency becomes more marked as the acid content of the copolymer is increased.

The poly(ethyl acrylate) emulsion used as a control did not show any such changes of the particles through the alkali–acid treatment.

These results indicate that, when the pH of an emulsion of EA copolymer containing carboxyl groups is adjusted to the alkaline side, the surface layers of the particles (where most of the copolymerized acid might be concentrated) are dissolved, and their cores swell. Then, when the pH of the emulsion is readjusted to the acid side, the solubility of the polymers which had been dissolved in the alkaline state decreases, and they coagulate. The coagulum is stabilized by adsorbing emulsifiers in aqueous phase.
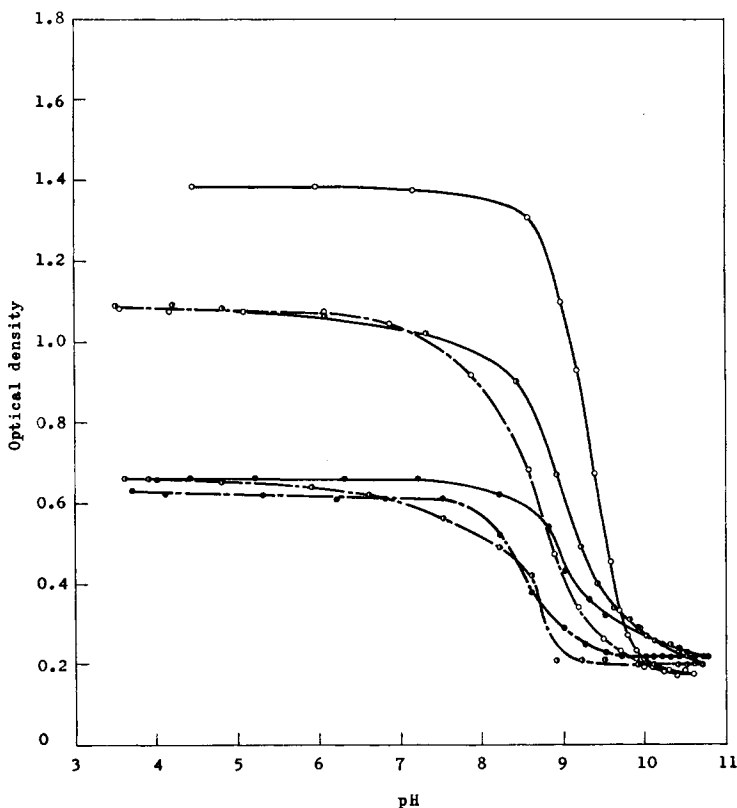
Fig. 8. Effect of repeating alkali–acid treatment cycle on change of optical density of EA copolymer (with 5 mole-% AA) emulsion vs. pH: (——) from low to high pH; (–·–) from high to low pH; (O) first cycle, (◑) second cycle, (●) third cycle.

Simultaneously, the swollen particle cores are dehydrated and shrink. The coagulum appears as tiny particles as seen in the bottom of Figures 6 and 7.

The fact that the difference between the optical density of the original emulsion and that of the emulsion subjected to the alkali–acid treatment becomes more marked with increasing amount of copolymerized acid indicates that the surface layer gradually thickens with increase of the acid. This is supported by the fact that the shrinkage of the original particles after the alkali–acid treatment becomes greater with the increased acid.

The reason why only one equivalence point based on the copolymerized acids is observed on conductometric titration curves of the copolymer emulsions with 2 mole-% of acid, whereas two points are seen on those of the copolymer emulsions with more than 5 mole-% of the acid (Figs. 1–3), is attributed to the thickening of the surface layers.

