Disintegration of Sulfonated Poly(1,4-piperazinediylterephthaloyl) Microcapsules by Poly(diallyldimethylammonium chloride)

Shiro SUZUKI and Tamotsu KONDO*,†

Department of Domestic Science, Ferris Women's College, Naka-ku, Yokohama 231

†*Faculty of Pharmaceutical Sciences, Science University of Tokyo, Shinjuku-ku, Tokyo 162*

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Partially sulfonated poly(1,4-piperazinediylterephthaloyl) microcapsules were found to undergo disintegration by the action of poly(diallyldimethylammonium) ions if the polycation concentration exceeded a certain value. The polycation concentration at which disintegration started was dependent on the degree of sulfonation of the microcapsules and pH of the medium. Exact electrical equivalence of the polyions involved was shown to be a necessary condition for disintegration of the microcapsules to take place. Disintegration of the microcapsules resulted in a formation of coacervate-like liquid drops. This formation of coacervate-like liquid was accelerated by mechanical and thermal agitation. Crosslinking among the polymers constituting the microcapsules prevented disintegration from occurring.

In a previous paper[1] the disintegration phenomenon of poly(N^α,N^ε-L-lysinediylterephthaloyl) microcapsules by poly(diallyldimethylammonium chloride) was reported. The cationic polyelectrolyte caused disintegration of the microcapsules if its concentration exceeded a certain value which was dependent on the pH of the medium while it acted on the microcapsules to bring about their aggregation at lower concentrations. In any case where disintegration was observed, exact electrical equivalence of the polyions involved was found to exist. The physical process of disintegration was indicated to be a formation of coacervate-like liquid.

As this way of the use of a polycation should be useful to probe the stability and exchangeability of the components of a coacervate film it will be worth while to extend our work to see if the mechanism established for the above system also works in other systems. In view of this, the present paper deals with disintegration of partially sulfonated poly(1,4-piperazinediylphthaloyl) microcapsules by poly(diallyldimethylammonium chloride) in terms of the degree of sulfonation of the polymer and the pH and ionic strength of the medium. The effect of crosslinking of the polymers constituting the microcapsules on disintegration will also be discussed.

Experimental

Preparation of Microcapsules. Sulfonated poly(1,4-piperazinediylterephthaloyl) microcapsules (SPP microcapsules) were prepared in a manner similar to that described in an earlier paper.[2] This way, SPP microcapsules with different degrees of sulfonation were prepared using mixtures of piperazine(Pip) and 4,4′-diaminostilbene-2,2′-disulfonic acid(DASSA) in varying ratios as water-soluble monomers in the interfacial polycondensation reaction between diamine and diacid dichloride, and named SPP-2, -3, and -5 microcapsules, respectively, according to the mixing ratio given in Table 1.

To 7.5 cm^3 of aqueous 1% polyethylene glycol(degree of polymerization 4000) solution in a 1 liter round bottom flask surrounded by ice was added an equal volume of 0.4 M solution of a mixture of Pip and DASSA in aqueous 0.45 M sodium carbonate solution containing 1% polyethylene glycol.

To this solution was added 75 cm^3 of the mixed solvent (chloroform-cyclohexane 1 : 3, v/v, containing 10% sorbitan trioleate as an emulsifier). The mixture was then mechanically emulsified with a constant speed stirrer for 5 min to yield a water-in-oil emulsion. The alkali served to neutralize hydrogen chloride formed during the polycondensation reaction. Without stopping the stirring, 75 cm^3 of terephthaloyl dichloride solution were quickly added to the emulsion, and the stirring was continued for further 3 min. The terephthaloyl dichloride solution was prepared just before use by adding 0.6 g of pure terephthaloyl dichloride to 75 cm^3 of the mixed solvent. SPP microcapsules thus obtained were separated from the organic phase by centrifugation at 1000 rpm for 3 min and washed with the mixed solvent containing no emulsifier on the centrifuge at least three times to remove the emulsifier. Then, the washed SPP microcapsules were transferred to aqueous phase with the aid of poly(oxyethylene) sorbitan monolaurate, washed repeatedly with deionized water on the centrifuge, and dialyzed in a Visking tube against distilled water for a week.

