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Studies on Microcapsules. XV. Electrophoretic Behavior of Carboxylated Polyphthalamide Microcapsules Containing Aqueous Solutions of Polyelectrolytes

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In an earlier paper of this series,[1] we reported that polyphthalamide microcapsules containing aqueous solution of anionic or cationic polyelectrolytes move towards the anode or cathode in an electric field according to the sign of charge on the encapsulated polyelectrolyte though the microcapsule membrane itself has no charge at all. Polyphthalamide microcapsules containing amphionic polyelectrolyte migrate either to the anode or to the cathode depending on the pH of the medium, showing the existence of an isoelectric point. All these findings indicated that the direction of electrophoresis of microcapsules containing aqueous solution of polyelectrolyte is determined by the sign of electric charge on the encapsulated polyelectrolyte.

However, if a certain portion of encapsulated polyelectrolyte molecules is supposed to have been chemically incorporated into the microcapsule membrane during the microencapsulation to give the membrane an electric charge, the direction in which microcap-

1) M. Shiba, Y. Kawano, S. Tomioka, M. Koishi, and T. Kondo, *Kolloid-Z. Z. Polym.*, **249**, 1056 (1971).

sules move in an electric field does not necessarily reflect the sign of charge on the encapsulated polyelectrolyte. Thus, for example, polyphthalamide microcapsules containing aqueous solution of bovine serum albumin migrated to the anode even at a lower pH than that of the isoelectric point of the protein.[2] This was interpreted as follows: A portion of the encapsulated bovine serum albumin molecules participates in the interfacial polycondensation reaction between diamine and acid dichloride, giving the membrane a negative charge since the protein has many amino groups reactive with acid dichloride and the charge on the encapsulated, unreacted protein molecules is screened by the charge of outer surface of microcapsule membrane.

The present study is aimed at confirming the dependence of the net charge of aqueous microcapsules containing polyelectrolyte upon the surface charge of their membrane. Poly-L-lysine phthalamide microcapsules containing aqueous solution of polyelectrolytes were prepared and their electrophoretic mobilities were determined at various hydrogen ion concentrations. The aqueous carboxylated polyphthalamide microcapsules containing polyelectrolyte are superior to the above-mentioned polyphthalamide microcapsules containing aqueous solution of bovine serum albumin in that the charge can be safely assumed to be uniformly distributed in the membrane since it consists of a single component and a free choice of polyelectrolyte to be encapsulated can be made.

Experimental

Materials. The polyelectrolytes were sodium heparinate (Daiichi Chemical Medicine Ind. Co., Tokyo) and 2-methyl-5-vinylpyridine–methyl acrylate–methacrylic acid copolymer (abbreviated hereafter as MPM) (Tanabe Pharmaceutical Co., Ltd., Osaka). Polyvinylpyrrolidone (PVP) was also used as electrically neutral polymer to be encapsulated.

L-Lysine of the highest purity available (Ajinomoto Co., Ltd., Tokyo) was used.

Preparation of Microcapsules. Poly-L-lysine phthalamide (PLPA) microcapsules containing aqueous polyelectrolyte solution were prepared by the same procedure as in a previous work.[3]

Measurements of Electrophoretic Mobilities. Electrophoretic mobility measurements on the carboxylated polyphthalamide microcapsules containing polyelectrolyte solution were carried out at room temperature in a quartz flat microelectrophoretic cell. For each measurement 40 microcapsules were timed in each direction to eliminate the polarization effect of the electrodes. The dispersion media were HCl-CH_3COONa (pH 2—3), acetate (pH 3—6), and phosphate (pH 6—8) buffers, the ionic strength of which was maintained at 1×10^{-1} or 2×10^{-3} with NaCl.

The samples for electrophoretic measurement were prepared by pipetting a few drops of the microcapsule suspension into a large volume of the dispersion media.

In view of the size of microcapsules (about 3 μm in diameter) and the ionic strength of the dispersion media (2×10^{-3} and higher), mobilities were converted into zeta-potentials ζ by means of the simple Smoluchowski equation

$$\zeta = \frac{4\pi\eta v}{D}$$

where v is the mobility, η and D are the viscosity and dielectric constants, respectively, of dispersion medium.

