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BI-IONIC POTENTIALS OF BOVINE LENS CAPSULES AND COLLODION MEMBRANES

NORIAKI TAKEGUCHI* AND MASAYUKI NAKAGAKI
Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto (Japan)

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SUMMARY

Concentration dependencies of bi-ionic potentials of well-cleaned bovine lens capsules *in vitro*, of collodion and of modified collodion membranes were studied. The lens capsules have positively fixed charges, and collodion membranes have negatively fixed charges. As these membranes are partially selectively permeable, both co-ions and counter-ions exist in the membrane. However, many studies on bi-ionic potentials have been limited to systems in which the membrane has extreme ionic selectivity and co-ions are completely excluded from the membrane. Experimental results agreed with theoretical values obtained by assuming the common ion concentration to be constant throughout the membrane for systems such as KCl(C)–membrane ($\theta > 0$, or $\theta < 0$)–NaCl(C), $NaNO_3$(C)–membrane ($\theta > 0$)–NaCl(C) and $CaCl_2(C_1)$–membrane ($\theta > 0$)–$NaCl(C_2)$ ($C_2/C_1 = 2$), where C is the bulk concentration. The theoretical reliability of this assumption was checked. When both electrolytes in solution were uni-univalent, the ratio of ionic mobilities of two counter-ions (or two co-ions) in all of these membranes was almost the same as the ratio obtained in bulk solution, while the ratio of ionic mobilities of the counter-ion and the co-ion was almost the same as the ratio obtained in bulk solution for the lens capsule, but different in the case of the collodion and modified collodion membranes.

INTRODUCTION

Charged membranes when used to separate two ionic solutions, each of which contains a different counter-ion and the same co-ion, give rise to a so-called bi-ionic potential. Here the counter-ion is a cation if the membrane is negatively charged. Many studies on bi-ionic potentials[1–14] have been limited to the case where membranes have extreme ionic selectivity, such as highly charged membranes and nerve membranes. In these cases the co-ion is completely excluded from the highly charged membranes, and hence the co-ion component does not appear in flux equations.

In this paper we study, for partially selectively permeable, positively or negatively fixed-charged membranes, the concentration dependencies of two kinds of membrane potential, *i.e.* the bi-ionic potential and the membrane potential that arises when charged membranes are used to separate two solutions, each of which contains

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* Present address: Faculty of Pharmaceutical Sciences, University of Toyama, Gofuku, Toyama, Japan.

a different co-ion and the same counter-ion. We designate the latter membrane potential a bi-ionic potential in the broader sense; this is not usually found in biological membrane systems because the fixed charge of most biological membranes is negative, and Na^+ and K^+ ion concentrations are high in the outer and inner phases of cell membranes, respectively, *i.e.* the counter-ions are different. But bovine lens capsule has positively fixed charges[15] so that it is necessary to study the bi-ionic potential in the latter case. Collodion membranes are used as partially selectively permeable and negatively fixed-charged membranes, and bovine lens capsules are used as partially selectively permeable and positively fixed membranes. In these cases, both co-ions and counter-ions exist in the membrane.

When two bulk concentrations, C(moles/l), are equal in the system of, for example, NaCl(C)–negatively charged membrane–KCl(C), the bi-ionic potential of the extremely selectively permeable membrane has been reported to be a function of the membrane selectivities of two counter-ions only[1–9,13,14], but the bi-ionic potential of the partially selectively permeable membrane are shown in this paper to be a function of concentration, membrane selectivities of the two counter-ions and the membrane selectivity of the common co-ion.

THEORETICAL

Two kinds of systems were studied: M_1A (Solution I)–membrane–M_2A (Solution II) and MA_1(I)–membrane–MA_2(II), where M_1, M_2 and M are the positive ions and A, A_1 and A_2 are the negative ions. In this paper we take M_2A and MA_2 to be uni-univalent electrolytes, and M_1 and A_1 to be univalent or multivalent ions for the sake of simplicity. These systems are isothermal and both solutions are at the same hydrostatic pressure. It is assumed that the contribution of the water flow can be neglected. The space coordinate x is taken in the direction of membrane thickness. Two membrane surfaces are in contact with Solution I and II at $x = 0$ and $x = \Delta x$, respectively.

M_1A (I)–membrane–M_2A (II)

We assume that all co-ions and counter-ions in the membrane, except fixed ions of the membrane, can move freely. Since no external electric field is applied across the membrane in the present system, the electric current density, I, is zero. From the condition $I = 0$, we have in the steady state at any point in the membrane[16]

$$\frac{d\psi}{dx}\left(\frac{-F}{RT}\right) = \frac{d\psi^*}{dx} = \frac{l_{M_1}^* Z_{M_1}\dfrac{d\bar{C}_{M_1}}{dx} + l_{M_2}^*\dfrac{d\bar{C}_{M_2}}{dx} - l_A^*\dfrac{d\bar{C}_A}{dx}}{l_{M_1}^* Z_{M_1}^2\bar{C}_{M_1} + l_{M_2}^*\bar{C}_{M_2} + l_A^*\bar{C}_A} \tag{1}$$

where ψ is the electric potential; $\bar{C}_k$ (k = M_1, M_2 and A) is the mobile ion concentration of the ion species k; l_k^*, its effective mobility; Z_k, its valencies; and F, R and T have their usual meaning. The requirement of electric neutrality in any element of the membrane gives

$$Z_{M_1}\bar{C}_{M_1} + \bar{C}_{M_2} - \bar{C}_A + \theta = 0 \tag{2}$$

where θ is the effective charge density of the membrane (moles/l). θ is the product of the real charge density of the membrane, X and the interaction parameter Φ that is characteristic of a given pair of membrane and electrolyte ($\theta = \Phi X$)[17–23]. θ is assumed not to change with bulk concentration with which the membrane is in contact. In most work on bi-ionic potential hitherto reported, the additional assumption is made that co-ions do not exist in the membrane[1–14] because of the extreme ionic selectivity of the membrane. But in systems of lens capsules ($\theta > 0$) and collodion membranes ($\theta < 0$) which are partially selectively permeable, we can not make the assumption that co-ions are completely excluded from the membrane.