TABLE 1. MOLAR MIXING RATIOS OF Pip TO DASSA IN DIAMINE MIXTURES USED FOR PREPARATION OF SPP MICROCAPSULES AND SULFUR CONTENTS IN SPP MICROCAPSULES

Microcapsule	Molar mixing ratio Pip : DASSA	Sulfur content %
SPP-2	2 : 1	3.82
SPP-3	3 : 1	3.53
SPP-5	5 : 1	2.89

Microscopic Observation of Microcapsule Disintegration. To the dialyzed suspension of each of SPP-2, -3, and -5 microcapsules in test tubes was added an equal volume of a series of various concentrations of aqueous poly(diallyldimethylammonium chloride)(PDADMA) solution. The pH and ionic strength of the medium were adjusted by the addition of HCl or NaOH and NaCl, respectively. The mixtures were allowed to stand for 1 h with occasional shaking in a thermostated bath kept at 30 °C. At the end of this period, a small portion of each of the mixtures was withdrawn by a capillary tube and placed on a slide glass to observe the state of the SPP microcapsules under an optical microscope. In some cases, the microcapsules were photographed.

Preparation of Dried Samples of SPP Microcapsule Membranes for Adsorption Experiments. Each of SPP-2, -3, and -5 microcapsules in the organic phase was washed repeatedly with the mixed solvent containing no emulsifier, thoroughly dried *in vacuo*, and ground down into fine powder in a porcelain mortar. The powdered samples were stored in a desiccator until the time of use.

Measurements of Adsorption of PDADMA to SPP Microcapsule Membranes. To 0.05 g of the powdered samples of SPP microcapsule membranes was added 50 cm^3 of various concentrations of aqueous PDADMA solution at different pH(7.0, 4.0, and 2.0) and ionic strengths (0.1 and 0.2). The pH and ionic strength of the medium were adjusted by the addition of HCl or NaOH and NaCl, respectively. The mixtures were permitted to stand for 1 h with continuous stirring in a thermostat maintained at 30 °C to ensure complete dispersion of the samples. At the end of this period, the mixtures were centrifuged at 2000 rpm for 5 min to settle the floating particles. Then, 10 cm^3 each of the supernatant solutions was withdrawn by a pipet and titrated with a standardized solution of potassium poly(vinylsulfonate) using toluidine blue as an indicator.[3] The end point of titration could easily be detected visually by the metachromatic color change from blue to purple of the indicator.

Measurements of Electrophoretic Mobility of SPP Microcapsules. To a dialyzed suspension of each of SPP-2, -3, and -5 microcapsules in test tubes was added an equal volume of a series of various concentrations of PDADMA solution. The mixtures were allowed to stand for 1 h with occasional shaking in a thermostated water bath kept at 30 °C. The pH and ionic strength of the medium were adjusted by the addition of the acid or alkali and the salt, respectively, as before.

At the end of this period, nondisintegrated microcapsules were separated from the mixtures by centrifugation at 2000 rpm for 3 min. A small portion of the separated SPP microcapsules as the top layer in the centrifuge tube was withdrawn by a capillary tube and put into a 10^{-3} M NaCl solution. The resulted suspension was used for electrophoresis measurement.

Electrophoretic mobility measurements of the SPP microcapsules were carried out at 30 °C using a microelectrophoresis apparatus(Rank Brothers Co., Ltd., England). For each measurement, at least 20 microcapsules were timed in each direction to eliminate the polarization effect of the electrodes. The mobility of the microcapsules thus obtained was converted into the zeta potential by the Smoluchowski equation.

A portion of disintegrated SPP microcapsules settled in the bottom of the centrifuge tube was also withdrawn by a capillary tube and put into a 10^{-3} M NaCl solution. The mobility of disintegrated SPP microcapsules was converted into the zeta potential in the same way as for nondisintegrated SPP microcapsules.

Preparation of Coacervate-like Liquid Drops from SPP Microcapsules and PDADMA and Measurements of Their Electrophoretic Mobility. On the basis of the microscopic observations of disintegration of SPP microcapsules described later, coacervate-like liquid drops were prepared from SPP-2 and -5 microcapsules and PDADMA under two extreme conditions, *i.e.*, the most favorable and unfavorable conditions for disintegration. In the case of SPP-2 microcapsules, equal volumes of microcapsule suspension and 1.73×10^{-1} N PDADMA solution at pH 7.0 and ionic strength 0.1 were mixed in a 100 cm^3 Erlenmeyer flask immersed in a thermostated water bath kept at 30 °C and the mixture was allowed to stand for 1 h. The mixture was then transferred to a 200 cm^3 beaker in a water bath at 40 °C, stirred for 30 min, and centrifuged at 2000 rpm for 5 min to sediment coacervate-like liquid.

