Disintegration of Sulfonated Poly(1,4-piperazinediylterephthaloyl) Microcapsules by 1-Dodecylpyridinium Chloride

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Partially sulfonated poly(1,4-piperazinediylterephthaloyl)(SPP) microcapsules were found to undergo disintegration by the action of dodecylpyridinium ions when the surfactant cation concentration exceeded a certain value which was dependent on pH of the medium. At their lower concentrations, dodecylpyridinium ions interacted with negatively charged SPP microcapsules to produce aggregation of the latter. A polyelectrolyte-type viscosity behavior was observed with the complex formed between SPP and dodecylpyridinium ions in the disintegration process of the microcapsules. Crosslinking of the terminal amino groups of SPP microcapsules prevented disintegration from taking place.

Since the earliest work was carried out on protein-anionic surfactant systems in the 1940's,[1] interactions in aqueous media between polyelectrolytes and oppositely charged surfactants have been under study for more than 30 years.[2-8] In almost all systems studied so far, the interaction causes precipitation of a complex which can be resolubilized by excess surfactant. In general, maximum precipitation seems to correspond to a single layer of surfactant adsorbed on the polymer, and the resolubilized form to a double layer of surfactant.

Meanwhile, it has become possible to prepare microcapsules composed of polyelectrolytes and to study their various physical properties.[9] Since such an electrically charged microcapsule can be regarded as a matrix of polyelectrolyte molecules assembled in a very thin spherical shell the interaction of the microcapsule with oppositely charged surfactants in aqueous media will be worth studying on the ground that understanding of this type of interaction should help us elucidate the mechanisms of the action of ionic surfactants on biological cells such as erythrocytes.[10]

The present paper deals with the interaction between partially sulfonated poly(1,4-piperazinediylterephthaloyl)(SPP) microcapsules and 1-dodecylpyridinium chloride(C_{12}PyCl) as a function of the cationic surfactant concentration at different degrees of sulfonation and pH of the medium, which leads to disintegration of the microcapsules at high concentrations of the surfactant. The effect of crosslinking with glutaraldehyde of the terminal amino groups of the polymers constituting the microcapsules on the interaction will also be discussed.

Experimental

Preparation of Microcapsules. SPP microcapsules were prepared by the method described in a previous paper.[11] The degree of sulfonation was varied by changing the molar ratio of 4,4′-diaminostilbene-2,2′-disulfonic acid to piperazine in the diamine mixture to be used as the water-soluble monomer in the preparation. When the ratio was fixed at 1:2, 1:3, and 1:5, the microcapsules obtained were named SPP-2, -3, and -5 microcapsules, respectively.

Microscopic Observation of Disintegration. To a dialyzed suspension of each of SPP-2, -3, and -5 microcapsules (*ca.* 5×10^7 capsules cm^{-3}) in test tubes was added an equal volume of various concentrations of aqueous C_{12}PyCl solution. The pH and ionic strength of the medium were adjusted by the addition of HCl or NaOH and NaCl, respectively.

The mixtures were then allowed to stand for 1 h with shaking in a thermostated water bath maintained at 35 °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 if SPP capsules were disintegrated or not.

Treatment of Microcapsules with Glutaraldehyde. The terminal amino groups of SPP microcapsules were crosslinked with glutaraldehyde in the same way as in the previous work.[11]

Adsorption of Dodecylpyridinium Ions to Microcapsules. Adsorption of C_{12}Py ions to noncrosslinked and crosslinked SPP microcapsules was measured by an equilibrium dialysis technique in the following manner.

Seventy cm^3 each of surfactant solution and microcapsule suspension were placed respectively in two compartments separated by a Cellophane membrane of an equilibrium dialysis cell made of methacrylate. The cell was immersed in a constant temperature bath kept at 35 °C. The content of each compartment was stirred with a two-blade glass stirrer. Equilibrium was attained within 4 h in all cases.

After equilibration, an aliquot of solution was withdrawn by a pipet from the compartment containing surfactant solution and its concentration was determined by the Few-Ottewill method.[12]

The amount of adsorption was calculated from the difference between the surfactant concentrations before and after adsorption.

Viscosity of Solubilized Complex. An Ostwald viscometer was used to measure the viscosity of solutions containing the solubilized complex formed between SPP and C_{12}Py ions. All measurements were made at 35 °C.