Results and Discussion

In Fig. 1 is shown the variation of the zeta-potential with the pH of the medium for PLPA microcapsules containing aqueous solution of PVP and for those containing aqueous solution of sodium heparinate. The electrophoretic behavior of PLPA microcapsules con-

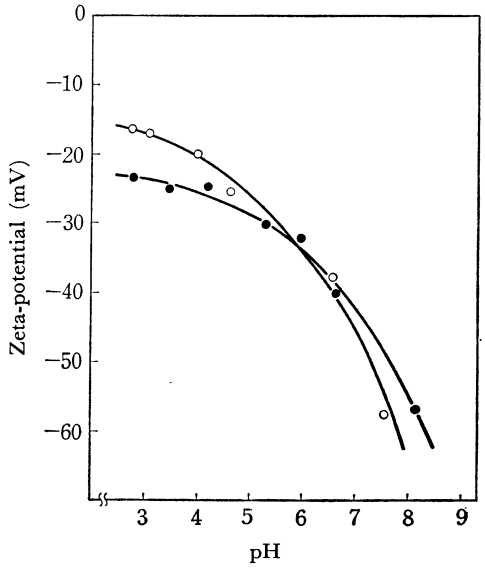

Fig. 1. Zeta-potential of carboxylated microcapsules containing 0.5% polymer solution as a function pH at an ionic strength of 2×10^{-3}. PVP, —○—, sodium heparinate, —●—.

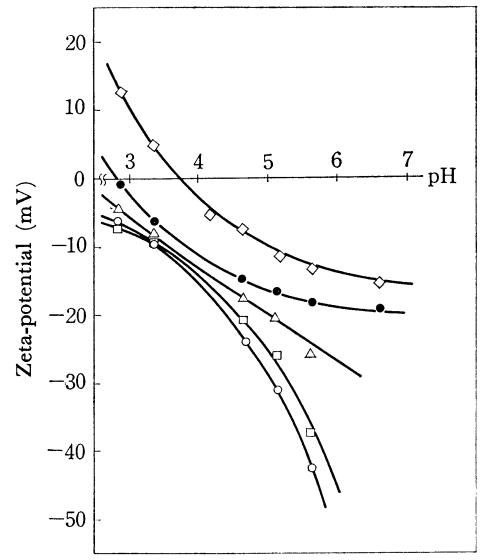

Fig. 2. Zeta-potential of carboxylated microcapsules containing MPM solution as a function of pH at an ionic strength of 1×10^{-2}. Concentration of MPM: —○— 0%; —□— 0.1%; —△— 0.3%; —●— 0.5%; —◇— 1.0%.

2) M. Shiba, Y. Kawano, S. Tomioka, M. Koishi, and T. Kondo, This Bulletin, **44**, 2911 (1971).

3) Y. Shigeri, M. Tomizawa, K. Takahashi, M. Koishi, and T. Kondo, *Can. J. Chem.*, **49**, 3623 (1971).

taining PVP was almost the same as that of those containing no polymer.[3] This is reasonable because PVP is electrically neutral and the zeta-potential of PLPA microcapsules is, therefore, determined solely by the charge of microcapsule membrane. In contrast, sodium heparinate seems to play an important role in determining the zeta-potential of PLPA microcapsules at low pH. Since the dissociation of carboxyl groups of PLPA should decrease with increasing hydrogen ion concentration, screening of the charge of the polyelectrolyte by the microcapsule membrane would be less significant with the lowering of pH of the medium. At high pH, the zeta-potential of PLPA microcapsules containing the polyelectrolyte was slightly less negative than that of those containing PVP. This may be due to the higher counter ion concentration near the membrane surface.

Figure 2 gives the plot of the zeta-potential against the pH of the medium for PLPA microcapsules containing aqueous solution of MPM, an amphionic polyelectrolyte having an isoelectric point at pH 4. The zeta-potential varied with both pH of the medium and the concentration of MPM. At low concentrations of MPM, PLPA microcapsules migrated to the anode independent of pH. When the microcapsules contained high concentrations of MPM, the direction in which they moved in an electric field reversed at low pH, while they still migrated towards the anode at high pH. This may result from the fact that some of MPM molecules are absorbed on the inner surface of microcapsule membrane to give it a positive charge which surpasses the negative charge of the outer membrane surface at low pH. We see from the figure that an increase in the concentration of MPM gives rise to a decrease in the absolute value of the zeta-potential of negatively charged PLPA microcapsules. The decrease in the zeta-potential may be caused by the increasing concentration of counter ions liberated from the encapsulated polyelectrolyte molecules.