A small portion of the bottom layer in the centrifuge tube was withdrawn by a microspatula and put into 100 cm^3 of 10^{-3}M NaCl solution. The electrophoretic mobility of the drops was measured in the same way as before. A similar procedure was employed to prepare coacervate-like liquid drops from SPP-5 microcapsules and 1.73×10^{-3} M solution of PDADMA. In this case, the pH and ionic strength of the medium were 2.0 and 0.2, respectively.

Treatment of SPP Microcapsules with Glutaraldehyde. The terminal amino groups of the constituent polymers of SPP-2 microcapsules were crosslinked with glutaraldehyde in the following way. Dialyzed suspension of SPP-2 microcapsules and 0.1 M NaCl solution were mixed in a 30 cm^3 Erlenmeyer flask. Then, the pH of the resultant suspension was adjusted to about 10 by dropwise addition of 0.1 M NaOH solution to ensure complete deprotonation of the terminal amino groups. Twenty five grams of 25% aqueous glutaraldehyde solution was added to the suspension in the flask and the mixture was kept at 30 °C for 1 h during which the flask was gently shaken. After this treatment, the mixture was centrifuged and the separated SPP-2 microcapsules were redispersed in a medium of pH 7.0 and ionic strength 0.1 containing 1.73×10^{-1} N PDADMA to observe if the polycations would cause disintegration of the aldehyde-treated microcapsules.

Results

Microscopic Observations. In Fig. 1 are shown photomicrographs of intact SPP microcapsules. They were all spherical in shape and well-dispersed in the medium.

Disintegration of SPP microcapsules by PDADMA was found to depend strongly on the polycation concentration, moderately on the pH of the medium, and slightly on the ionic strength of the medium. In Table 2 is shown the dependency of the disintegration phenomenon on the three variables.

At any pH and ionic strength of the medium, disintegration of SPP microcapsules was observed only when the polycation concentration exceeded a certain value though the polycations caused aggregation of the microcapsules at lower concentrations. It was also observed that large microcapsules are readily ruptured by the action of the polycations as compared with small ones.

On the other hand, disintegration was apparently affected by the degree of sulfonation of SPP microcapsules since the pH dependence of the minimum PDADMA concentration required for the microcapsules to undergo disintegration varied with the degree of sulfonation as shown in Table 2. That is to say, disintegration of SPP-5 microcapsules with the lowest degree of sulfonation was prevented at low pH while SPP-2 microcapsules of the highest degree of sulfonation were ruptured independently of the pH of the medium above a certain polycation concentration.

Although the influence of the ionic strength of the medium on disintegration of SPP microcapsules was generally insignificant, it was appreciable in the case of SPP microcapsules of low degree of sulfonation at low pH.

Figure 2 gives the process of disintegration of SPP-2 microcapsules under the most favorable condition for disintegration in the present work, *i.e.*, at pH 7.0 and ionic strength 0.1 when the PDADMA concentration is increased.

At first, a low concentration of PDADMA caused

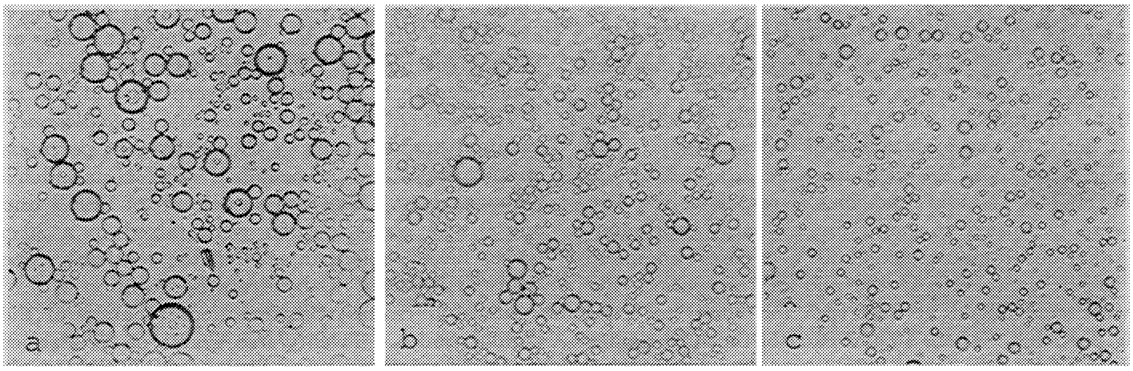

Fig. 1. Photomicrographs of intact SPP-2 (a), -3 (b), and -5 (c) microcapsules (×150).