Here, in order to study these partially selectively permeable membranes, we use the experimental condition that two concentrations of the common ion A (M in the system of MA_1–membrane–MA_2) in Solutions I and II are equal. Under this condition, we make the additional assumption that $d\bar{C}_A/dX = 0$, *i.e.* $\bar{C}_A$ is constant throughout the membrane. (We attempt to check the reliability of this assumption in the appendix.) Integrating Eqn. 1 with the assumption $d\bar{C}_A/dX = 0$ and phase boundary conditions, $\bar{C}_{M_2} = 0$ at $x = 0$ and $\bar{C}_{M_1} = 0$ at $x = \Delta x$, we have for the biionic potential

$$-\Delta\psi^* = [(l_{M_2}^*/l_{M_1}^* - 1)/(l_{M_2}^*/l_{M_1}^* - Z_{M_1})] \ln (1 + \bar{C}_{M_2}^{II}/k_A') \quad (3)$$

and

$$K_A' = [(Z_{M_1} + l_A^*/l_{M_1}^*)\bar{C}_A - Z_{M_1}\theta]/(l_{M_2}^*/l_{M_1}^* - Z_{M_1}) \quad (4)$$

where $\bar{C}_{M_2}^{II}$ is the concentration of M_2 ion at the membrane surface which is in contact with Solution II. As limiting forms of Eqn. 3 at the lowest and at the highest concentrations, we have

$$\Delta\psi^* = 0 \qquad \text{for } \theta > 0 \text{ and } C/\theta \ll 1 \quad (5)$$

$$\Delta\psi^* = -[(l_{M_2}^*/l_{M_1}^* - 1)/(l_{M_2}^*/l_{M_1}^* - Z_{M_1})] \ln [(l_{M_2}^*/l_{M_1}^* + l_A^*/l_{M_1}^*)/(Z_{M_1} + l_A^*/l_{M_1}^*)]$$
$$\text{for } \theta > 0 \text{ and } C/\theta \gg 1 \text{ and for } \theta < 0 \text{ and } C/|\theta| \gg 1 \quad (6)$$

and

$$\Delta\psi^* = -[(l_{M_2}^*/l_{M_1}^* - 1)/(l_{M_2}^*/l_{M_1}^* - Z_{M_1})] \ln (l_{M_2}^*/l_{M_1}^* Z_{M_1})$$
$$\text{for } \theta < 0 \text{ and } C/|\theta| \ll 1 \quad (7)$$

in the derivation of which concentrations in the membrane are calculated from the Donnan equilibrium and the electric neutrality condition[15]. The limiting Eqn. 7 is the same equation as that derived by MICHAELIS[1] and holds where the co-ion is completely excluded from the membrane and only counter-ions exist in the membrane (*i.e.* $C/|\theta| \ll 1$).

$MA_1(I)$–*membrane*–$MA_2(II)$

Following similar treatment to that applied for the M_1A–membrane–M_2A system, we have for the bi-ionic potential of the present system

$$\Delta\psi^* = [(l_{A_2}^*/l_{A_1}^* - 1)/(l_{A_2}^*/l_{A_1}^* + Z_{A_1})] \ln (1 + \bar{C}_{A_2}^{II}/K_p') \quad (8)$$

and

$$K_p' = [(l_M^*/l_{A_1}^* - Z_{A_1})\bar{C}_M - l_{A_1}^* Z_{A_1}\theta]/(l_{A_2}^*/l_{A_1}^* + Z_{A_1}) \tag{9}$$

in the derivation of which we assume $d\bar{C}_M/dX = 0$. For limiting forms of Eqn. 8, we have

$$\Delta\psi^* = [(l_{A_2}^*/l_{A_1}^* - 1)/(l_{A_2}^*/l_{A_1}^* + Z_{A_1})] \ln (-l_{A_2}^*/l_{A_1}^* Z_{A_1})$$
$$\text{for } \theta > 0 \text{ and } C/\theta \ll 1 \tag{10}$$

and

$$\Delta\psi^* = [(l_{A_2}^*/l_{A_1}^* - 1)/(l_{A_2}^*/l_{A_1}^* + Z_A)] \ln [(l_M^*/l_{A_1}^* + l_{A_2}^*/l_{A_1}^*)/(l_M^*/l_{A_1}^* - Z_{A_1})]$$
$$\text{for } \theta > 0 \text{ and } C/\theta \gg 1. \tag{11}$$

MATERIALS AND METHODS

The salts used were analytical grade reagents. The pH of aqueous salt solutions in equilibrium with laboratory air was about 5.8.

