CHEMISTRY LETTERS, pp.493-496, 1974. Published by the Chemical Society of Japan

A SELECTIVITY STUDY ON THE ION-SELECTIVE ELECTRODE WITH A LIQUID MEMBRANE

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The selectivity coefficient of a liquid ion-exchange membrane, in which an ion-exchange site and counter ions are at almost complete dissociation, was studied by a kind of the bi-ionic membrane potential methods. A limiting selectivity coefficient was introduced as an intrinsic quantity of a pair of counter ions for a given membrane and shown to be consistent with the Sandblom-Eisenman-Walker theory on the relation between the selectivity coefficient and ionic parameters.

The potential of a liquid membrane electrode for a sample solution containing a number of species of univalent ions has been found to obey the following empirical equation[1,2]:

$$E = \text{const.} - (RT/F)\ln(a_i + \sum_j K^{pot}_{i,j}\, a_j) \qquad (1)$$

Here a_i and a_j are activities of a primary ion i and any other ion j. $K^{pot}_{i.j}$ is the potentiometric selectivity coefficient of the ion j over the primary ion. The selectivity coefficient computed by means of Eq.(1), in most cases, was observed to vary with the conditions of a sample solution and an electrode membrane such as the concentrations of the sample solution and of the ion exchanger in the membrane. Such a variation of the selectivity coefficient was described to be due to the changes of the ion-exchange selectivity coefficient with the external solution concentration[2,3] and of the physical properties of the membrane.[4]

This letter preliminarily reports the effect of the change of the ionic composition at the membrane-solution interface on the variation of the selectivity coefficient and proposes the selectivity coefficient intrinsic to a pair of counter ions in the liquid membrane electrode of the complete dissociation type.

Membrane potentials were measured by means of the cell:

SCE | KCl-agar bridge | Solution(') | Liquid membrane | Solution(") | KCl-agar bridge | SCE

Crystal Violet (CV) was used as the ion-exchange site in the membrane. Nitrobenzene was used as the membrane solvent. With the systems containing perchlorate ion, NH_4Cl-agar bridges were used in replacement of KCl-agar bridges. The experimental cell used was a U-shaped glass tube with 12 cm^3 of membrane phase at the bottom and 10 cm^3 of each aqueous solution above. Ionic activities necessary for the evaluation of the selectivity coefficient were obtained from the Kielland's table[5] or the concentration potential measured by using an appropriate liquid membrane. In most experiments, the concentration ranges of the ion exchanger in the membrane and of aqueous solutions were chosen so as not to cause the elution of the ion exchanger into adjacent aqueous solutions. All the membrane potentials were measured by a Takeda Riken Electrometer TR 8651 at room temperature (23±3°C), after the cells had been constructed.

In the case of two counter anions, X and Y, the membrane potential of the cells described above may be expressed by:

$$E_M = (RT/F)\cdot \ln \frac{a_X'' + K_{X,Y}^{pot}\, a_Y''}{a_X' + K_{X,Y}^{pot}\, a_Y'} \qquad (2)$$

Here the symbols (') and (") are used to designate the solutions of both sides of the membrane. The membrane potential E_M is the electric potential difference between the solutions (") and (').

Fig.1 shows the selectivity coefficient $K_{SCN^-,ClO_4^-}^{pot}$ for the bi-ionic system $SCN^-(')-ClO_4^-('')$, in which the membrane (CV·SCN in nitrobenzene) is interposed between NaSCN and $NaClO_4$ solutions of the same concentration. The selectivity coefficient was calculated from the measured potential by the use of Eq.(2) with $a_{ClO_4^-}' = 0$ and $a_{SCN^-}'' = 0$. It is observed that the selectivity coefficient varies with the concentrations of the ion exchanger in the membrane and of the aqueous solutions. However, with the membrane having a given concentration of the exchanger, the selectivity coefficient approaches a limiting value (indicated by the dashed line in the figure) with the increasing concentration of the aqueous solutions. With the solutions having a given concentration of the electrolytes, the selectivity coefficient also tends toward the same limiting value as the exchanger concentration decreases. The deviation of the parenthesized value from the limiting one is presumably due to the incomplete exclusion of the co-ion (sodium ion) from the membrane. Almost similar results were obtained for the bi-ionic systems $NaI-NaClO_4$ and NaI-NaSCN, by the use of the nitrobenzene solutions of CV·I as the liquid ion-exchange membranes.$^{6)}$

The variation of the selectivity coefficient in Fig.1 should be ascribed to a straightforward application of Eq.(2) to the cell systems, without taking account of the change of the ionic composition at the membrane-solution interface. Before the liquid membrane and aqueous solutions are in contact with each other, the solution (') and the membrane contain the same counter ion X, whereas the solution (") contains a different counter ion Y. After the construction of the cell, the ion-exchange occurs between the solution (") and the membrane, and diffusion layer is formed at the interface. Since the change of the ionic composition, caused by the ion-exchange, at the interface will depend on both the concentrations of the solution and of an ion exchanger in the membrane, the selectivity coefficient evaluated without this ion-exchange effect accounted for may show the kind of variation observed here. However, in the situation where the concentration of the solution (") is sufficiently high in comparison with that of the ion exchanger in the membrane, the initial counter ion X in the membrane side of the interface will be mostly replaced by the ion Y and in the aqueous side of the interface the presence of the exchanged ion X is minor and will give only a negligible contribution to the inter-