Table 2. Disintegration of SPP microcapsules by PDADMA

Micro-capsule	pH	Ionic strength	PDADMA concn (N) 0.23×10^{-3}	0.33×10^{-3}	1.65×10^{-2}	1.73×10^{-1}	1.77
SPP-2	7.0	0.1	–	–	–	+	++
		0.2	–	–	–	+	++
	4.0	0.1	–	–	–	+	++
		0.2	–	–	–	+	++
	2.0	0.1	–	–	–	+	++
		0.2	–	–	–	+	++
SPP-3	7.0	0.1	–	–	–	+	++
		0.2	–	–	–	+	++
	4.0	0.1	–	–	–	+	++
		0.2	–	–	–	+	++
	2.0	0.1	–	–	–	+	++
		0.2	–	–	–	±	++
SPP-5	7.0	0.1	–	–	–	+	++
		0.2	–	–	–	+	++
	4.0	0.1	–	–	–	+	+
		0.2	–	–	–	±	+
	2.0	0.1	–	–	–	–	+
		0.2	–	–	–	–	+

–: Aggregation alone; ±: very slight disintegration; +: slight disintegration; ++: moderate disintegration.

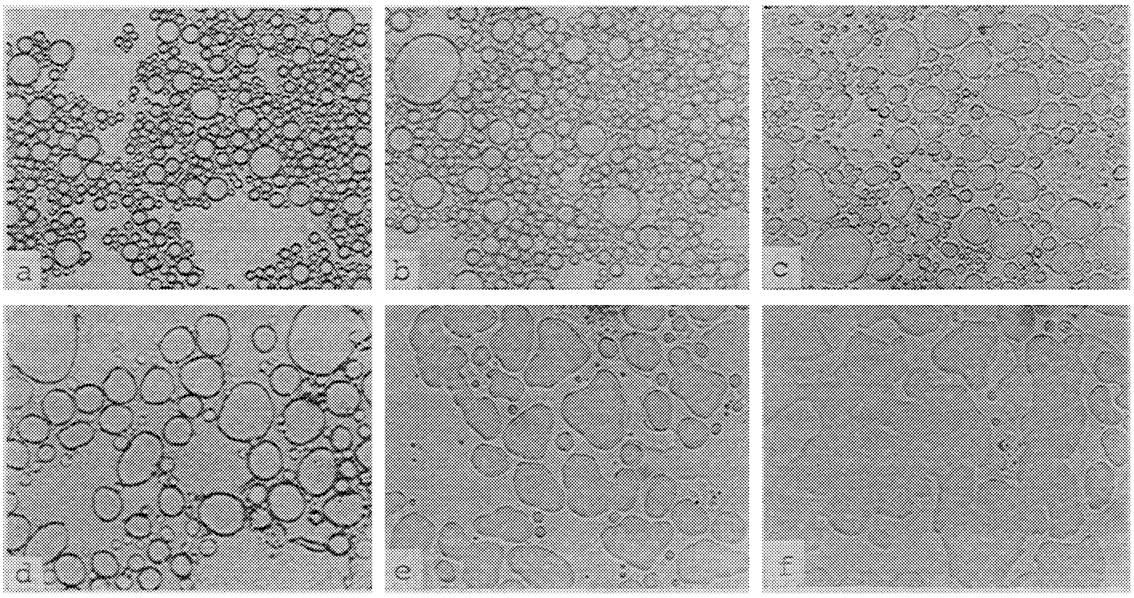

Fig. 2. A series of photomicrographs showing the process of disintegration of SPP-2 microcapsules by PDADMA at pH 7.0 and ionic strength 0.1. PDADMA concentration increases in the alphabetical order of the photos.

aggregation of the microcapsules(a); fusion among the aggregated microcapsules began here and there as the polycation concentration increased, large capsules having been liable to be the centers of fusion(b); the number of the centers from which fusion spread increased rapidly with further increase in the polycation concentration(c); the fusion developed further and large coacervate-like drops were formed(d); coalescence among the large drops proceeded(e); and finally, the microcapsule membranes were almost completely broken to the extent that their original form could not be seen.