Sample solutions were prepared by diluting the solubilized complex solution with NaCl solutions of appropriate concentrations. The ratio of the specific viscosity to the dilution was defined as the viscosity number.

Results

Microscopic Observation. Disintegration of SPP microcapsules by C_{12}Py ions was dependent greatly on the surfactant cation concentration and slightly on the pH of the medium. The degree of sulfonation and the ionic strength of the medium had no effect on the disintegration phenomenon.

SPP microcapsules were disintegrated by the action of C_{12}Py ions when their concentration exceeded a certain value at all pH studied. Lower concentrations

Table 1. Disintegration of SPP microcapsules by $C_{12}PyCl$[a)]

$C_{12}PyCl$ concn M	pH 2.0		pH 4.0		pH 7.0	
	Microcapsule					
	SPP-2	SPP-5	SPP-2	SPP-5	SPP-2	SPP-5
1×10^{-6}	−	−	−	−	−	−
1×10^{-5}	−	−	−	−	−	−
1×10^{-4}	−	−	−	−	−	−
1×10^{-3}	−	−	−	−	−	−
1×10^{-2}	−	−	−	−	−	−
3×10^{-2}	−	−	−	−	−	−
5×10^{-2}	−	−	−	−	+−	+−
7×10^{-2}	+−	+−	+−	+−	+	+
1×10^{-1}	+	+	+	+	+	+

a) −, aggregation; +−, partial disintegration; +, disintegration.

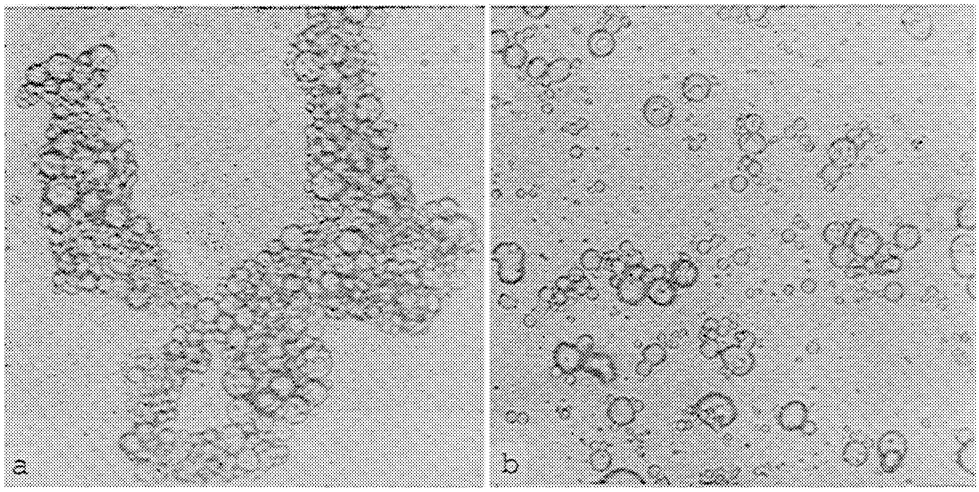

Fig. 1. Photomicrographs of SPP-5 microcapsules aggregated by 10^{-4} M $C_{12}PyCl$ (a) and partially redispersed by 10^{-2} M $C_{12}PyCl$ (b) at pH 7.0 and ionic strength 0.1.

of the surfactant cation caused aggregation of the microcapsules. Complete disintegration of the microcapsules was observed at surfactant concentrations higher than 7×10^{-2} M.** The minimum surfactant concentration needed for complete disintegration slightly decreased with increasing pH of the medium.

Table 1 gives the dependence of the phenomenon on the two variables at an ionic strength of 0.1.

Disintegration of glutaraldehyde-treated SPP microcapsules was never observed even when the highest concentration of $C_{12}PyCl$ was used. Instead, redispersion of the crosslinked microcapsules aggregated by low concentrations of $C_{12}PyCl$ took place in the presence of a large excess of the surfactant as shown in Fig. 1.

Surfactant Adsorption. Adsorption of $C_{12}Py$ ions on SPP microcapsules was affected by the surfactant cation concentration, the pH of the medium, the degree of sulfonation, and crosslinking of the terminal amino groups.