Guziak and Maclay[9] have also shown that in emulsion copolymerization of styrene, 2-ethylhexyl acrylate, and methacrylic acid a considerable
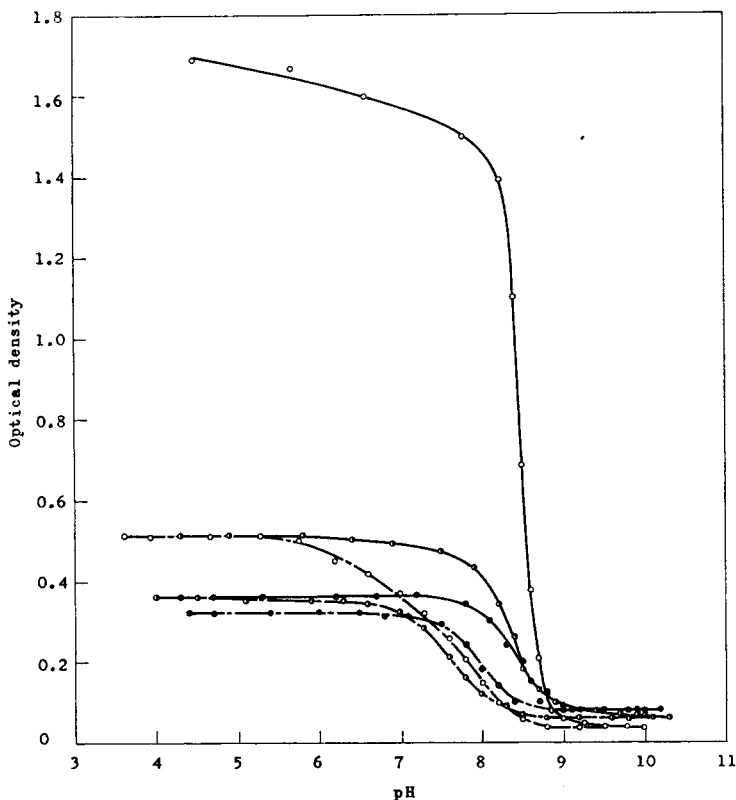
Fig. 9. Effect of repeating alkali–acid treatment cycle on change of optical density of EA copolymer (with 10 mole-% AA) emulsion vs. pH: (———) from low to high pH, (–·–) from high to low pH; (O) first cycle, (◑) second cycle, (●) third cycle.

portion of methacrylic acid is distributed at the surface of the emulsion particles.

In a subsequent experiment, the alkali–acid treatment cycle was repeated with emulsions of copolymers containing 5 and 10 mole-% AA. The optical density on the acid side gradually decreases when the cycle is repeated, but the difference between the optical density of the second cycle and that of the third cycle is very slight, as shown in Figures 8 and 9. In both figures the curves of the first cycle are given for comparisons.

It is seen in Figures 8 and 9 that the critical pH at which the optical density of the emulsion levels off shifts toward high pH when the cycle is repeated. Figures 4 and 5 show that this pH shifts to higher values with decreasing amount of copolymerized acid. As a result, it may be concluded that the acid content of the particles decreases from the surface toward the center of the particles.

Water-Soluble Polymers

Water-soluble polymers formed in the course of the emulsion copolymerizations were separated by two methods. In method 1, an emulsion

was dried by placing it on glass plate. The dried material was dissolved in approximately 20% acetone. Then, the water-insoluble polymers were precipitated from this solution by adding water and centrifugation. The precipitated polymers were again dried and dissolved in acetone. The aqueous solutions were combined after repeating this treatment four times. In method 2, a previously diluted emulsion containing approximately 5% solid was frozen in Dry Ice–methanol at $-10°C$. for about 24 hr. and then the coagulated polymers were separated by centrifugation.

The amounts of water-soluble polymers obtained by method 1 are un-realistically high because small quantities of water-insoluble polymers (in fact, aqueous acetone-insoluble polymers) are stably dispersed and it is impossible to separate the dispersed polymers completely by centrifugation. This tendency is more marked for the copolymers with MAA than in those with AA, and increased with increasing amount of the acid used in copolymerization. On the other hand, the amounts of water-soluble polymers obtained by method 2 are unrealistically low, because some water-soluble polymers may be adsorbed on the particles.