Adsorption of PDADMA to SPP Microcapsule Membrane. In Fig. 3 is shown the effect of the degree of sulfonation on the adsorption of PDADMA upon SPP microcapsule membranes at pH 7.0 and ionic strength 0.1. The abscissa represents the logarithm of the initial PDADMA concentration.

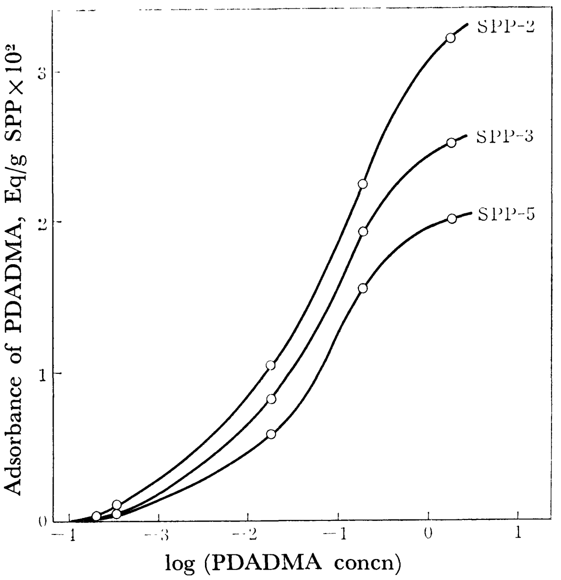

Fig. 3. Adsorption isotherms of PDADMA on SPP microcapsule membranes in a medium of pH 7.0 and ionic strength of 0.1 at 30 °C.

In any case, the PDADMA adsorption increased steeply first and then showed a tendency to saturate as the polycation concentration increased beyond 1.73×10^{-1} N. The adsorption was strongly dependent on the degree of sulfonation. Namely, it increased with increasing degree of sulfonation at all polycation concentrations. Variations in the pH and ionic strength of the medium did not alter this trend though not given here.

The effects of the pH and ionic strength of the medium on the polycation adsorption are illustrated in Fig. 4 for SPP-3 microcapsules.

As the pH was increased the adsorption rose remarkably. An increase in the ionic strength brought about a decrease in the adsorption. The adsorption decrease became less pronounced when the pH was lowered. Similar results were obtained with SPP-2 and -5 microcapsules.

Electrophoretic Behavior of SPP Microcapsules in the Presence of PDADMA. Figure 5 shows the zeta potential of nondisintegrated SPP-3 microcapsules as a function of the polycation concentration and the pH and ionic strength of the medium. The values of these variables are those employed in the preparation of the samples for electrophoresis experiment.

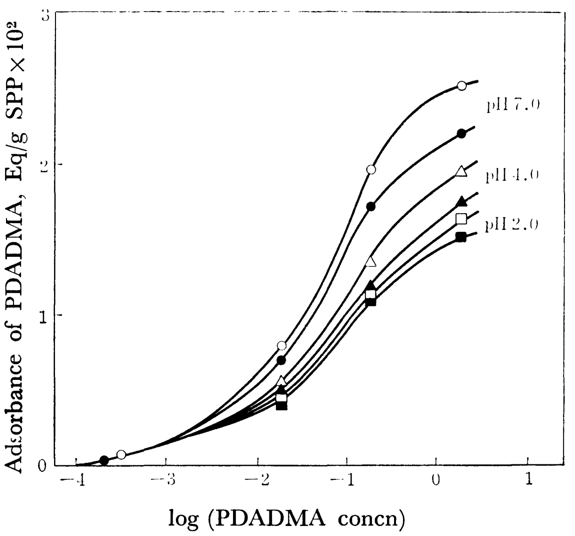

Fig. 4. Adsorption isotherms of PDADMA on SPP-3 microcapsule membranes at 30 °C. Ionic strength: 0.1 (open symbols) and 0.2 (closed symbols).

