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Dynamic Differential Effect of Alkali Ions on the Desorption of Calcium Ion from Lipid Film

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The study of the interaction between the surface film and the solute of an underlying solution is essential in order to elucidate the reactions occurring at the interface of the cellular membrane. Recently, some evidence has been accumulated to show that Ca^{2+} is involved in regulating the ion movement across the cell membrane.[1] It is of importance, therefore, to examine the interactions between Ca^{2+} and other ions within lipid film. Since the phenomenon of ion movement is kinetic in nature, it may be more intimately related to the rate of adsorption or desorption than to any static property such as the equilibrium adsorption. It was shown in the preceding papers that the rate of desorption of Ca^{2+} brought about by K^+ was greater than that brought about by Na^+, whereas the equilibrium adsorptions were almost the same.[2] This differential effect was tentatively explained by assuming that the rate-determining step in the exchange reactions is the removal of the water molecule from the hydrated K^+ and Na^+. A further test of this hypothesis would require similar experiments by the use of other alkali ions such as Li^+, more hydrated than Na^+, and such as Cs^+ and Rb^+, less hydrated than K^+. This paper will describe the result of experiments carried out with these ions.

The samples as well as the apparatus used have been described elsewhere;[2] the temperatures were 25±1°C. The films of stearic acid or phospholipid were spread over the 5 m*l* of a solution containing radioactive calcium, and the calcium bound to the lipid film was measured with the G-M counter. When the equilibrium had been attained, 1 m*l* of a solution of alkali chloride was injected into the underlying solution by means of a syringe and the time-dependence of the desorption of Ca^{2+} was measured.[2] The results are shown in Figs. 1 and 2 together with the preceding results.[2] It may be seen in these figures that Li^+ acts like Na^+, whereas Rb^+ and Cs^+ behave like K^+, *i. e.*, the former indicates the induction period prior to the Ca^{2+} desorption, while the latter cause the desorption immediately. In contrast to the desorption behavior, the equilibrium adsorptions were nearly the same. These phenomena were found to be reproducible regardless of the concentrations of the alkali chloride solutions.

The results of the present paper, together with those of preceding papers,[2] suggest that the alkali ions may be classified into two groups, the 1st consisting of Li^+ and Na^+, and the 2nd, of K^+, Rb^+, and Cs^+, according to their dynamic behaviors at the interface. In addition, it may be pointed out that this classification may be attributed to the kinetic property of the alkali ion itself, since the phenomena are independent of the kind of anionic site.

According to Samoilov,[3] alkali ions are divided

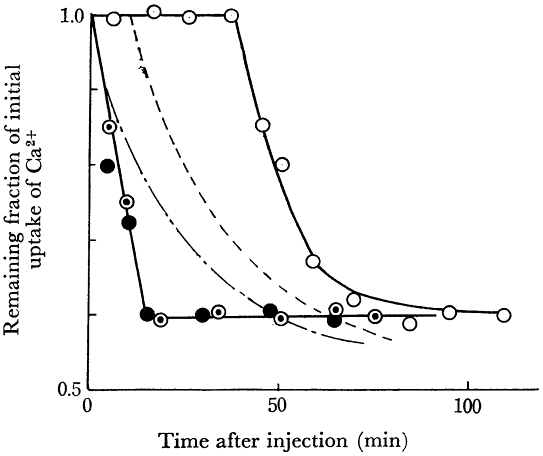

Fig. 1. Desorption of Bound Ca^{2+} from stearate film with time.
Open, dotted and filled circles indicate the effect of Li^+, Rb^+ and Cs^+, respectively. Concentration of Ca^{2+} was 4.72×10^{-5} M and those of the alkali ions, 0.1 M (pH, 7.1—7.2).
Dotted and broken lines indicate the effect of Na^+ and K^+, respectively.[2] Concentration of Ca^{2+} was 1.62×10^{-5} M and those of Na^+ and K^+, 0.4 M (pH, 8.0—8.2).

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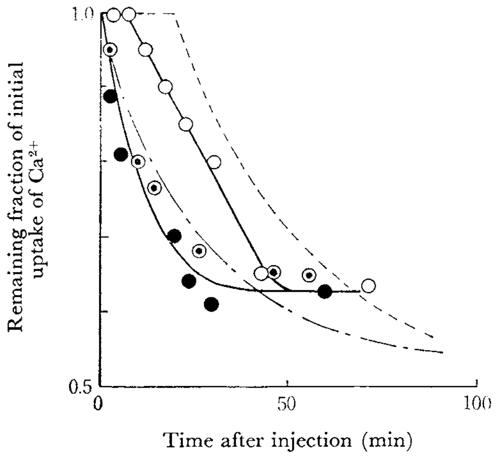

Fig. 2. Desorption of bound Ca^{2+} from lipid film with time.
Open, dotted and filled circles indicate the effect of Li^+, Rb^+ and Cs^+, respectively. Concentration of Ca^{2+} was 2.15×10^{-4}M and those of alkali ions, 1M (pH, 7.1—7.2).
Dotted and broken lines indicate the effect of Na^+ and K^+, respectively.[2] Concentration of Ca^{2+} was 5×10^{-4}M and those of alkali ions, 1.12M (pH, 7.1—7.2).

into two groups on the basis of the kinetic features of hydrated water, *i. e.*, the ions of positive hydration, Li^+ and Na^+, and those of negative hydration, K^+, Rb^+, and Cs^+. The hydrated water molecules of the former and of the latter are, respectively, less and more labile than molecules of pure water. This proposal corresponds to the concept of the structural temperature[4] or the order-disorder structure[5] of hydrated water.

Thus, this concept of the state of hydration may offer a plausible explanation for the present results providing that the rate-determining step of the ion-exchange reaction occurring at the surface film is the dehydration process of the alkali ion.

The similar differentiation has already been established in some biophysicochemical properties, such as the movements of alkali ions across the cell membrane[6] and the activation phenomena of some enzymes by those ions.[7] Since these phenomena are also kinetic in nature, it is conceivable that these biophysicochemical properties are closely related to the kinetic behavior of alkali ions at boundaries.

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