The Thermal Membrane Potential as a Function of the Apparent Ionic Transport Number of Membranes

By Toshio IKEDA, Masao TSUCHIYA* and Masaru NAKANO**

(Received April 20, 1964)

Some aspects of the "thermal membrane potential" (TMP) have previously been reported by one of us[1,2] in relation to its general properties and the theoretical basis for it. TMP is an EMF that appears at an ion-selective membrane, M, placed between two identical electrolytic solutions of the same concentration, m, in contact with one another, the two solutions are, however, kept at different temperatures, T and $T+\Delta T$. TMP can be measured by the the following cell system:

$$\underset{T}{\mathrm{Hg/HgCl}},\ \underset{T}{\mathrm{RX}(m)}\ \vdots\ \underset{T+\Delta T}{\mathrm{RX}(m)},\ \underset{T}{\mathrm{HgCl/Hg}} \qquad (1)$$
$$\mathrm{M}$$

where R represents the cation species, and X, the anion species, reversible to the electrodes of insoluble mercurous salt, HgX. On the other hand, the EMF of cell 1, and consequently the TMP, is very sensitive to the ionic permeability of the membrane used. The purpose of the present work is to find experimentally the relation between the EMF or its temperature coefficient (i.e., the thermoelectric power) and the ionic permeability of the membrane used in the cells of type 1, where the apparent ionic transport number of the membrane was adopted to represent the degree of the ionic permselectivity of the membrane.

Experimental

Materials. — GR chemicals were used without further purification in most cases. Ordinary distilled water was used in preparing the solutions. The mercury used for the calomel electrodes was purified by vacuum distillation after making the usual chemical refinements. Mercurous chloride, which was washed in advance by repeated decantation with the same solution of potassium chloride as that used for the meaurements, was used for the preparation of calomel electrodes. A pair of calomel electrodes was prepared after the usual manner in an identical way by the use of the same solution of potassium chloride as that used for the measurements of the TMP. Prior to the use of these calomel electrodes, they were let stand at least for five days in order to age them.

The Preparation of Membranes.—*Cation Permeable Membranes.* — An "oxidized" collodion membrane, according to Gregor and Sollner,[3] is advantageous because of its high cationic selectivity even with low electric resistance. The "oxidized" collodion membranes used in the present work were prepared according to the method found by one of us for getting membranes of graded cationic permeability.[4]

Anion Permeable Membranes. — A weak base-type cellophane matrix membrane of aniline-formaldehyde resin was prepared in the following way. A piece of cellophane membrane was cleaned by washing it with ether and water and was then tied with cotton thread at the end of a beaker cut off at its bottom. The beaker thus provided with a cellophane bottom was immersed in aqueous 1 M aniline hydrochloride, and a 5% aqueous formaldehyde solution acidified with a small amount of hydrochloric acid was placed on the cellophane membrane to let aniline-formaldehyde resin form in the membrane phase by means of diffusion. The most convenient temperature for the practical control of the resin-forming process was about 30°C. After about half an hour the membrane became yellowish orange as the result of the formation of the aniline-formaldehyde polymer. This cellophane

* Present address: Tokyo Metropolitan Isotope Centre, Tokyo.
** Present address: Japan Balqua Ind. Co., Tokyo.

1) T. Ikeda, *J. Chem. Phys.*, **28**, 166 (1958); **31**, 267 (1959).
2) T. Ikeda, *Rep. Liberal Arts Sci. Fac., Shizuoka Univ., Nat. Sci.*, **2**, 237 (1960).
3) H. P. Gregor and K. Sollner, *J. Phys. Chem.*, **50**, 53 (1946).
4) T. Ikeda and K. Tarumoto, *Rep. Liberal Arts Sci. Fac., Shizuoka Univ., Nat. Sci.*, **3**, 109 (1961); **3**, 165 (1962).

polymer matrix was washed with water overnight and stored for ready use in the electrolytic solution to be used for the experiment. Membranes prepared in such a way were found to be permselective to anions, exhibiting an anionic transport number of about 0.9 or less for the chloride ions. On the other hand, the anionic transport number of membranes of this type gradually diminishes down to about 0.6 in about two months when they are stored in aqueous media, presumably because of hydrolysis, but the rate of its change is so slow that this change will not practically disturb measurements that can be performed within a short time (about half an hour). This characteristic is, in a reverse sense, rather convenient for getting a serial run of measurements for different values of transport numbers; the same membrane can even be used if an appropriate interval is allowed for.

Cell System.—The cell system used in the present work was nearly the same as that reported on in a previous paper,[2] but some improvements were made in it. The cell is divided into two symmetrical compartments by a water-tight membrane which was placed between the brims of these two cell parts, sandwiched between two rubber sheets. This cell is suited also for measuring the isothermal membrane potential with the same membrane as was used for measuring the TMP. The cell used in the present work is sketched in Fig. 1. Here,

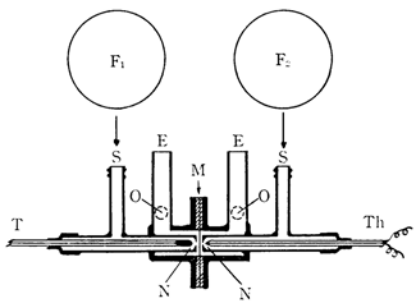

Fig. 1. Cell system.