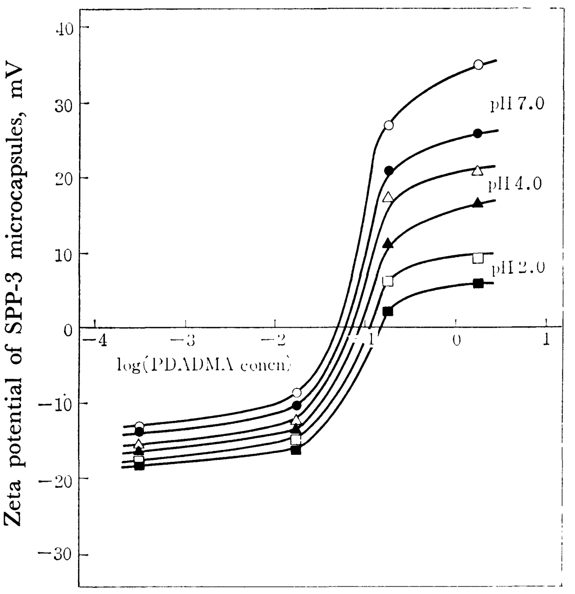

Fig. 5. Zeta potential of SPP-3 microcapsules at 30 °C as a function of PDADMA concentration, pH, and ionic strength. Ionic strength: 0.1 (open symbols) and 0.2 (closed symbols).

In all cases, the zeta potential changed its sign when the polycation concentration attained a value between 1.65×10^{-2} and 1.73×10^{-1} N. The polycation concentration at which the zeta potential reversed its sign shifted downward as the hydrogen ion concentration and ionic strength of the medium were reduced. A decrease in the degree of sulfonation gave rise to an increase in the polycation concentration required to cause reversal of the sign of the zeta potential.

The zeta potential of disintegrated SPP-3 microcapsules is shown in Fig. 6 as a function of the polycation concentration and the pH and ionic strength of the medium used for the preparation of the samples for electrophoresis.

Reversal of the sign of the zeta potential was observed as the polycation concentration increased beyond 1.65×10^{-2} N as in the case of nondisintegrated SPP microcapsules. The positive zeta potential after the sign reversal was at most as high as 7 mV and insensitive to changes in the pH and ionic strength of the medium.

Electrophoretic Behavior of Coacervate-like Liquid Drops Prepared from SPP Microcapsules and PDADMA. In Fig. 7 is given a photomicrograph of coacervate-like liquid drops prepared from SPP-2 microcapsules and PDADMA.

The zeta potentials of coacervate-like liquid drops prepared from SPP-2 and -5 microcapsules and PDADMA were almost zero or slightly positive, being indicative of a very low, if any, electric charge of the drops and they were almost independent of the degree of sulfonation and pH and ionic strength of the medium at which the drops were prepared.

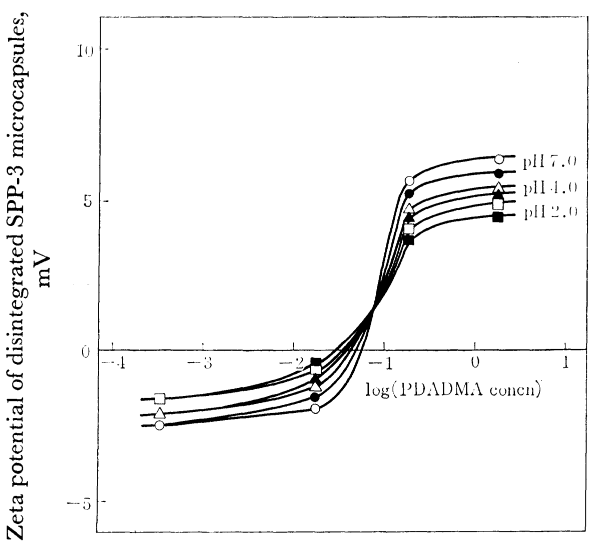

Fig. 6. Zeta potential of disintegrated SPP-3 microcapsules at 30 °C as a function of PDADMA concentration, pH, and ionic strength. Ionic strength: 0.1 (open symbols) and 0.2 (closed symbols).

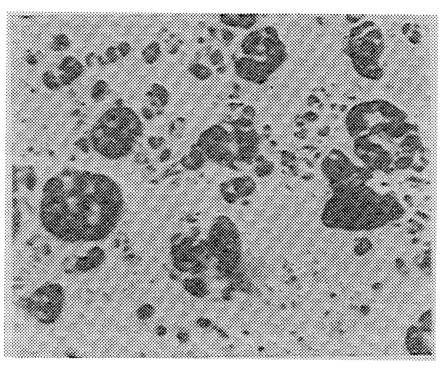

Fig. 7. Photomicrograph of coacervate-like liquid drops prepared from SPP-2 microcapsules and PDADMA.