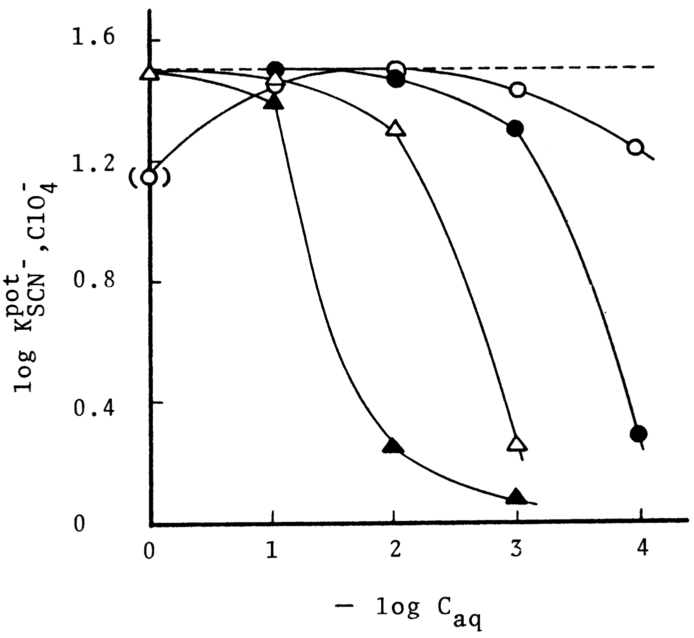

Figure 1. Variation of selectivity coefficient with aqueous solution concentration, C_{aq} (molarity), and exchanger concentration

Membrane:

○ 5 X 10^{-5} M
● 5 X 10^{-4} M
△ 5 X 10^{-3} M
▲ 5 X 10^{-2} M

CV·SCN in nitrobenzene

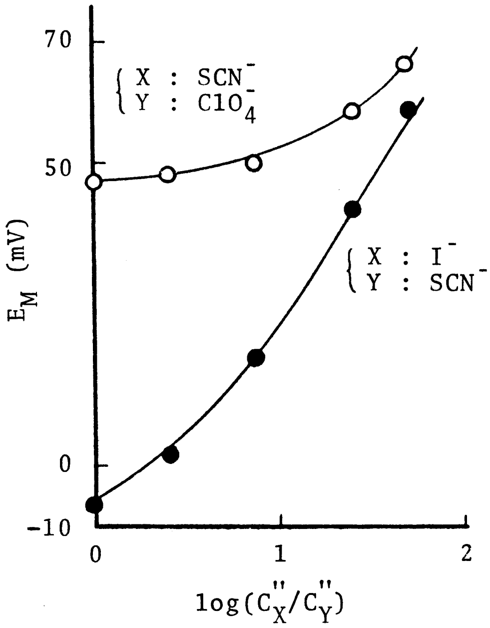

Figure 2. Comparison of experimental potentials with the calculated ones for mixed electrolyte systems

Cell:NaX (C_X') | Membrane | NaX (C_X''), NaY (C_Y'')

$C_X' = 1 \times 10^{-2}$ M

C_X'' = variable, $C_Y'' = 2 \times 10^{-3}$ M

Membrane: 10^{-4}M CV·X in nitrobenzene

facial potential. Eq.(2) with $a_Y' = 0$ and $a_X'' = 0$ should be applied to such a situation of the cell and the limiting value of the selectivity coefficient (limiting selectivity coefficient) is considered to be a parameter correctly describing the properties of the membrane.

The limiting selectivity coefficient will also be applied to mixed electrolyte solutions, in the case where the change of the ionic composition in the interface is expected not to be large at contact of the membrane with the solution. Typical data for the mixed electrolyte systems are shown in Fig.2. The circles represent the observed potential for the mixed solutions containing a pair of counter ions, either SCN^--ClO_4^- or I^--SCN^-. The curves were drawn according to Eq. (2) with the limiting selectivity coefficient values obtained in the corresponding bi-ionic systems. The agreement of the observed potential with the calculated one is seen to be excellent.

Because of the high dielectric constant of nitrobenzene, the degree of ion-pair formation in the membrane, over the exchanger concentration range investigated here, will be small, and virtually negligible at the lower exchanger concentrations.[7)] According to the Sandblom-Eisenman-Walker theory on the membrane potential of the liquid membrane with complete dissociation, the selectivity coefficient between the counter ion species X and Y is given by Eq.(3).[8)]

$$K^{pot}_{X,Y} = \overline{u}_Y k_Y \ / \ \overline{u}_X k_X \qquad (3)$$

where $\overline{u}_X$ and $\overline{u}_Y$ are the mobilities of the ions X and Y in the membrane, and k_X and k_Y are the single-ion partition coefficients between the membrane solvent and water. The value k_Y/k_X was obtained from the square of the ratio of the distribution coefficients of the fuchsin basic salts of the appropriate anions at infinite dilution between nitrobenzene and water. The distribution coefficients of the iodide, perchlorate and thiocyanate salts were observed to be 7.40, 68.1, and 13.1 at 25.0°C, respectively. The values of $\overline{u}_Y/\overline{u}_X$ were obtained from the limiting conductivity data.[9,10] Table 1 presents the comparison between experimental and calculated selectivity coefficients, indicating that the theoretical relation is quantitatively satisfied.

Table 1. Comparison of experimental limiting selectivity coefficients with calculated values

X	Y	$\log K^{pot}_{X,Y}$	
		experimental	calculated
I^-	ClO_4^-	1.96	1.85
SCN^-	ClO_4^-	1.5	1.3
I^-	SCN^-	0.47	0.52

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(Received March 4, 1974)