Membranes

The anterior lens capsule was removed using the method previously described by us[15]. Physicochemical properties of the well-cleaned lens capsules were stable for one or two weeks[15,24]. Collodion membranes were prepared according to the method of Gregor and Sollner[25] (collodion), and an oxidized collodion membrane was prepared by immersing the collodion membrane in 1 M NaOH solution for 4 min (C-Oxid$_{14}$). A collodion–polystyrene (the degree of sulfonation was 76 %) membrane was kindly presented to this laboratory by N. Kamo and Y. Kobatake at Osaka University (C-HPSS). From measurements of the membrane potential[17] (NaCl–membrane–NaCl system), effective charge densities θ' (NaCl–NaCl) were calculated to be $-1.2_0 \cdot 10^{-1}$ M for C-HPSS, $-2.3_5 \cdot 10^{-2}$ M for C-Oxid$_{14}$ and $-4.2_0 \cdot 10^{-3}$ M for the collodion membrane.

Bi-ionic potential

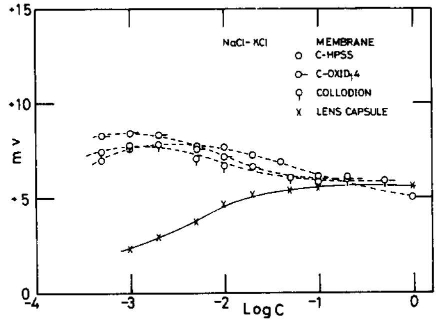
In this paper, the electrolyte in Solution II was always NaCl (M_2A = NaCl or MA_2 = NaCl), and the anterior lens capsule was always set so that Solution II was in contact with the front surface of the lens capsule and Solution I was in contact with the inner surface of the lens capsule. The electric potential was measured by means of a reed vibrating electrometer (Toshiba Co., Tokyo, UFE-26301 Type). Ag–AgCl electrodes were used when the system had Cl^- as the common ion (for example, NaCl–membrane–KCl system), and Na glass electrodes were used when the system had Na^+ as the common ion (for example, NaCl–membrane–$NaNO_3$). A plus sign of $\Delta\psi$ indicates that ψ^{II} (the electrical potential in Solution II) was positively higher than ψ^I. All measurements were made in duplicate or triplicate at 25°.

RESULTS AND DISCUSSION

We classify our experimental results and discussion into three categories: M_1A(KCl or LiCl or HCl)(C)–membrane ($\theta > 0$ or $\theta < 0$)–M_2A(NaCl)(C), MA_1($NaNO_3$ or NaBr)(C)–membrane ($\theta > 0$)–MA_2(NaCl)(C) and M_1A($CaCl_2$, $MgCl_2$, $SrCl_2$, $BaCl_2$ or $LaCl_3$)(C_1)–membrane ($\theta > 0$)–M_2A(NaCl)(C_2) where $C_2/C_1 = 2$ (or 3 for $LaCl_3$). Under the experimental condition where two concentrations of the common ion are equal, $d\bar{C}_A/dX = 0$ and $d\bar{C}_M/dX = 0$ are considered to be satisfied in the first and second categories, respectively, and in the last category $d\bar{C}_A/dX = 0$ is considered to be satisfied with a maximum error of 10 % (or 15 % for $LaCl_3$) (see the APPENDIX).

M_1A(KCl, LiCl or HCl)(C)-membrane($\theta > 0$ or $\theta < 0$)-NaCl(C)

Fig. 1 represents experimental results of bi-ionic potentials for KCl–membrane–NaCl systems. The bi-ionic potential for C-HPSS, C-Oxid$_{14}$ and collodion membranes had essentially a similar nature despite a broad distribution of values of the effective charge density (see MATERIALS AND METHODS). As C decreased, the bi-ionic potential for these collodion and modified collodion membranes ($\theta < 0$) tended to positive limiting values but the bi-ionic potential for lens capsule 11 ($\theta > 0$) tended to zero, tendencies also expected theoretically from Eqns. 5 and 7. As C increased, the bi-ionic potential for both these positive and negative membranes approached similar values. The parameters that characterize the system are $l_A^*/l_{M_1}^*$, $l_{M_2}^*/l_{M_1}^*$ and θ (see Eqns. 3 and 4).



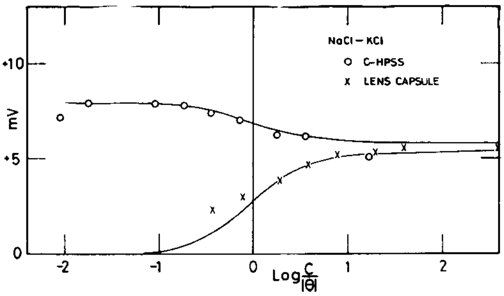


Fig. 1. Experimental curves of bi-ionic potentials measured with Ag–AgCl electrodes for KCl(C)–membrane–NaCl(C).

Fig. 2. Plots of bi-ionic potentials against *log* C/|θ| for KCl(C)–lens capsule 11–NaCl(C) (C = 0.001–1 M) and KCl(C)–C-HPSS–NaCl (C = 0.0005–1 M) indicated × and ○, respectively, where $\theta = 2.5_8 \cdot 10^{-3}$ M and $\theta = -60._0 \cdot 10^{-3}$ M are used, respectively. Solid lines represent theoretical curves calculated from Eqn. 3 with $l_{Na}^*/l_K^* = 0.61$ and $l_{Cl}^*/l_{Na}^* = 1.6_3$ for lens capsule 11 and with $l_{Na}^*/l_K^* = 0.74$ and $l_{Cl}^*/l_{Na}^* = 0.40$ for C-HPSS.

