Transport Behavior of Ferric, Aluminum and Cupric Ions across the Alginate and the Other Membranes

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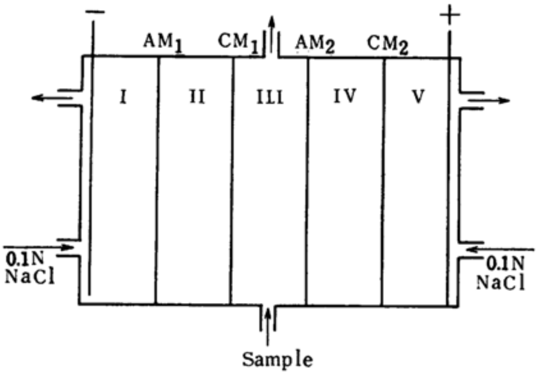
Recently many attempts have been undertaken to separate various species of ions by the electrodialyses using the ion-selective membranes, but there is no report as to the selective permeability of heavy metal ions. One of the objects of this study is to describe the transport behavior of ferric, aluminum and cupric ions across the ion-selective membranes. Another is to examine the permeability of ferric ion across the alginate membrane which is prepared from alginic acid. It is known that alginic acid adsorbs preferentially the ferric ion[1].

The electrodialyses were carried out at the constant current densities, $(0.33\sim2.50)\times10^{-2}$ amp./cm^2, for one hour, using a five-compartment cell which was schematically Shown in Fig. 1.



AM$_1$, SAM ; CM$_2$, SCM

Fig. 1. A five-compartment cell for the electrodialyses.

Into the central compartment, the solution containing 5∼10 meq./l. of ferric and aluminum chloride or ferric and cupric chloride and being adjusted to be about pH 1.3 (ca. 0.05N HCl) were fed at the flow-rate of about 1 l./hr. The amounts of ions transferred to the adjacent compartments, which were filled with the same solution beforehand, across the ion-selective membranes were measured. The analyses were done by the simultaneous colorimetric methods[2]. The ion-selective membranes were heterogeneous and were prepared from Amberlite resins in the authors' laboratory*. The alginate membrane

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[1] M. Senō and T. Yamabe, This Bulletin, to be published.

[2] R. E. Kitson, *Anal. Chem.*, 22, 664 (1950); K. Motojima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 76, 903 (1955).

* From the four kinds of Amberlite resins, IR-120, IRC-50, IRA-400 and IR-4B, the corresponding ion exchange membranes were prepared. These are a strongly and a weakly dissociated cation-selective membrane and a strongly and a weakly dissociated anion-selective membrane, which are abbreviated as SCM, WCM, SAM and WAM. Similarly the alginate membrane is designated as ACM in Table II.

was prepared from polyvinylchloride and alginic acid crosslinked with formaldehyde[3], using cyclohexanone as a mixing agent. The obserbed membrane potentials of these membranes are 80~90% of the theoretical (S.C.E. | 0.1N KCl | memb. | 0.01N KCl | S.C.E.).

A part of the experimental results was given in Tables I and II. The following facts are to be noticed.

TABLE I. PERMEABILITIES OF HYDROGEN, FERRIC, ALUMINUM AND CUPRIC IONS ACROSS A STRONGLY DISSOCIATED CATION-SELECTIVE MEMBRANE

Current densities	Concentration ratios*					
	Fe-Al system			Fe-Cu system		
amp./cm^2×10^2	H	Fe	Al	H	Fe	Cu
0.33	1.99	0.84	0.79	1.88	0.78	0.72
0.83	2.60	1.02	1.26	2.41	1.13	1.78
1.67	3.36	1.15	1.39	4.28	2.18	3.28
2.50	4.90	2.26	2.49	4.70	2.41	4.30

* These are ratios of concentrations of a given ion in the compartment II before and after electrodialysing.

TABLE II. PERMSELLCTIVITY COEFFICIENTS ACROSS THE VARIOUS ION-SELECTIVE MEMBRANES AT 0.0083 amp./cm^2

Ion-selective membrane system (CM1-AM2)	Permselectivity coefficients*			
	T_{Fe}^{Al}	T_{Fe}^{Cu}	T_{Fe}^{H}	
SCM-SAM	1.23	1.57	2.55	2.13
WCM-SAM	1.27	1.32	2.49	2.00
WCM-WAM	1.07	1.30	2.06	2.35
ACM-SAM	1.03	1.70	1.72	2.50
ACM-WAM	1.01	1.51	1.75	2.06

* $T_A^B = \frac{[B]_f [A]_i}{[B]_i [A]_f}$

where $[A]_i$, $[B]_i$; concentration of A or B ion in the initial solution filling the compartment II, respectively; $[A]_f$, $[B]_f$; concentration of ion A or B in the final (concentrated) solution in the compartment II, respectively.

** In the first column, the values obtained for Fe-Al system were shown and in the second column, those for Fe-Cu system were presented.

(1) The order of permeabilities of these cations across the cation-selective membranes is as follows; $Fe^{3+} < Al^{3+} < Cu^{2+} < H^+$, excepting the case at the lowest current density**.

(2) This order remains invariable, independently of the various combinations of the ion-selective membranes. The permeability of the ferric ion across the alginate membrane is nearly the same as that in the other membrane systems. There is no parallel relationship between the selectivity in the ion exchange equilibria[1] and the permselectivity in this experiment, of the various ion-selective membranes.

(3) Some amount of the ferric ion transports across the anion-exchange membranes and this behavior seems to be due to the formation of a complex anion. A further investigation is carried out now, for the experimental error of this research prevents from giving a final conclusion to this problem.

The full data will be presented in the near future.

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[3] T. Yamabe, Y. Tanka and M. Senō, *Industrial Science* (*Seisan Kenkyu*), **9**, 476 (1959).

** This order does not depend on the current density higher than 0.0083 amp./cm^2. The diffusion of ions through membrane and the migration of water due to the electro-osmosis make a contribution to the transport behavior to some extent. On this account, the concentration ratio of the metal ions shown in Table I is smaller than unity at the current density, 0.0033 amp./cm^2. When the current density is high enough and the same membrane used as AM1, the permselectivity coefficient T_A^B defined in Table II is considered to be a relative measure of the permeabilities of the cations across the cation-exchange membrane CM1.