CHEMISTRY LETTERS, pp. 483-486, 1975. Published by the Chemical Society of Japan

ANOMALOUS RESPONSE OF LIQUID MEMBRANE ELECTRODE BASED ON NEUTRAL CARRIER

Hideaki SETO, Akinori JYO, and Nobuhiko ISHIBASHI*
Department of Applied Analytical Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka 812

The non-Nernstian anomalous response of a neutral carrier-based liquid membrane electrode was studied, and the equation on the membrane potential of the electrode was derived on the basis of the Teorell-Meyer-Sievers theory. The relationship between the anomalous behavior of the electrode and the composition of the electrode membrane was successfully explained by the equation.

Boles et al. have shown that the valinomycin based potassium ion-selective electrode showed anomalous responses, such as a decreased slope of a potential-activity curve and an anion response, for aqueous solutions of potassium salts of large halides, pseudo-halides and most organic anions.1) It has been shown by Morf et al. that such anion interferences could be reduced by incorporating a lipophilic anion, such as tetraphenylborate, into the membrane.2) Both research groups also have treated such an anomalous behavior theoretically. However, the relationship between the anomalousness and the composition of the membrane is not fully clarified. In this study, the dependence of the anomalous response on the composition of the membrane has been examined, and discussed according to the Teorell-Meyer-Sievers (TMS) theory.

Electrode membranes used were an organic solution containing potassium dipicrylaminate and a neutral carrier (NC). As NC, dibenzo-18-crown-6 and polynactin were used.3,4) The concentrations of the dipicrylaminate and NC in the membrane were 10^{-5} - 10^{-4} M and 10^{-4} - 10^{-2} M, respectively. Nitrobenzene (NB), chloroform (CF) and 1,2-dichloroethane (DCE) were used as the solvent of the membrane. A membrane potential was obtained by subtracting the potentials of the reference silver/ silver chloride electrodes from the electromotive force of the following electrochemical cell (1):

$$(-)\ \mathrm{Ag/\ AgCl/\ Sample\ Solution\ ('')/\ Liquid\ Membrane\ (*)/\ Reference\ Solution\ (')/\ AgCl/\ Ag}\ (+) \qquad (1)$$

Activity coefficients of ions were calculated by means of the Debye-Hückel equation with ion size parameters of Kielland.5) The set-up of the cell and the procedure of the potential measurement were described in a previous paper.6) An aqueous solution of potassium chloride was used as reference and sample solutions.

As can be seen in Figs. 1 and 2, the electrodes show the anomalous response at high salt concentration even for the sample solution containing hydrophilic chloride ion. The negative slope of a potential-activity curve was observed on the NB

---

* To whom any correspondence should be addressed.

membrane (Fig. 1). The anomalous response begins at lower salt concentration of the sample solution, on the membrane with higher NC concentration (Fig. 2). It was also observed that the anomalous response began at lower concentration of the sample solution, on the membrane with lower concentration of the dipicrylaminate.

By analyzing the membrane system according to the TMS theory under the following assumptions from (1) to (4),

(1) A monovalent cation forms a 1:1 complex with NC,

(2) An ion-pair of the complex cation with a lipophilic anion (X) or co-ion (Y) dissociates completely in the membrane,

(3) Donnan equilibrium exists between the membrane and each of the outside solutions at the respective boundaries,

(4) A distribution of a lipophilic anion in the membrane is uniform,

the membrane potential, E_M, can be expressed as follows:

$$E_M = \frac{u^*_{is} - u^*_y}{u^*_{is} + u^*_y}\frac{RT}{F}\ln\frac{u^*_{is}C^{*\prime\prime}_{is} + u^*_y(C^{*\prime\prime}_{is} - C^*_x) + u^*_xC^*_x}{u^*_{is}C^{*\prime}_{is} + u^*_y(C^{*\prime}_{is} - C^*_x) + u^*_xC^*_x} + \frac{RT}{F}\ln\frac{a^{\prime\prime}_{is}C^{*\prime}_{is}}{a^{\prime}_{is}C^{*\prime\prime}_{is}} \qquad (2)$$