For negatively fixed-charged membranes, we can determine $l_A^*/l_{M_1}^*$ and $l_{M_2}^*/l_{M_1}^*$ from two limiting values at the highest concentration and the lowest concentration using Eqns. 6 and 7. Using the obtained values for $l_A^*/l_{M_1}^*$ and $l_{M_2}^*/l_{M_1}^*$, we calculated the bi-ionic potential as a function of C for an arbitrary value of θ from Eqn. 3. The calculated bi-ionic potential is represented in Fig. 2 by solid lines as a function of *log* C/|θ|. Because the experimental curve in Fig. 1 is a function of *log* C, and the theoretical curve in Fig. 2 is a function of *log* C/|θ|, the parameter θ can be calculated by the proper superimposition of these two curves. Using θ obtained from the above-mentioned method, we also represent the experimental data for C-HPSS ($\theta = -6.0_0 \cdot 10^{-2}$ M) (indicated ○) in Fig. 2. The theoretical curve fitted experimental data well over a wide range of concentrations. The parameters obtained are listed in Table I.

TABLE I

VALUES OF PARAMETERS FROM BI-IONIC POTENTIALS

M_1A–membrane–M_2A	$\theta \cdot 10^3$	$l_{Na}^*/l_{M_1}^*$	l_{Cl}^*/l_{Na}^*
KCl–collodion–NaCl	-7.4_2	0.74	0.40
KCl–C-Oxid$_{14}$–NaCl	$-15._9$	0.73	0.50
KCl–C-HPSS–NaCl	$-60._0$	0.74	0.40
KCl–lens capsule 11–NaCl	2.5_8	0.61	1.6_3
(bulk, KCl–NaCl)		($l_{Na}/l_K = 0.68$)	($l_{Cl}/l_{Na} = 1.47$)
LiCl–C-HPSS–NaCl	$-36_{4.0}$	1.2_2	0.91
LiCl–lens capsule 12–NaCl	1.5_9	1.3_2	1.6_3
(bulk, LiCl–NaCl)		($l_{Na}/l_{Li} = 1.30$)	($l_{Cl}/l_{Na} = 1.47$)
HCl–C-HPSS–NaCl	$-61._7$	0.22	0.23
HCl–lens capsule 30–NaCl	$25._1$	0.14	1.6_3
(bulk, HCl–NaCl)		($l_{Na}/l_H = 0.14$)	($l_{Cl}/l_{Na} = 1.47$)

MA_1–membrane–MA_2	$\theta \cdot 10^3$	$l_{Cl}^*/l_{A_1}^*$	l_{Cl}^*/l_{Na}^*
NaNO$_3$–lens capsule 23–NaCl	5.3_8	1.0_1	1.3_4
(bulk, NaNO$_3$–NaCl)		($l_{Cl}/l_{NO_3} = 1.07$)	($l_{Cl}/l_{Na} = 1.47$)
NaBr–lens capsule 28–NaCl	4.6_8	0.93	3.8_2
(bulk, NaBr–NaCl)		($l_{Cl}/l_{Br} = 0.98$)	($l_{Cl}/l_{Na} = 1.47$)

M_1A–membrane–M_2A	$\theta \cdot 10^3$	$l_{Na}^*/l_{M_1}^* = l_{Na}/_{M_1}$	l_{Cl}^*/l_{Na}^*
CaCl$_2$–lens capsule 13–NaCl	1.1_5	1.68	1.0_3
MgCl$_2$–lens capsule 14–NaCl	1.0_0	1.89	1.1_5
SrCl$_2$–lens capsule 14–NaCl	6.9_2	1.69	1.2_1
BaCl$_2$–lens capsule 14–NaCl	8.3_2	1.57	0.95
LaCl$_3$–lens capsule 12–NaCl	1.4_5	2.16	0.58

The ratio of mobilities of two counter-ions in collodion, and modified collodion membranes ($l_{Na}^*/l_K^* = 0.74$ for collodion, 0.73 for C-Oxid$_{14}$ and 0.74 for C-HPSS) was roughly the same as l_{Na}/l_K in bulk solution (0.68), but the ratio of mobilities of the co-ion and the counter-ion in collodion and modified collodion membranes was very different from that in bulk solution ($l_{Cl}^*/l_{Na}^* = 0.40$ for collodion and C-HPSS, $l_{Cl}^*/l_{Na}^* = 0.50$ for C-Oxid$_{14}$ and $l_{Cl}/l_{Na} = 1.47$ in bulk solution). (The value of mobilities of ions in bulk solution was taken from ref. 26). Our interpretation of these facts is as follows: There is no great difference between βl_A^* and l_A where A is the co-ion and β is the tortuosity of the membrane. There are great differences between $\beta l_{M_1}^*$ and l_{M_1} and between $\beta l_{M_2}^*$ and l_{M_2}, where M_1 and M_2 are the counter-ions, because the counter-ion in the membrane interacts with the fixed charge of the membrane. That is, $l_{M_1}^* = (\alpha/\beta) l_{M_1}$ and $l_{M_2}^* = (\alpha'/\beta) l_{M_2}$ where α and α' are the interaction parameters. Therefore, $l_A^*/l_{M_1}^* = l_A/\alpha l_{M_1}$ and $l_{M_2}^*/l_{M_1}^* = (\alpha'/\alpha) l_{M_2}/l_{M_1}$. For C-HPSS, α was calculated to be 3.69 and α'/α to be 1.09 ($\alpha' = 4.02$).