All adsorption isotherms exhibited a definite step in the surfactant concentration range of 10^{-2} to 10^{-3} M. The number of $C_{12}Py$ ions adsorbed on the microcapsules increased with increasing pH of the medium. This trend was more remarkable at low concentrations than at high concentrations of the surfactant cation. Increase in the degree of sulfonation gave rise to an increase in the amount adsorbed of $C_{12}Py$ ions.

Some of the adsorption isotherms for SPP-2 and SPP-5 microcapsules at an ionic strength of 0.1 are shown in Figs. 2 and 3, respectively, where the number of $C_{12}Py$ ions adsorbed on unit weight of the microcapsules is plotted against the initial surfactant concentration in logarithmic scale.

Crosslinking with glutaraldehyde of the terminal amino groups of SPP microcapsules caused a significant decrease in the number of adsorbed $C_{12}Py$ ions. Examples of the adsorption isotherms obtained at pH 7.0 and an ionic strength of 0.1 are given in Fig. 4 where isotherms for noncrosslinked SPP microcapsules are also shown for comparison.

Viscosity Behavior. The viscosity of solubilized complex formed between SPP molecule and $C_{12}Py$ ions exhibited a concentration dependence which is characteristic of polyelectrolytes.

The viscosity number of the solubilized complex

** 1 M=1 mol dm^{-3}.

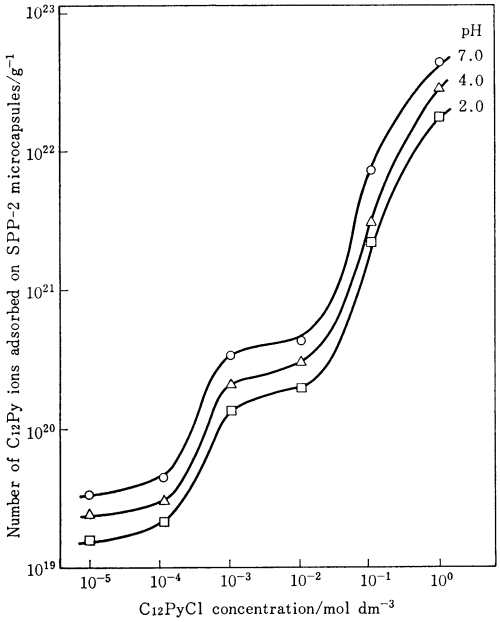

Fig. 2. Adsorption isotherms of $C_{12}Py$ ions on SPP-2 microcapsules at different pH and ionic strength 0.1 (35 °C).

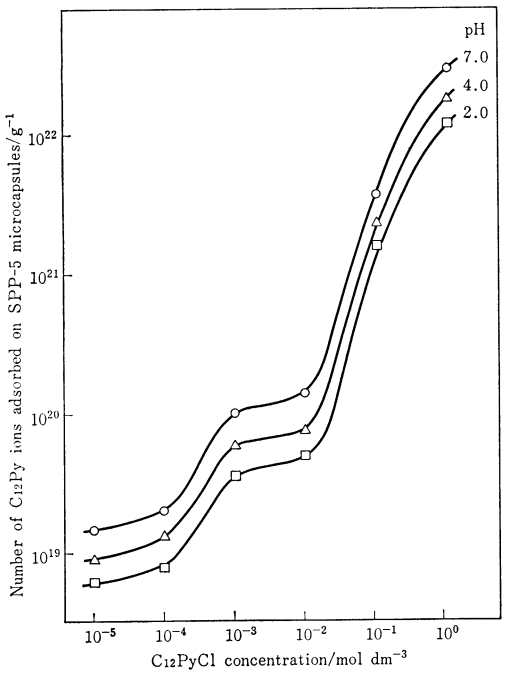

Fig. 3. Adsorption isotherms of $C_{12}Py$ ions on SPP-5 microcapsules at different pH and ionic strength 0.1 (35 °C).

at high ionic strength decreased linearly with increasing dilution while that at low ionic strength showed an uprising tendency at high dilutions. At intermediary ionic strength, the viscosity curve lay on a position between those at lower and higher ionic strengths. An example is illustrated in Fig. 5.