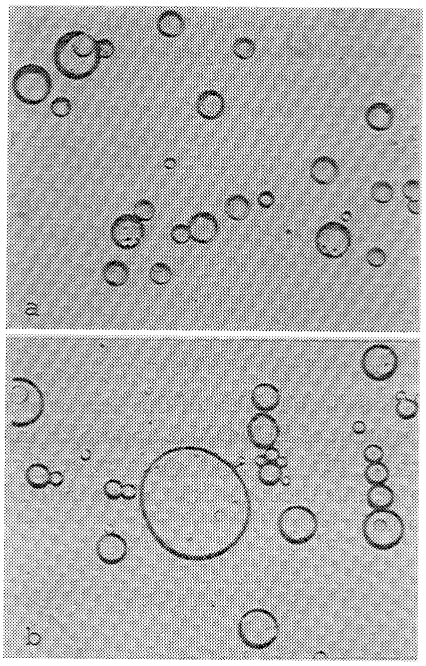

Fig. 8. Photomicrographs of glutaraldehyde-treated SPP-2 microcapsules taken in the absence (a) and presence (b) of PDADMA (×150).

Effect of Glutaraldehyde Treatment on Disintegration of SPP Microcapsules. As described already, SPP-2 microcapsules were appreciably ruptured in 1 h at pH 7.0 and ionic strength 0.1 when the polycation concentration was 1.73×10^{-1} N. On the contrary, glutaraldehyde-treated SPP-2 microcapsules were hardly disintegrated by the action of PDADMA under the same condition. Photomicrographs of glutaraldehyde-treated SPP-2 microcapsules taken in the absence(a) and presence(b) of PDADMA are shown in Fig. 8.

Discussion

As is apparent from the polycondensation reaction utilized in the preparation, SPP microcapsules have a number of sulfonato groups on their constituent polymer molecules as the ionizable group. Disintegration of the microcapsules is clearly caused by the electrostatic interaction between the negatively charged microcapsules and the oppositely charged polycations in the aqueous medium. Namely, it is a prerequisite for disintegration of the microcapsules that PDADMA ions are adsorbed on the sulfonato groups of the microcapsules. However, there seems to be a minimum number of sulfonato groups on the microcapsules for their disintegration to occur because SPP-5 microcapsules are not disintegrated at the PDADMA concentration of 1.73×10^{-1} N when the pH is low though this concentration produces disintegration of the microcapsules with higher degrees of sulfonation at the same pH(Table 2). It is reasonable that the pH effect on disintegration is less significant for SPP microcapsules than for PPL[††] microcapsules which have carboxyl groups as the ionizable group since $-SO_3H$ group has

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[††] Abbreviation for poly(N^{α},N^{ε}-L-lysinediylterephthaloyl).

Table 3. Numbers of quarternary ammonium groups of PDADMA ions adsorbed on SPP microcapsules

Micro-capsule	pH	Ionic strength	PDADMA concn (N)				
			0.23×10^{-3}	0.33×10^{-3}	1.65×10^{-2}	1.73×10^{-1}	1.77
SPP-2	7.0	0.1	5×10^{18}	1.3×10^{19}	6.02×10^{21}	1.32×10^{22}	1.89×10^{22}
		0.2	5×10^{18}	1.3×10^{19}	5.41×10^{21}	1.20×10^{22}	1.74×10^{22}
	4.0	0.1	3×10^{18}	9×10^{18}	3.91×10^{21}	1.08×10^{22}	1.50×10^{22}
		0.2		9×10^{18}	3.61×10^{21}	9.93×10^{21}	1.38×10^{22}
	2.0	0.1		6×10^{18}	3.61×10^{21}	9.03×10^{21}	1.26×10^{22}
		0.2		6×10^{18}	3.31×10^{21}	8.72×10^{21}	1.17×10^{22}
SPP-3	7.0	0.1	2×10^{18}	6×10^{18}	4.81×10^{21}	1.17×10^{22}	1.57×10^{22}
		0.2	2×10^{18}	6×10^{18}	4.21×10^{21}	1.02×10^{22}	1.32×10^{22}
	4.0	0.1		5×10^{18}	3.31×10^{21}	8.12×10^{21}	1.17×10^{22}
		0.2		5×10^{18}	2.70×10^{21}	6.92×10^{21}	1.05×10^{22}
	2.0	0.1		3×10^{18}	2.70×10^{21}	7.22×10^{21}	9.93×10^{21}
		0.2		3×10^{18}	2.40×10^{21}	6.65×10^{21}	9.03×10^{21}
SPP-5	7.0	0.1		5×10^{18}	3.31×10^{21}	9.33×10^{21}	1.20×10^{22}
		0.2		5×10^{18}	2.70×10^{21}	7.22×10^{21}	9.33×10^{21}
	4.0	0.1		3×10^{18}	2.40×10^{21}	5.71×10^{21}	8.72×10^{21}
		0.2		3×10^{18}	1.86×10^{21}	5.41×10^{21}	6.32×10^{21}
	2.0	0.1			2.10×10^{21}	4.81×10^{21}	7.52×10^{21}
		0.2			1.86×10^{21}	4.21×10^{21}	6.02×10^{21}