The magnitude of $|\theta|$ for these membranes increased in the order of collodion $<$ C-Oxid$_{14}$ $<$ C-HPSS as in the system of NaCl–membrane–NaCl.

The effective charge density θ ($= \Phi X$) (KCl–NaCl) of these membranes in the present system was different from θ' ($= \Phi' X$) (NaCl–NaCl) (see Table I and MATERIALS

AND METHODS). This means $\Phi \neq \Phi'$ ($\Phi'/\Phi = \theta'/\theta = 2.0_0$ for C-HPSS, 1.4_8 for C-Oxid$_{14}$ and 0.57 for collodion).

Next we consider parameters for positively charged membranes. For the KCl–lens capsule 11–NaCl system, $\Delta\psi$ was +5.5 mV at an adequately high concentration and tended to zero as C decreased. (The number placed after the lens capsule indicates the individual membrane.) Because the value of zero at the limit of low concentration is estimated from Eqn. 5, the value of zero does not give any information on the two parameters $l_{M_2}*/l_{M_1}*$ and $l_A*/l_{M_1}*$ in Eqn. 3. Because the lens capsule is composed of a collagenous protein[27] and has several kinds of negatively fixed charges as well as several kinds of positively fixed charges (the net charge is positive and small compared with collodion and modified collodion membranes), fixed charges of the lens capsule interact with both co-ions and counter-ions, and therefore the effect of the interaction might not be characteristic of co-ions and counter-ions. On the other hand, fixed charges of collodion and modified collodion membranes are mainly composed of carboxyl groups, and therefore their interaction with counter-ions might be characteristic. Here these two parameters were determined following a working hypothesis based on the above consideration. First, in the lens capsule, the ionic mobilities of K^+ and Cl^-, which have the same mobility in bulk solutions, were assumed to be equal, *i.e.* $l_K* = l_{Cl}*$, although $l_K* \neq l_{Cl}*$ in collodion membranes. Second, $l_{Na}*/l_K*$ was calculated from Eqn. 6 together with the assumption $l_K* = l_{Cl}*$ and the experimental value of $\Delta\psi$ at the highest concentration. Third, if the value of $l_{Na}*/l_K*$ calculated is equal to l_{Na}/l_K, the assumption $l_K* = l_{Cl}*$ may be considered to be valid. For the present system, introducing $\Delta\psi = +5.5$ mV and $l_K* = l_{Cl}*$ into Eqn. 6, we have $l_{Na}*/l_K* = 0.61_4$ (therefore $l_{Cl}*/l_{Na}* = 1.6_3$). This value of $l_{Na}*/l_K*$ is near the value $l_{Na}/l_K = 0.68_2$, and therefore the above working hypothesis may be correct. Thus, unlike collodion and modified collodion membranes, two interactions between the lens capsule and the co-ion, and between the lens capsule and the counter-ion, can be expressed by approximately the same factor, and the effect of the interaction might be cancelled out if we took the ratio of mobilities of the co-ion and the counter-ion.

From the superimposition technique, θ was calculated to be $2.5_8 \cdot 10^{-3}$ M for the KCl–lens capsule 11–NaCl system. In Fig. 2, experimental data are plotted (×) and the theoretical curve (solid line) fits experimental data well except at the highest dilution.

For LiCl–C-HPSS–NaCl, LiCl–lens capsule 12–NaCl, HCl–C-HPSS–NaCl and HCl–lens capsule 30–NaCl systems, the parameters of ionic mobility and effective charge density were determined following the method described in the KCl–membrane–NaCl system.

For C-HPSS membrane, $l_{Na}*/l_{Li}*$ (1.2_2) and $l_{Na}*/l_H*$ (0.22) were close to l_{Na}/l_{Li} (1.3_0) and l_{Na}/l_H (0.14), respectively, but the values for $l_{Cl}*/l_{Na}*$ (0.91 for LiCl–C-HPSS–NaCl and 0.23 for HCl–C-HPSS–NaCl) were greatly different from l_{Cl}/l_{Na} (1.47). These findings were similar in the KCl–C-HPSS–NaCl system.

For lens capsules, $l_{Cl}*/l_{Na}* = 1.63$ was assumed. $l_{Na}*/l_{Li}*$ (1.3_2) and $l_{Na}*/l_H*$ (0.14) agreed well with l_{Na}/l_{Li} (1.32) and l_{Na}/l_H (0.14), respectively. This good agreement might suggest that the working hypothesis and discussion with respect to the KCl–lens capsule–NaCl system are correct.

Experimental values of the bi-ionic potential for the LiCl–membrane–NaCl and

HCl–membrane–NaCl systems are plotted in Fig. 3 and Fig. 4, respectively, using θ obtained by superimposition. The experimental data fitted the theoretical curves (solid lines) calculated from Eqn. 3 for the LiCl–C-HPSS–NaCl (Fig. 3), LiCl–lens capsule 12–NaCl (Fig. 3) and HCl–C-HPSS–NaCl (Fig. 4) systems. But in the case of the HCl–lens capsule 30–NaCl system, the coincidence of the theoretical curve (solid line) and experimental data (×) was not good (Fig. 4). As the lens capsule is mainly composed of a collagenous protein, the state of dissociation of the membrane might change and therefore the real charge density X might change from concentration to concentration. In the range of $C/\theta < 1$, the deviation owing to the change of X clearly occurred. (But this discrepancy does not seem to arise totally from the change of X; the discrepancy might partly be the same as that which appeared at the highest dilution in the case of the KCl–lens capsule 11–NaCl system).