M is the membrane, N is a fixed nozzle about 1 mm. in diameter at its orifice, S is the inlet for the solution by means of a siphon, and O is the outlet for the solution if it overflows. E is the connection for the terminal calomel electrode. F_1 and F_2 are flasks of about 3 l. which contain identical solutions. F_1 was kept at room temperature, while F_2 was kept in a bath whose temperature was controlled by a weak electric heater. F_2 was provided with an effective reflux condenser. These two solutions, identical but controlled at different temperatures, were let flow from F_1 and F_2 into the respective cell compartments through the respective nozzle, N, by means of polyvinyl chloride tube siphons at a rate above 50 cc./min. (This rate was the lowest limit for producing a stationary value of the EMF of the cell used; the flow rate employed by us was between 50 and 120 cc./min.). The solutions were then let spout against the respective sides of the membrane, M, to produce a clear-cut temperature gradient at the membrane. T is a mercury thermometer with 0.1°C divisions to be used for reading the temperature of the solution of F_1 at the instant immediately before it runs out of the orifice of the left-side nozzle to strike the left side of the membrane. On the other hand, Th is a thermister of the pencil type, which is convenient for reading the instantaneous variation in temperature of the solution of F_2 immediately before it runs out of the orifice of the right-side nozzle to strike the right side of the membrane.

To eliminate the heterogeneous thermocell effect, two calomel electrodes were kept at the same, constant temperature by placing them together in moderately running service water, whose temperature fluctuation did not exceed even ± 0.1°C per hour. TMP is substantially so small that every care must be taken not to introduce stray EMF's such as that coming from the drift of the electrode potentials due to a mechanical shock imposed accidentally upon the calomel electrodes, and such as those due to some thermoelectric effects of any sort which happen to occur in the system.

TMP was measured to a precision down to 0.1 μV. with a Yokogawa P-7-type potentiometer for low-voltage use by the aid of a highly sensitive galvanometer as a zero indicator. Here, we have adopted the convention for marking the EMF of this cell positive when the sign of the hot-side electrode is more positive. The apparent transport number of the membrane was detrermined from the isothermal membrane potentials observed at a concentration ratio of 0.05 M potassium chloride/0.1 M potassium chloride immediately before or after the TMP measurements.

Results and Discussion

The plots of EMF against T are shown in Figs. 2 and 3 for membranes with different degrees of ionic permselectivity. The EMF of cell 1 under the isothermal conditions is not always zero; it differs from run to run, presumably because of the asymmetry of the conditions of the two terminal electrodes. However, as long as such an asymmetric potential maintains itself at a constant value during the measuring run, it will not interfere with the present purpose of determining the thermoelectric power, dE/dT. The EMF, E, of cell 1 was found to be practically linear with the temperature difference, ΔT, and to respond well to the change in temperature of the solutions on either side of the membrane, irrespective of the degree of ionic permselectivity of the membrane used. When the flows of the solution on either side of the membrane were stopped, TMP returned immediately to the original isothermal value, but it promptly recovered its proper value when the flow of the solution was resumed. If these conditions could not be satisfied, the attempt to observe EMF was abandoned as not possible. The other properties were entirely the same

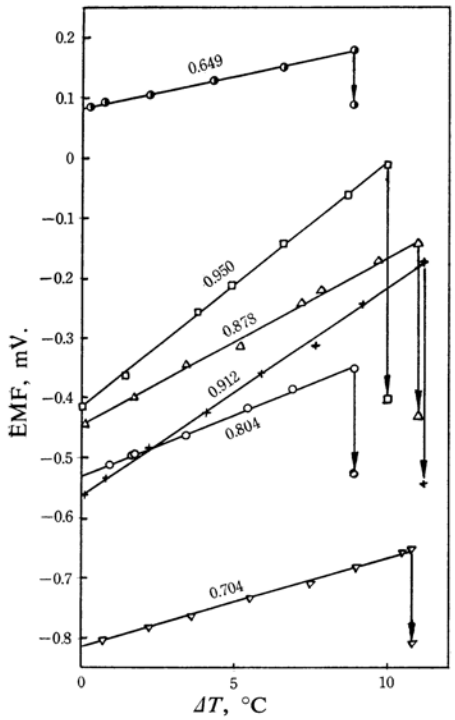

Fig. 2. EMF for oxidized collodion membranes in 0.1 M KCl. Figure attached to each line represents the apparent cationic transport number, t'_+, of the membrane applied. Vertical arrows show the return of potential to the isothermal value on stopping the flow.