The amounts of the water-soluble polymers determined by the two methods mentioned above are summarized in Table IV. The values listed in Table IV obtained by method 1 are the total amounts of the water-soluble polymers and the dispersed polymer, that is, the amounts of the separated substances minus total amounts of the emulsifiers and initiator charged. Both of these were considered to be extracted in the aqueous phase of the treatments. On the other hand, the values obtained by method 2 give the total amounts of the separated substances, because in this case a great portion of the emulsifiers may have been adsorbed on the

TABLE IV
Amounts and Acid Contents of Water-Soluble Polymers
Formed in Emulsion Copolymerization

Emulsions	Acid in monomers, mole-%	Method 1		Method 2	
		Amount, wt.-%[a]	Acid content, mole-%	Amount, wt.-%[b]	Acid content, mole-%
EA–AA	0	−1.26	—	—	—
	2	4.00	6.1	1.19	31.6
	5	3.39	13.9	1.01	43.2
	10	4.05	25.8	2.07	36.1
	15	3.61	14.7	2.08	39.7
EA–MAA	2	2.18	7.6	2.22[c]	7.8[c]
	5	5.27	4.5	1.24	13.4
	10	11.50	18.4	1.54	18.8

[a] Total amounts of emulsifiers and initiator charged in emulsion copolymerization were subtracted.
[b] All water-soluble components.
[c] Emulsion state was not completely destroyed by freezing.

particles, and determining the amounts of the water solubles separate from the polymers is extremely difficult.

The amounts of water-soluble polymers obtained by method 1 differ from those by method 2. The difference becomes greater with increased dispersion of the insoluble polymers. The most reasonable conclusion to be drawn from the data shown in Table IV is that the amounts of water-soluble polymers formed in the course of the emulsion copolymerization are considerably smaller than expected, approximately 3–4% or slightly more, and are nearly constant, regardless of the amount and type of the copolymerized acid.

The water-soluble polymers were titrated potentiometrically in order to determine the acid contents of the polymers. The results are listed in Table IV. All of the water-soluble polymers obtained by the two methods are not pure, and consequently the acid contents also can not be exact. It is possible, however, to discuss relative effects of various factors on the acid contents from the data of the water-soluble polymers obtained by the method 2, assuming that the amount of emulsifier adsorbed on the particles is constant for all samples.

As a result, it appears that the acid contents are scarcely affected by the amounts of the copolymerized acids, and that the acid contents are higher in the copolymers with AA than in those with MAA. This shows that MAA copolymerizes better with EA than AA does.

Although it is impossible to determine the exact acid content, the data obtained here indicate that the water-soluble polymers are copolymers of the unsaturated acids with EA.

CONCLUSION

The present study shows that the unsaturated acids are concentrated in the surface layers of the particles in the course of emulsion copolymerization, as expected from their chemical structure. The surface layers are dissolved, and the particle cores are quite swollen at above a characteristic pH for the emulsions. This pH is lower for emulsions of the copolymer with acrylic acid than for those with methacrylic acid at the same acid concentration. The pH decreased with increasing amounts of the copolymerized acid. This may explain the empirical fact that, in alkali-thickening of an unsaturated acid copolymer emulsion, copolymerization with acrylic acid is more effective than that with methacrylic acid. Furthermore, the fact that poly(ethyl acrylate) emulsions containing carboxyl groups are markedly swollen at high pH explains the empirical fact that copolymerization with an unsaturated acid improves film-forming properties of the copolymer emulsion in spite of elevation of the glass transition temperature of the resulting copolymer.[10]

The polymers dissolved at alkaline pH precipitated out when the pH was lowered, because their solubility decreased. In this case it is of great interest that these polymers coagulated, forming extremely tiny spherical

particles. The surface tension may be a factor in forming spherical particles. However, the exact mechanism is not clear at present.