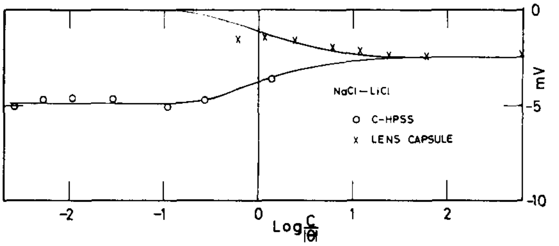


Fig. 3. Plots of bi-ionic potentials against *log* C/|θ| for LiCl(C)–lens capsule 12–NaCl(C) (C = 0.001–0.5 M) and LiCl(C)–C-HPSS–NaCl (C = 0.001–0.5 M) and LiCl(C)–C-HPSS–NaCl (C = 0.001–0.5 M) indicated × and ○, respectively, where $\theta = 1.5_9 \cdot 10^{-3}$ M and $\theta = -36_4 \cdot 10^{-3}$ M are used, respectively. Solid lines represent theoretical curves calculated from Eqn. 3 with $l_{Na}^*/l_{Li}^* = 1.3_2$ and $l_{Cl}^*/l_{Na}^* = 1.6_3$ for lens capsule 12 and with $l_{Na}^*/l_{Li}^* = 1.2_2$ and $l_{Cl}^*/l_{Na}^* = 0.91$ for C-HPSS.

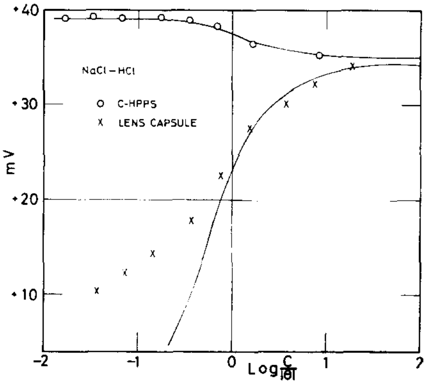


Fig. 4. Plots of bi-ionic potentials against *log* C/|θ| for HCl(C)–lens capsule 30–NaCl(C) (C = 0.001–0.5 M) and HCl(C)–C-HPSS–NaCl(C) (C = 0.001–0.5 M) indicated × and ○, respectively, where $\theta = 25._1 \cdot 10^{-3}$ M and $\theta = -61._7 \cdot 10^{-3}$ M are used, respectively. Solid lines represent theoretical curves calculated from Eqn. 3 with $l_{Na}^*/l_H^* = 0.14$ and $l_{Cl}^*/l_{Na}^* = 1.6_3$ for lens capsule 30 and with $l_{Na}^*/l_H^* = 0.22$ and $l_{Cl}^*/l_{Na}^* = 0.23$ for C-HPSS.

MA_1 ($NaNO_3$ or NaBr) (C)–membrane ($\theta > 0$)–NaCl (C)

Introducing two limiting values at $C \gg \theta$ and $C \ll \theta$ into Eqns. 10 and 11, respectively, we determined two parameters, $l_{Cl}^*/l_{A_1}^*$ and l_{Cl}^*/l_{Na}^*, simultaneously. For $NaNO_3$–lens capsule 23–NaCl, $l_{Cl}^*/l_{NO_3}^*$ (1.0_1) and l_{Cl}^*/l_{Na}^* (1.3_4) were close to l_{Cl}/l_{NO_3} (1.07) and l_{Cl}/l_{Na} (1.47), respectively. For NaBr–lens capsule 28–NaCl, l_{Cl}^*/l_{Br}^* (0.93) was very close to l_{Cl}/l_{Br} (0.98), but l_{Cl}^*/l_{Na}^* (3.8_2) was different from l_{Cl}/l_{Na} (1.47). As absolute values of these bi-ionic potentials were small and a small change in the bi-ionic potential provoked a large change in l_{Cl}^*/l_{Na}^*, the experimental error of l_{Cl}^*/l_{Na}^* for the NaBr–lens capsule 28–NaCl system should be considered. Furthermore the order of $l_{Cl}^* > l_{Na}^*$ obtained was the same as the order in bulk solution ($l_{\mathrm{Cl}} > l_{\mathrm{Na}}$). (But for M_1A–collodion-based membranes–M_2A systems, $l_{\mathrm{Cl}}^* < l_{\mathrm{Na}}^*$.)

From the facts observed in the present systems that two parameters of ionic mobility in the lens capsule determined without any working assumption had approximately equal values in bulk solution, the working hypothesis adopted in the M_1A–lens capsule–M_2A systems is suggested to be correct.

Experimental values of bi-ionic potentials are plotted in Fig. 5. (ό, $NaNO_3$–lens capsule 23–NaCl; ○, NaBr–lens capsule 28–NaCl) and theoretical curves based on Eqn. 8 fit experimental data well.

M_1A ($CaCl_2$, $MgCl_2$, $SrCl_2$, $BaCl_2$ or $LaCl_3$) (C_1)–membrane ($\theta > 0$)–NaCl (C_2)

The ratio C_2/C_1 was set constant so that the common ion concentration in in Solutions I and II were equal. In these systems $d\bar{C}_A/dX = 0$ is shown to be satisfied with a maximum error of 10 % (15 % for the $LaCl_3$-membrane ($\theta > 0$)–NaCl system) in the APPENDIX.