Discussion

It is quite obvious that aggregation of SPP microcapsules observed at low surfactant concentrations is

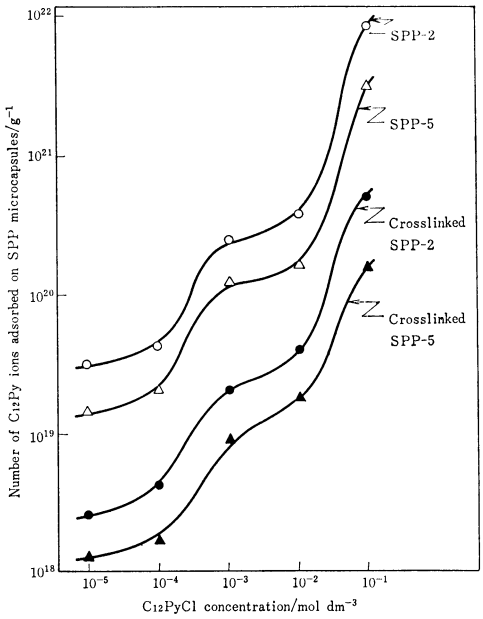

Fig. 4. Adsorption isotherms of $C_{12}Py$ ions on crosslinked and noncrosslinked SPP microcapsules at pH 7.0 and ionic strength 0.1 (35 °C).

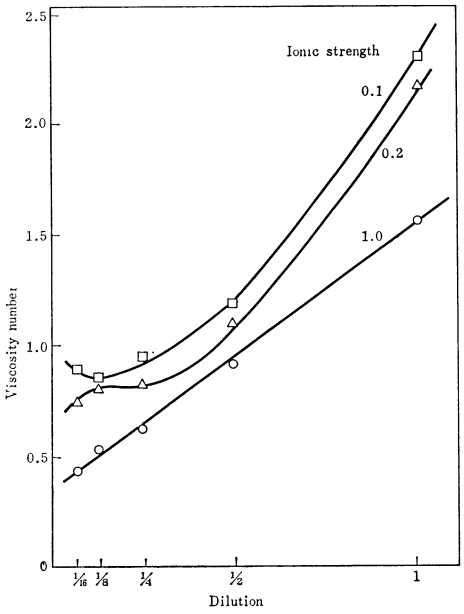

Fig. 5. Viscosity of solubilized $C_{12}Py$-SPP complex as a function of dilution at 35 °C.

caused by adsorption of $C_{12}Py$ cations with their hydrophobic tails directing outwards on sulfonato groups of the polymers constituting the microcapsules to form a hydrophobic complex. As the number of sulfonato groups on the polymers is slightly pH dependent, this head-to-head adsorption is also slightly pH dependent. This type of adsorption of the surfactant cations diminishes the electrostatic repulsion and at the same time augments the van der Waals attraction between the microcapsules, thus causing their aggregation.

When the $C_{12}Py$ ion concentration is increased beyond a value of 10^{-2} M adsorption of the surfactant cations rises steeply to form a step on the adsorption

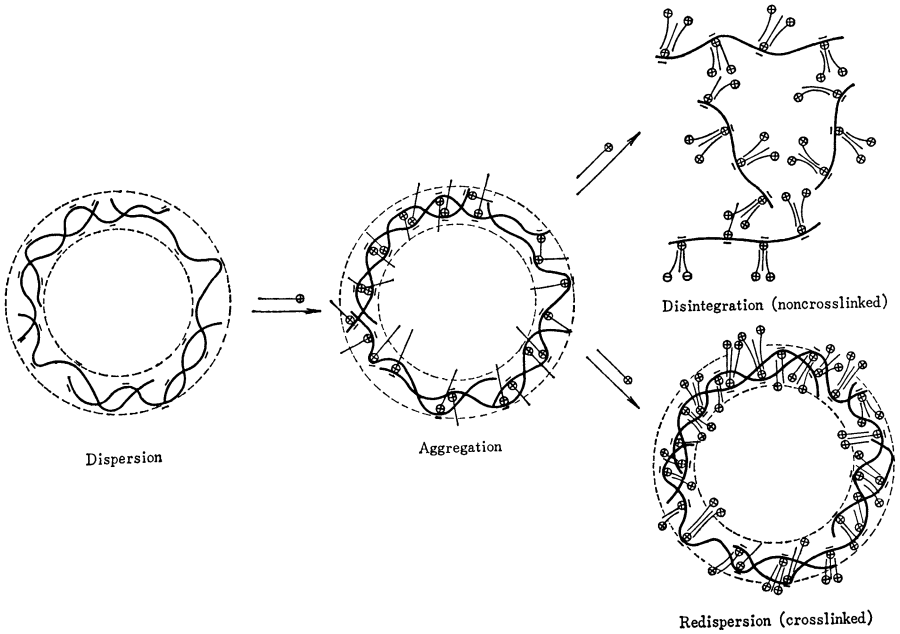

Fig. 6. Model for aggregation, disintegration, and redispersion of SPP microcapsules caused by $C_{12}Py$ ions.