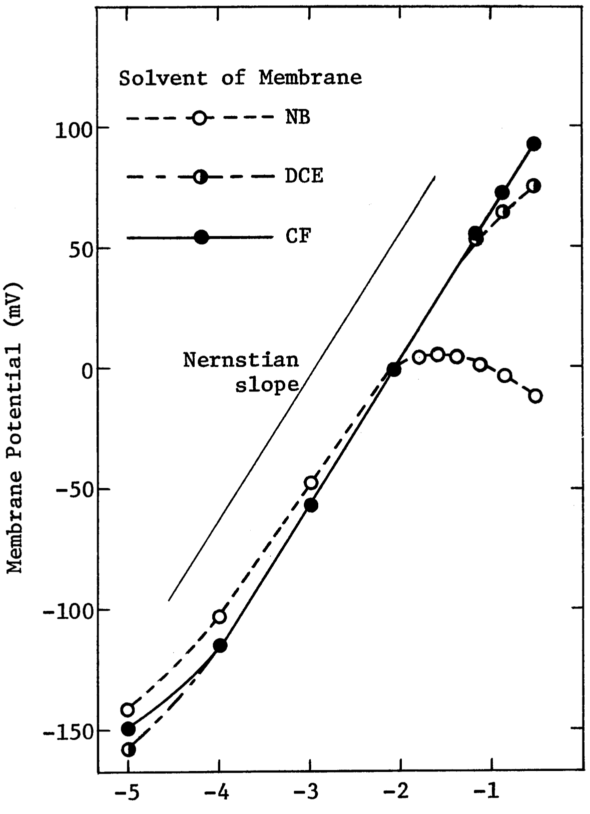

Fig. 1. Responses of electrode membranes with dibenzo-18-crown-6

Membrane: Organic solution of potassium dipicrylaminate(10^{-5}M) and dibenzo-18-crown-6(10^{-2}M), Temp: 28 ± 1 °C.

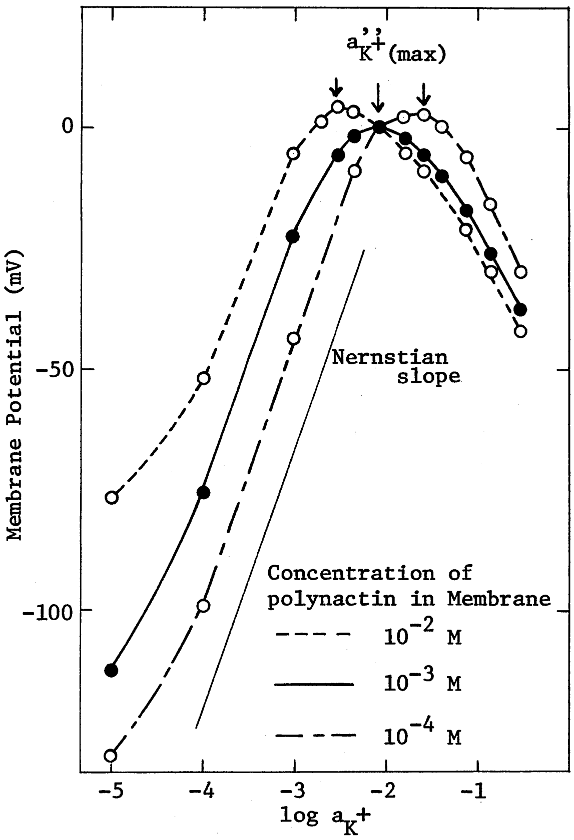

Fig. 2. Responses of electrode membranes with polynactin

Membrane: Potassium dipicrylaminate (10^{-5}M) and polynactin in NB, Temp. 28 ± 1 °C.

where $C^*_{is} = C^*_x/2 + ((C^*_x/2)^2 + k_{is}k_yK_{is}(a_i)^2C_s)^{1/2}$, and $a_{is} = K_{is}a_iC_s$.

