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Bi-ionic Potentials in Anion Exchange Membranes

We would like to report some of the recent studies of bi-ionic potentials in anion exchange membranes. The bi-ionic potential (bip) is the membrane potential of a bi-ionic cell containing two electrolytes, MX and MY, separated by a membrane. Interdiffusion of X and Y through the membrane gives rise to the potential which will be more negative in the solution containing the counterion of lower mobility, lower valence, or lower affinity for the membrane. This is true of an anion exchange membrane, and the reverse is true of a cation exchange membrane.

The total bip may be considered in accordance with the concepts of Teorell[1-3] and Meyer and Sieves[4] as being made up of three potentials (two Donnan potentials and one diffusion potential). Assuming the absence of coions and convection in the membrane, Helfferich[5,6] has given a complete mathematical discussion of bi-ionic potentials under conditions of (a) membrane diffusion control, (b) film diffusion control, and (c) coupled membrane and film diffusion control.

In this note, we will present some of the results of the measurement of bip in various quaternary, strong-base, anion exchange membranes. The significance of these measurements will be discussed.

EXPERIMENTAL

All of the vinyl benzyl chloride copolymer and terpolymer were prepared via emulsion polymerization and quaternized with $(CH_3)_3N$ in DMF solution. The quaternary ion exchange membrane was cast from the above polymer in DMF solution. All the anion-exchange membranes are about 1-mil thick and are permselective anion-exchange membranes (permeating anions and rejecting cations).

The bi-ionic cell consisted of two halves of a cell and O-rings. The ion exchange membrane is held between the O-ring partitions and two halves of the cell. Calomel electrodes were inserted into the cell, and the bi-ionic potential was measured with a Leeds and Northrup potentiometer.

RESULTS

Table I shows the bip's between various pairs of ions in three different types of anion exchange membranes. For the same system, the magnitude of the bip's lie in the order of BA/VBC/ST > VBC/ST > AN/VBC/ST. (All polymer abbreviations are described in Table I.) The additive rule[7,8] of bip follows in all three anion exchange membranes, and the sign of bip reflects that the affinity of the anions in all three anion exchange membranes increases in the order $ClO_4^- > NO_3^- > Cl^-$.

TABLE I
Bi-ionic Potentials for Various Anions Paired Across Anion Exchange Membranes

Membrane[a]	System	bip, mv
VBC/ST	0.1*N* KCl/0.1*N* KNO_3	12.2
VBC/ST	0.1*N* KNO_3/0.1*N* $KClO_4$	33.6
VBC/ST	0.1*N* KCl/0.1*N* $KClO_4$	44.0
AN/VBC/ST	0.1*N* KCl/0.1*N* KNO_3	0.3
AN/VBC/ST	0.1*N* KNO_3/0.1*N* $KClO_4$	13.2
AN/VBC/ST	0.1*N* KCl/0.1*N* $KClO_4$	13.9
BA/VBC/ST	0.1*N* KCl/0.1*N* KNO_3	28.1
BA/VBC/ST	0.1*N* KNO_3/0.1*N* $KClO_4$	44.0
BA/VBC/ST	0.1*N* KCl/0.1*N* $KClO_4$	72.0

[a] VBC/ST = Vinyl benzyl chloride/styrene copolymer quaternized with $(CH_3)_3N$; AN/VBC/ST = acrylonitrile/vinyl benzyl chloride/styrene terpolymer quaternized with $(CH_3)_3N$; BA/VBC/ST = butyl acrylate/vinyl benzyl chloride/styrene terpolymer quaternized with $(CH_3)_3N$. All ionic membranes contain about 1.2 meq./gram polymer.

Table II shows the bip of KCl/KI pair ions in an interpolymer type of anion exchange membrane. The higher the charge density of the membrane, the lower is the bip value. This indicates that bip is dependent on the charge density of polymer. The different values of bip in two directions of composite membranes indicate the asymmetric properties of these composite ion exchange membranes. The bip in a composite membrane is also shown between those of individual component membranes.

DISCUSSION

According to Helfferich,[6] the bip can be expressed as

$$E_B{}^A = \frac{RT}{Z_A F} \ln \frac{\overline{D}_A a'_A \overline{\gamma}_B}{\overline{D}_B a''_B \overline{\gamma}_A} \tag{1}$$

where Z_A is the valence of ion A, $\overline{D}_A$, and $\overline{D}_B$ are the diffusion constants of ions A and B in the membrane, a'_A and a''_B are the activity of ions A and B in the solutions in the left and right side of the membrane, and $\overline{\gamma}_A$ and $\overline{\gamma}_B$ are the activity coefficient of ions A and B in the membrane.

The above equation is only valid under the following conditions: (1) bip is membrane-diffusion controlled, (2) relative selectivity and diffusion constant for counterions are constant in the membrane, and (3) counterions are of equal valence. Thus, one can show the additive rule for bip for different sets of counterions for eq. (1).[7]

The additive properties and the magnitude of bip for the combination pairs of ClO_4^-, NO_3^-, and Cl^- in BA/VBC/ST, VBC/ST, and AN/VBC/ST ion exchange membranes indicate that the bip is a membrane diffusion control mechanism instead of film diffusion control. Also, the relative selectivity and diffusion constant for ClO_4^-, NO_3^-, and Cl^- are almost independent of the concentration. If the bip is a liquid film diffusion control, the bip will be primarily determined by the relative diffusion constant of ions in the solutions. In this case, the sign of bip for the pair Cl^-/ClO_4^- will be negative due to the larger diffusion constant for Cl^-. This is contrary to our experimental results. Thus, the relative affinity of counterions in the ion exchange membrane (i.e., the ratio of the activity coefficients) primarily determines the value of bip.

The different values of bip in the various ion exchange membranes also indicate that various ion exchange polymers have different transport properties toward different ions. The composition of polymer in the ion exchange membrane, indeed, is very important in the determination of transport of any particular ion in the membranes.

The charge density of ion exchange membranes is also important in the determination of bip. The higher the charge density of the membrane, in general, the lower is the value of bip.

The anisotropic properties of bip in the composite membrane consisted of different charge density membranes and are consistent with the anisotropic permeation rate for ions observed in this laboratory. It was found that the anisotropic ratio[9] for permeation rate can be as high as 2 in a composite membrane.

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TABLE II
The Bi-ionic Potentials in Composite Anion Exchange Membranes

Membrane[a]	System	bip, mv
A	0.1*N* KCl/0.1*N* KI	73.6
B	0.1*N* KCl/0.1*N* KI	79.6
A/B	0.1*N* KCl/0.1*N* KI	76.3
B/A	0.1*N* KCl/0.1*N* KI	78.5

[a] A = Interpolymer poly(*N*-butylvinylpyridium bromide)/copoly(acrylonitrile/vinylidine chloride 60/40 wt ratio), 20/80 by wt; B = interpolymer poly(N-butylvinylpyridium bromide/copoly(acrylonitrile/vinylidine chloride 60/40 wt ratio), 9/91 by wt; A/B = A and B composite membranes.

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