isotherm (Figs. 2 and 3). The rise in adsorption is likely to correspond to the start of tail-to-tail adsorption onto the anionic sites modified by head-to-head adsorption and hydrophobic binding onto lipophilic sites on the polymer chains of $C_{12}Py$ ions. This view is supported by the fact that the number of the surfactant cations adsorbed at the concentration of 10^{-2} M on the capsules is comparable to that of anionic sites on the polymer chains.[11] Both types of adsorption generate positive charges on the polymer chains. The number of positive charges thus created will be larger, though not remarkably, at higher pH of the medium because the number of anionic sites along the polymer chains increases slightly with increasing pH as dissociation of sulfonato groups on the polymer proceeds while the number of lipophilic sites is independent of pH. It continues to increase with further rise in the surfactant cation concentration and the amount of adsorbed surfactant cations will then be enough to solubilize the polymer chains since the number of adsorbed surfactant cations reaches a value far larger than that of sulfonato groups on the polymer chains (Figs. 2 and 3).[11]

As the degree of sulfonation rises the number of sulfonato groups on the polymer chains also increases, and this in turn brings about an increase in the number of adsorbed $C_{12}Py$ ions as indicated from comparison of Fig. 2 with Fig. 3.

Increase in the number of positive charges on the constituent polymer chains of the microcapsules will cause dissociation of the chains, which leads to disintegration of the microcapsules, owing to the increased electrostatic repulsion between the chains. As is seen from Fig. 5, the viscosity of solubilized complex undergoes a marked increase with dilution when the ionic strength of the medium is low. This behavior of viscosity is characteristic of polyelectrolytes. Hence, each of the dissociated and solubilized polymer chains can be regarded as a polyelectrolyte.

Crosslinking of the constituent polymer chains prevents them from separating each other though they acquire some positive charges as a result of adsorption of $C_{12}Py$ ions on them. Consequently, disintegration of the microcapsules is never observed and instead redispersion occurs. Adsorption is rather limited in this case as the positively charged polymer chains are connected to each other by covalent bonds, and hence, an electric field exists around each capsule which is strong enough to repel the free surfactant cations approaching from the bulk of solution after adsorption proceeds to a certain degree (Fig. 4).

Figure 6 gives a proposed model for disintegration and redispersion of SPP microcapsules by the action of $C_{12}Py$ ions based on the experimental findings described in the previous section and the arguments made so far.

References

1) F. W. Putnam and H. Neurath, *J. Am. Chem. Soc.*, **66**, 672, 1992 (1944).
2) F. Karush and M. Sonenberg, *J. Am. Chem. Soc.*, **71**, 1369 (1949).
3) E. D. Goddard and B. A. Pethica, *J. Chem. Soc.*, 2659 (1951).
4) S. Saito, *Kolloid Z.*, **143**, 66 (1955).
5) M. N. Jones, *J. Colloid Interface Sci.*, **23**, 36 (1967).
6) E. D. Goddard, T. S. Phillips, and R. B. Hannan, *J. Cosmet. Chem.*, **26**, 461 (1975).
7) E. D. Goddard and R. B. Hannan, *J. Colloid Interface Sci.*, **55**, 73 (1976).
8) E. D. Goddard and R. B. Hannan, *J. Am. Oil Chem. Soc.*, **54**, 561 (1977).
9) T. Kondo, "Surface and Colloid Science", ed by E. Matijevic, Plenum Press, New York and London (1978), Vol. 10, pp. 1—43.
10) T. Kondo, *Adv. Colloid Interface Sci.*, **6**, 139 (1976).
11) S. Suzuki and T. Kondo, *Bull. Chem. Soc. Jpn.*, **52**, 1330 (1979).
12) A. V. Few and R. H. Ottewill, *J. Colloid Sci.*, **11**, 34 (1956).