[Chem. Pharm. Bull. 17(5)1073—1075(1969)]

UDC 615.453.4.011.4

Studies on Microcapsules. III.[1] Permeability of Polyurethane Microcapsule Membranes

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(Received January 31, 1969)

The membrane permeability is one of the important properties of the microcapsules prepared by the interfacial polycondensation method, because these microcapsule membranes have been found to be semipermeable. However, very few reports have been published so far on the permeability characteristics of microcapsules. This situation has prompted us to obtain further information about the permeability of microcapsules.

The present paper constitutes the first report on this subject and describes the permeability of polyurethane microcapsule membranes toward several inorganic electrolytes.

Experimental

Preparation of Polyurethane Microcapsules——Each of aqueous 1N solutions of cesium, sodium, and lithium chlorides, and sodium bromide, sodium sulfate, and sodium chromate was microencapsulated within polyurethane membranes. The polyurethane microcapsules were prepared by the same method as in the previous paper[3] except that the mechanical agitation in the emulsification and polycondensation processes was performed with a Model B-100 Chemistirrer (Tokyo Rika Kikai Co., Ltd.) at 620 rpm instead of a magnetic stirrer.

Permeability of Microcapsule Membranes toward Inorganic Electrolytes——The permeability was estimated from the change in electrical conductance of the dispersions of the microcapsules containing inorganic electrolyte solution.

The electrical conductance measurements were made by a Model CM-1DB Conductance Meter (Toa Electronics Co., Ltd., Tokyo) at $30 \pm 0.1°$. The measurements were started immediately after dispersing the newly formed microcapsules into aqueous Tween 20 solution in a conductance cell immersed in a thermostat. The conductance readings were taken at suitable time intervals.

Calculation of Permeability Constants——Assuming the simple diffusion of the ions in the microcapsule membranes, the permeability constants, P (cm/min), were calculated by the following equation,[4]

$$P = -\frac{1}{tA(1/V_1 + 1/V_2)} \ln \frac{1 - C_2/C_1}{1 + V_2/V_1 \cdot C_2/C_1}$$

where C_1 and C_2 are the concentrations of the electrolyte concerned inside and outside the microcapsules at a time t, V_1 and V_2 are the total volume of the microcapsules and the volume of the dispersion medium, and A is the total surface area of the microcapsules.

The value of C_1 at a time t was calculated from the difference between the value of C_2 at the same t and that at distribution equilibrium. In determining the C_2 value at each time from electric conductance measurements, the conductance due to the unreacted diamine, residual sodium carbonate, and sodium chloride formed during the polycondensation reaction had to be subtracted from the measured conductance. The conductance to be subtracted was estimated from separate measurements on the change in electrical conductance with time of the dispersion of microcapsules prepared in the absence of the electrolyte concerned.

The total volume of the microcapsules, V_1, was assumed to be equal to the product of the total volume of the dispersion and the ratio of the final equilibrium concentration to the initial one of the electrolyte concerned inside the microcapsules. The value of V_2 was then given by the difference between the total volume of the dispersion and V_1.

1) Part II: M. Koishi, N. Fukuhara, and T. Kondo, *Chem. Pharm. Bull.* (Tokyo), **17**, 804 (1969).
2) Location: *No. 12, Funagawara-machi, Shinjuku-ku, Tokyo.*
3) S. Suzuki, T. Kondo, and S.G. Mason, *Chem. Pharm. Bull.* (Tokyo), **16**, 1629 (1968).
4) M. Nakagaki, M. Koga, and S. Iwata, *Yakugaku Zasshi*, **82**, 1134 (1962).

The total surface area of the microcapsules, A, was evaluated from their mean diameter and concentration in the dispersion.

Results and Discussion

The distribution equilibrium was established between the inside and outside of the microcapsules within a few hours for all inorganic electrolytes studied.

Fig. 1 and 2 show the plots of the permeability constants of the membranes toward the inorganic electrolytes calculated by the equation given in the preceding section against time.

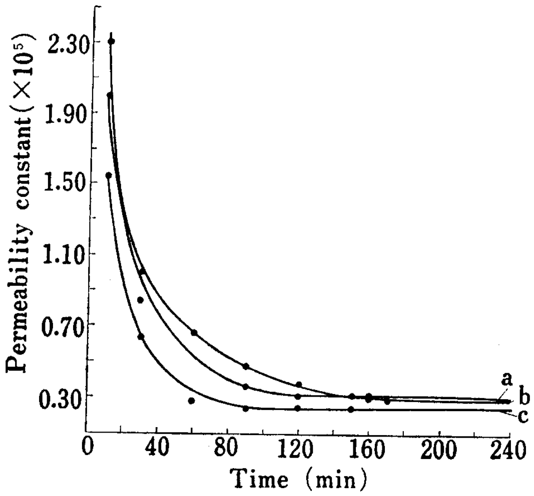

Fig. 1. Relationship between Permeability Constant and Time for Cesium Chloride (a), Sodium Chloride (b), and Lithium Chloride (c)

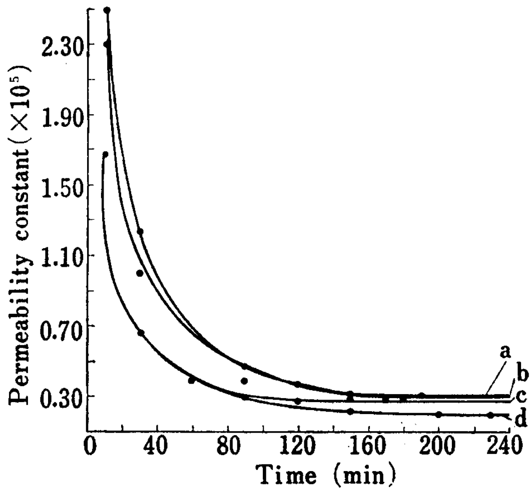

Fig. 2. Relationship between Permeability Constant and Time for Sodium Bromide (a), Sodium Chloride (b), Sodium Sulfate (c), and Sodium Chromate (d)

The permeability constants evidently decrease with time and then level off, although the equation predicts them to be constant independent of time provided that the membrane structure remains unchanged throughout the permeation process. The time-dependent permeability constants obtaind will, therefore, result from the gradual modification of the microcapsule membranes by the adsorption of Tween 20 molecules during the permeation process. This is quite possible because Tween 20 molecules must flow into the microcapsules across the membranes from the dispersion medium and some of the molecules will be trapped by the membranes during the passage. When the adsorption comes to a saturation, the membrane structure will no longer change. The permeability constants will thereafter assume a constant value.

In Table I are listed the final permeability constants of the membranes toward the inorganic electrolytes.

Table I. Permeability Characteristics of Polyurethane Microcapsules

Electrolyte	Permeability constant $P\times 10^5$ (cm/min)	Electrolyte	Permeability constant $P\times 10^5$ (cm/min)
CsCl	0.32	NaBr	0.31
NaCl	0.30	Na_2SO_4	0.28
LiCl	0.25	Na_2CrO_4	0.20

An inspection of the table indicates that the values for the members having cholride ion as the common anion are in the order,

$$Cs^+ > Na^+ > Li^+,$$

and those for the salts with sodium ion as the common cation in the order,

$$Br^- > Cl^- > SO_4^{2-} > CrO_4^{2-}.$$

These orders for the cations and anions are in accordance with those of decreasing hydration for these ions.[5] It may be concluded, therefore, that the rate of permeation of electrolytes through the microcapsule membranes is highly dependent on the hydration of ions involved.

5) **T. Sasaki,** *Kagaku No Ryoiki*, **2,** 378 (1948).