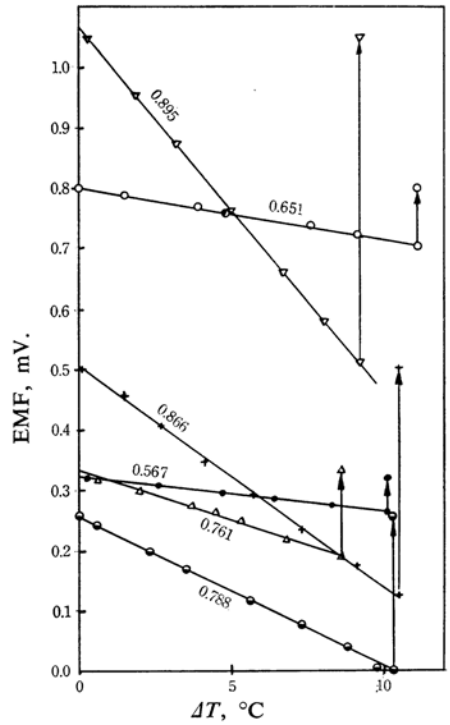

Fig. 3. EMF for aniline-formaldehyde resin-cellophane matrix membranes in 0.1 M KCl. Figure attached to each line represents the apparent anionic transport number, t'_-, of the membrane applied. Vertical arrows show the return of the potential to the isothermal value on stopping the flow.

as those found in previous works,[1,2] so the details are omitted here.

In Figs. 4 and 5 the values of dE/dT were plotted against the apparent ionic transport number, t'_+ or t'_- of the membranes. Here we found that the dE/dT values were characteristic of the nature of the membrane used, with negative signs for positive membranes ($t'_- > 0.5$), and positive signs for negative membranes ($t'_+ > 0.5$). In either negative or positive membranes, the absolute value of dE/dT is reduced practically to zero by the extrapolation at $t'_- = 0.5$ (or at $t'_+ = 0.5$); it gradually increases when the degree of the ionic permselectivity of the membrane is increased, and it precipitously reaches the highest limit characteristic of the nature of the membane at the extreme transport numbers of $t'_- = 1$ (or $t'_+ = 1$). In general, the absolute value of dE/dT for positive membranes was found always to be much higher than that for negative membranes at the equivalent values of the degree of the ion permselectivies of these two membranes.

According to our theory on the TMP,[2] dE/dT should be linear with the apparent transport number, t'_k, of the membrane used,

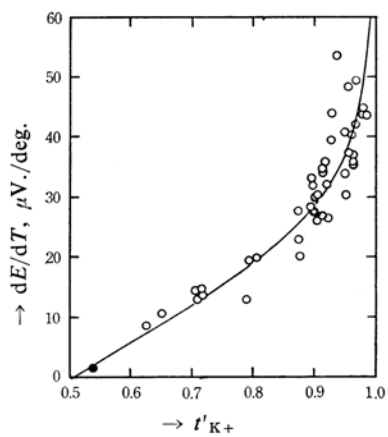

Fig. 4. Relation between thermoelectric power and apparent cationic transport number of oxidized collodion membranes in 0.1 M KCl. Black circle indicates the value for cellophane.

provided that the heats of the transfer of ions in the membrane phase are constant. However, as is clear in Figs. 4 and 5, this is not the case. This fact might indicate that the heats of the transfer of ions in the membrane phase

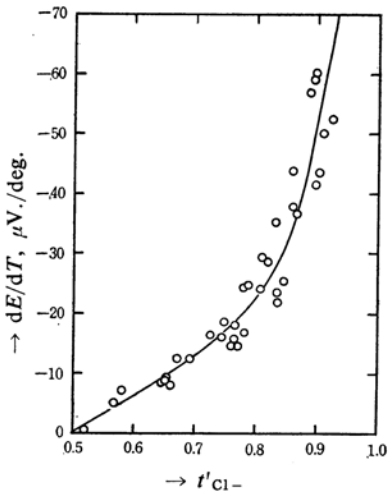

Fig. 5. Relation between thermoelectric power and apparent anionic transport number of aniline-formaldehyde resin-cellophane matrix membranes in 0.1 M KCl.

should be a function of the apparent ionic transport number of that membrane. This conclusion is very plausible; since the heats of the transfer of ions are substantially of a kinetic nature, accordingly the value of ionic heats of transfer in the membrane phase should depend on the membrane structure or on its measure, such as the apparent ionic transport number of the membrane. The relation between the ionic heat of transfer in the membrane phase and the apparent ionic transport number of the membrane has not yet been clarified, but it should be studied.

Summary

The thermal membrane potential (TMP) has been studied as a function of the apparent ionic transport number of ionselective membranes. The temperature coefficient of TMP, the thermoelectric power, has been found to be a continuously increasing function of the apparent ionic transport number of the membranes used, starting from zero at the neutral point, where the membrane exhibits no selectivity for ions, and approaching with acceleration when the ionic transport number of the membrane is increased until it reaches its highest limit at the perfect ion permselectivity. The sign of the thermoelectric power has been found to be positive for negative membranes, and negative for positive membranes. The absolute value of the thermoelectric power is higher for positive membranes than for negative membranes at equivalent degrees of ion permselectivity.

Department of Chemistry
Shizuoka University
Oiwa, Shizuoka