a lower p*K* value than –COOH group.

The disintegration phenomenon, polycation adsorption, and zeta potential of SPP microcapsules are closely interrelated. When the PDADMA concentration exceeds a value of 1.65×10^{-2} N the polycation adsorption to the microcapsules begins to increase abruptly (Figs. 3 and 4), disintegration of the microcapsules starts, and the zeta potential of the microcapsules reverses its sign (Fig. 5). In order to give this interrelationship a quantitative basis on which it rests, the numbers of sulfonato groups per unit weight of SPP-2, -3, and -5 microcapsules were first calculated from the sulfur contents. They were 7.08, 6.64, and 5.40×10^{21}, respectively. Secondly, calculations were made of the numbers of quarternary ammonium groups of the PDADMA ions adsorbed on unit weight of the microcapsules based on the adsorption data. The results are given in Table 3.

Interestingly enough, the number of sulfonato groups on the constituent polymers of the microcapsules and that of quarternary ammonium groups on the adsorbed polycations are nearly equal to each other in the polycation concentration region where the disintegration phenomenon is observed. This means that there exists an exact or nearly exact electrical equivalence between the polyanions and the polycations involved in disintegration. In fact, as mentioned before, coacervate-like liquid drops prepared from the microcapsules and the polycations under the conditions favorable to disintegration to occur bear no or little electrical charge, indicating that the electrical equivalence holds in these cases.

Inspection of Fig. 6 seems to give a clue to elucidate the mechanism of disintegration of the microcapsules. Disintegrated SPP microcapsules still have positive zeta potentials though not so high in the polycation concentration region in which coacervate-like liquid drops carry no or little electrical charge. This can be interpreted as showing that interminglement of the polyanions and the polycations is not sufficient and the latter component is still more abundant than the former in the surface layer of the disintegrated microcapsules, thus giving them positive zeta potentials though both components exist on the whole in approximately equivalent amounts in the capsules. Application of thermal and mechanical agitations to the disintegrated capsules should bring about a complete interminglement of the polyion components and this really happens in the preparation of coacervate-like liquid drops. If there are crosslinks among the constituent polymers of the microcapsules random mixing of the polyanions of the microcapsules and the polycations must be prevented and therefore no disintegration is observed.

Interaction between a strongly acidic polyanion and strongly basic polycation in aqueous solution usually yields a colloidal precipitate rather than a gelatinous coacervate.[4,5] The reason why coacervate-like liquid drops were formed in the present work instead of colloidal precipitates as a result of the interaction between SPP polymers and PDADMA polycations both of which are strong polyelectrolytes would presumably be due to a very low charge density of the former as compared with the latter.

It is obvious from the way in which the foregoing argument has been developed that PDADMA ions adsorb on the surface of SPP microcapsules to interact electrostatically with sulfonato groups on the constituent polymers of the microcapsules, causing disintegration of the microcapsules which leads to a complex coacervation under favorable conditions. The electrical equivalence holds in the coacervation and the effects of the degree of sulfonation and the pH and ionic strength of the medium on the disintegration phenomenon can be explained in terms of the effects of these variables on the electrostatic interaction between the polyions involved. The effect of the molecular sizes of the components is left to be studied in future because there is no way of obtaining samples of the polyanions and the polycations of definite molecular dimensions at present.

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