In the present study, it is not evident whether the phenomena described above are characteristic only for the emulsions of acrylic or methacrylic acid copolymers with ethyl acrylate or general for emulsions containing carboxyl groups.

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Résumé

Les comportements à la titration conductométrique et potentiométrique d'émulsions de copolymères d'acrylate d'éthyle avec l'acide acrylique et méthacrylique ont été étudiés. On peut observer deux points d'équivalence sur les courbes de titration conductométrique d'émulsions des copolymères contenant plus de 5% molaire en acide; on en observe toutefois un seul sur les courbes de titration potentiométrique. Pratiquement, tout l'acide copolymérisé peut être détecté au moyen des deux méthodes de titration. Les variations de densité optique des émulsions diluées avec le pH ont été mesurées. Les particules de ces émulsions ont été étudiées au moyen d'un microscope électronique. Ces résultats montrent que lorsque le pH des émulsions est augmenté, les couches en surface des particules commencent à se dissoudre et gonflent jusqu'à un pH voisin de leur premier point d'équivalence. Lorsque ce pH est à nouveau abaissé les polymères dissous coagulent, formant de petites particules et les centres gonflés sont à nouveau déshydratés. Les couches en surface deviennent plus épaisses en accroissant la quantité d'acide copolymérisé. Ces comportements sont très similaires aux émulsions des copolymères avec l'acide acrylique et l'acide méthacrylique. Des quantités de polymères solubles dans l'eau formés en cours de la copolymérisation en émulsion était approximativement de 3–4% ou légèrement plus. Cette quantité dépend peu de la quantité et de la nature de l'acide copolymérisé. La teneur en acide des polymères solubles dans l'equ était plus élevée dans le cas d'un copolymère d'acide acrylique que dans ceux des de l'acide méthacrylique. Aucun rapport avec la quantité de l'acide copolymérique n'a été établi.

Zusammenfassung

Das konduktometrische und potentiometrische Titrationsverhalten der Emulsionen von Äthylacrylat-Acrylsäure- und -Methacrylsäurekopolymeren wurde untersucht. Auf den konduktometrischen Titrationskurven der Emulsionen von Kopolymeren mit mehr als 5 Mol% Säuregehalt wurden zwei Äquivalenzpunkte in Bezug auf die kopolymerisierte Säure gefunden. Auf den potentiometrischen Titrationskurven fand sich jedoch nur ein Äquivalenzpunkt. Fast die ganze kopolymerisierte Säure konnte mit beiden Titrationsverfahren gefunden werden. Die Änderung der optischen Dichte der

verdünnten Emulsionen in Abhängigkeit vom pH-Wert wurde gemessen. Die emulgierten Teilschen wurden elektronenmikroskopisch untersucht. Die Ergebnisse zeigten, dass bei Erhöhung des pH-Werts der Emulsionen die äusseren Schichten der Partikeln sich aufzulösen begannen und eine Quellung des Partikelinneren in der Nähe des pH-Werts des ersten Äquivalenzpunkts einsetzte. Setzte man den pH-Wert wieder herab, so koagulierten die gelösten Polymeren und bildeten winzige Partikel. Gleichzeitig wurden die gequollenen Partikelkerne dehydratisiert. Die Dicke der Oberflächenschicht nahm mit steigender Menge an kopolymerisierter Säure zu. Darin verhielten sich die Emulsionen von Acrylsäure- und Methacrylsäurekopolymeren sehr ähnlich. Der Anteil an wasserlöslichen Polymeren, die im Verlauf der Emulsionskopolymerisation gebildet wurden, betrug etwa 3–4% oder etwas mehr. Diese Menge war nur wenig von der Menge und Art der kopolymerisierten Säure abhängig. Bei den Acrylsäurekopolymeren war der Säuregehalt des wasserlöslichen Polymeren höher als bei den Methacrylsäure kopolymeren. Es konnte keine Abhängigkeit von der Menge der kopolymerisierten Säure festgestellt werden.