At low concentration of the sample solution, the hydrophilic co-ion is completely rejected by the membrane. Thus, $C^{*''}_{is}$ might be equal to C^*_x and also to $C^{*'}_{is}$. Equation (2) is, therefore, simplified:

$$E_M = \text{Const.} + RT/F \ln a_i'' \tag{3}$$

Equation (3) implies that the electrode response for the sample solution should be Nernstian in lower concentration of the sample solution, and this agrees with the experimental results. At higher concentration of the sample solution, however, $C^{*''}_{is}$ can exceed C^*_x owing to the invasion of the sample salt into the membrane from the aqueous sample phase as the ion-pair of the complex cation with the hydrophilic co-ion. In such a case, the electrode response will be no longer Nernstian. The slope of the potential-activity curve might diminish and the maximum potential might be observed. In the extreme case, the potential-activity curve will be expressed by the following equation (4):

$$E_M = \text{Const.} + (u^*_{is} - u^*_y)/(u^*_{is} + u^*_y)\cdot RT/F \ln a_i'' \tag{4}$$

Since the size of the complex cation is generally larger than that of the co-ion, it is reasonably assumed that the mobility of the complex cation may be smaller than that of the co-ion. Thus, Equation (4) implies that the electrode will show an response to the hydrophilic co-ion. These predictions are in good agreement with the experimental results qualitatively, as shown in Fig. 2.

At the maximum potential, the relation, $dE_M/da_i'' = 0$, leads to:

$$a''_{i(max)} = \text{Const.}\cdot(k_s)^{1/2}(k_{is}k_yK_{is}C^*_s)^{-1/2}(C^*_x) \tag{5}$$

where $a''_{i(max)}$ is the activity of the objective cation at the maximum potential. From the mass balance of the neutral carrier species in the membrane, we have

$$C^{*Tot}_s = C^*_s + C^*_{is} \tag{6}$$

As C^*_s is much greater than C^*_{is} in this work, Equation (6) is simplified:

$$C^{*Tot}_s = C^*_s \tag{7}$$

From Equations (5) and (7), the following relation (6) is obtained.

$$a''_{i(max)} = \text{Const.}\cdot(k_s)^{1/2}(k_{is}k_yK_{is}C^{*Tot}_s)^{-1/2}(C^*_x) \tag{8}$$

It is, thus, expected that $a''_{i(max)}$ is proportional to -1/2 power of the total concentration of NC in the membrane, and also proportional to the concentration of the lipophilic anion in the membrane. The results are also in good agreement with this theoretical expectation, as illustrated partly in Fig. 2.

The authors are grateful to Chugai Pharmaceutical Co. Ltd. for a gift of polynactin and for the financial support given to this work by the Ministry of Education (General Research B, Grant No. 847042, 1974).

Notation

i = free cation subscript.
s = neutral carrier subscript.
x = lipophilic anion subscript.
y = co-ion subscript.
is = neutral carrier-cation complex subscript.

a = activity.
C = concentration.
u = mobility.
k = partition coefficient between water and the solvent of the membrane.
K_{is} = stability constant of the complex in an aqueous phase.

$C^{*\prime}_{is}$ = concentration of the complex in the membrane at the reference solution-membrane interface.
$C^{*\prime\prime}_{is}$ = concentration of the complex in the membrane at the sample solution-membrane interface.
C^{*Tot}_{is} = total concentration of the neutral carrier in the membrane.

Asterisk (*) denotes a quantity in the membrane.
Prime (') and double prime ('') denote quantities in reference and sample solutions, respectively.

References

1) J. H. Boles, and R. P. Buck, Anal. Chem., 45, 2057 (1973).
2) W. E. Morf, G. Kahr, and W. Simon, Anal. Lett., 7, 9 (1974).
3) C. J. Pedersen, J. Amer. Chem. Soc., 89, 7017 (1967).
4) It was informed by Chugai Pharmaceutical Co. Ltd. that polynactin was the 1:4:5 mixture of dinactin trinactin and tetranactin.
5) J. Kielland, J. Amer. Chem. Soc., 59, 1675 (1937).
6) N. Ishibashi, and H. Kohara, Anal. Lett., 4, 785 (1971).

(Received April 3, 1975)