Again we met the difficulty which appeared in the KCl–membrane ($\theta > 0$)–NaCl system in determining the two parameters of ionic mobility from Eqns. 5 and 6 without ambiguity. For the lens capsule the interaction between the co-ion and the membrane was assumed not to be characteristic in the multi-univalent electrolyte–membrane ($\theta > 0$)–NaCl system. This assumption was shown to be valid in systems of two uni–univalent electrolytes–lens capsules, collodion and modified collodion membranes. Introducing the value of the bi-ionic potential at the highest concentration and the assumption that $l_{\mathrm{Na}}^*/l_{\mathrm{M_1}}^* = l_{\mathrm{Na}}/l_{\mathrm{M_1}}$ (Na and M_1 are both co-ions) into Eqn. 6, we obtained another parameter, $l_{\mathrm{Cl}}^*/l_{\mathrm{Na}}^*$. The values of $l_{\mathrm{Cl}}^*/l_{\mathrm{Na}}^*$ obtained are listed in Table I and were different from $l_{\mathrm{Cl}}/l_{\mathrm{Na}}$, although for systems of two uni–univalent electrolytes and lens capsules, $l_{\mathrm{Cl}}^*/l_{\mathrm{Na}}^* \doteqdot l_{\mathrm{Cl}}/l_{\mathrm{Na}}$ and $l_{\mathrm{Na}}^*/l_{\mathrm{M_1}}^* \doteqdot l_{\mathrm{Na}}/l_{\mathrm{M_1}}$. Therefore, the validity of the assumption made here was not clear. (Inversely,

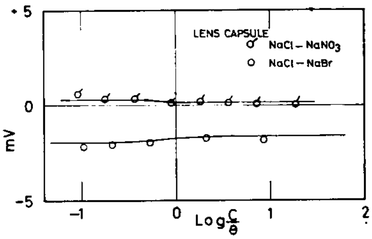


Fig. 5. Plots of bi-ionic potentials against *log* C/θ for $NaNO_3$(C)–lens capsule 23–NaCl(C) (C = 0.0005–0.1 M) and for NaBr(C)–lens capsule 28–NaCl(C) (C = 0.0005–0.04 M) indicated ό and ○, respectively, where $\theta = 5.3_8 \cdot 10^{-3}$ M and $\theta = 4.6_8 \cdot 10^{-3}$ M are used, respectively. Solid lines represent theoretical curves calculated from Eqn. 8 with $l_{\mathrm{Cl}}^*/l_{\mathrm{NO_3}}^* = 1.0_1$ and $l_{\mathrm{Cl}}^*/l_{\mathrm{Na}}^* = 1.34$ for $NaNO_3$–lens capsule 23–NaCl and with $l_{\mathrm{Cl}}^*/l_{\mathrm{Br}}^* = 0.93$ and $l_{\mathrm{Cl}}^*/l_{\mathrm{Na}}^* = 3.8_2$ for NaBr–lens capsule 28–NaCl.

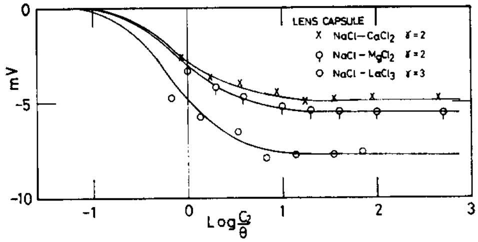


Fig. 6. Plots of bi-ionic potentials *log* C_2/θ for $CaCl_2(C_1)$–lens capsule 13–$NaCl(C_2)$ (C_2 = 0.001–0.5 M), $MgCl_2(C_1)$–lens capsule 14–$NaCl(C_2)$ (C_2 = 0.001–0.5 M) and $LaCl_3(C_1)$–lens capsule 12–$NaCl(C_2)$ (C_2 = 0.001–0.1 M) indicated ×, ọ and ○, respectively, where $\theta = 1.1_5 \cdot 10^{-3}$ M, $\theta = 1.0_0 \cdot 10^{-3}$ and $\theta = 1.4_5 \cdot 10^{-3}$ M are used, respectively. Solid lines represent theoretical curves calculated from Eqn. 3 with $l_{\mathrm{Na}}^*/l_{\mathrm{Ca}}^* = 1.6_8$ and $l_{\mathrm{Cl}}^*/l_{\mathrm{Na}}^* = 1.0_3$ for $CaCl_2$–NaCl system, with $l_{\mathrm{Na}}^*/l_{\mathrm{Mg}}^* = 1.8_9$ and $l_{\mathrm{Cl}}^*/l_{\mathrm{Na}}^* = 1.1_5$ for $MgCl_2$–NaCl system and with $l_{\mathrm{Na}}^*/l_{\mathrm{La}}^* = 2.1_6$ and $l_{\mathrm{Cl}}^*/l_{\mathrm{Na}}^* = 0.5_8$ for $LaCl_3$–NaCl system.

introducing the value of the bi-ionic potential at the highest concentration and $l_{Cl}^*/l_{Na}^* = 1.63$ using the same method as for the KCl–lens capsule–NaCl system, we could not find an answer for $l_{Na}^*/l_{M_1}^*$.) The interaction between the univalent counter-nion and the lens capsule when the system had a multivalent co-ion, was found to become more complicated than when the system had uni-univalent electrolytes only. As the method adopted to determine the two parameters of ionic mobilities for the multi-univalent electrolyte–lens capsule–uni-univalent electrolyte system, was arbitrary and as the meanings of these parameters are ambiguous, we need further independent experiments such as isotope experiments to determine the ratio of ionic mobilities. Using these two parameters, we calculated the bi-ionic potential from Eqn. 3 as a function of *log* C_2/θ (solid lines in Fig. 6). Experimental data are also plotted in Fig. 6 and the agreement between theory and experimental data was good. Therefore $d\bar{C}_A/dX = 0$ may be satisfied for these systems including the multivalent ion in the first approximation.

In conclusion, experimental results agreed with theoretical values obtained from the assumption that the common ion concentration is constant throughout the membrane for systems such as KCl(C)–membrane ($\theta > 0$, or $\theta < 0$)–NaCl(C), $NaNO_3$(C)–membrane ($\theta > 0$)–NaCl(C) and $CaCl_2(C_1)$–membrane ($\theta > 0$)–$NaCl(C_2)$ ($C_2/C_1 = 2$) except at the highest dilution. When both electrolytes in solution were uni-univalent, the ratio of ionic mobilities of two counter-ions (or two co-ions) in the lens capsule and in the collodion and modified collodion membranes, had approximately the same value as in bulk solution while the ratio of ionic mobilities of the counter-ion and the co-ion was same in bulk solution for the lens capsule, but different for the collodion and modified collodion membranes. When the system had multivalent ions, the ratio of ionic mobilities in the lens capsule was somewhat ambiguous and requires further study.

APPENDIX

Theoretical reliability of assumptions $d\bar{C}_A/dX = 0$ *and* $d\bar{C}_M/dX = 0$

In the derivation of Eqns. 3 and 8, we have used the assumptions $d\bar{C}_A/dX = 0$ and $d\bar{C}_M/dX = 0$, respectively.

In systems of uni-univalent electrolyte solution (C)–membrane–uni-univalent electrolyte solution (C), two concentrations of the common ion at two phase boundaries in the membrane, $\bar{C}_M^I$ (at $x = 0$) and $\bar{C}_M^{II}$ (at $x = \Delta x$) or $\bar{C}_A^I$ and C_A^{II}, are calculated to be equal from the Donnan equilibrium and the electric neutrality condition, and therefore the total concentration gradient of the common ion across the membrane becomes zero. Considering this evidence, we can assume with high reliability that the concentration of the common ion is constant throughout the membrane phase, *i.e.* $d\bar{C}_M/dX = 0$ or $d\bar{C}_A/dX = 0$ in these systems.

In systems of multi-univalent (or uni-multivalent) electrolyte solution (C_1)–membrane–uni-univalent electrolyte solution (C_2) and $C_2/C_1 =$ constant at which two bulk concentrations of the common ion are provided to be equal, two concentrations of the univalent common ion at two phase boundaries in the membrane are calculated not to be equal. In Fig. 7, $|R$ is represented as a function of *log* $C_2/|\theta|$, where $|R$ is the concentration ratio of the common ion in the membrane at two phase boundaries, *i.e.* $|R = \overline{C}_A$ (at $x = 0$)/$\overline{C}_A$ (at $x = \Delta x$) or $|R = \overline{C}_M$ (at $x = 0$)/$\overline{C}_M$ (at $x = \Delta x$). The solid line represents $|R$ in the system of $CaCl_2(C_1)$-membrane ($\theta > 0$)-$NaCl(C_2)$, $C_2/C_1 = 2$; the broken line represents $|R$ in the system of $LaCl_3(C_1)$-membrane ($\theta > 0$)-$NaCl(C_2)$, $C_2/C_1 = 3$; and the dotted line represents $|R$ in systems of $Na_2SO_4(C_1)$-membrane ($\theta > 0$)-$NaCl(C_2)$, $C_2/C_1 = 2$ and $CaCl_2(C_1)$-membrane ($\theta < 0$)-$NaCl(C_2)$, $C_2/C_1 = 2$. In systems represented by solid line and broken line, $|R$ deviates from unity in the region of $0.1 < C_2/|\theta| < 10$ and its maximum deviations are 10% and 15%, respectively. In these systems, therefore, $d\overline{C}_A/dX = 0$ is considered to be satisfied with maximum errors of 10% and 15%, respectively. But in systems represented by the dotted line, $|R$ diverges systematically from unity as $C_2/|\theta|$ becomes small, and therefore the assumption $d\overline{C}_A/dX = 0$ or $d\overline{C}_M/dX = 0$ cannot be true in the range of $C_2/|\theta| < 10$.

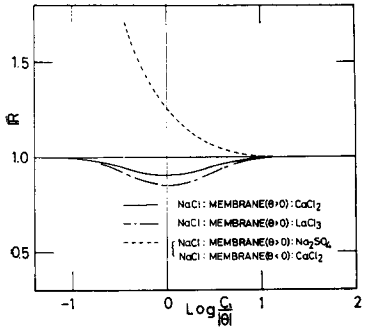


Fig. 7. $|R$ is represented as a function of *log* $C_2/|\theta|$ for various systems, where $|R$ is the concentration ratio of the common ion at two phase boundaries in the membrane, *i.e.* $|R = \overline{C}_A$ (at $x = 0$)/$\overline{C}_A$ (at $x = \Delta x$) or $|R = \overline{C}_M$ (at $x = 0$)/$\overline{C}_M$ (at $x = \Delta x$).

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