Table 5 is compiled from results for dipole–elastic relaxation in the same polymers. These data introduce nothing fundamentally new, but merely confirm the general principle that elongation of the side-chain by an increase in size of the alkyl group shortens the relaxation time for the dipole–elastic process. This effect can be partly compensated by the introduction of a polar group, *e.g.* a CCl dipole, into the side-chain.

The higher values of tan δ_{max} for PVA and PCVP can be explained by a decrease in dipole correlation within the chain, since the effective dipole moment calculated from values of the dielectric permeability corresponding to the dipole–elastic region of relaxation (according to the cyclic diagrams) is greater for PVA than for PMA.

The value of the distribution parameter α for relaxation times of dipole–elastic processes is considerably higher than analogous values for dipole–radical processes, and may approach unity, as in the case of PVB at 30°. This is common to all polymers, and can be interpreted as evidence that a polymer has a more homogeneous structure in the rubberlike state.

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Institute of Macromolecular Compounds,
Academy of Sciences of the USSR

ELECTRODE PROPERTIES OF ION-EXCHANGE MEMBRANES

E. A. Materova and F. A. Belinskaya

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I. INTRODUCTION

During recent years a large number of papers have appeared both in our own country and abroad on the theory and practical application of membranes made of ion-exchange materials. Such membranes can find wide use as indicator electrodes in potentiometric analysis, as well as in various processes of electrodialysis.

The study of ion-exchange membranes had already begun in the previous century. It was then discovered accidentally that, during the separation of electrolyte solutions by some plant and animal membranes, a potential difference is produced at the membrane–solution boundary. These membranes were termed "semipermeable" or "selective" membranes, since they allowed some substances to pass through and prevented others from doing so. Since then, the electrochemical properties of selective membranes have been studied by biologists and physical chemists [1-10].

Work on the glass electrode has assisted the development of the electrochemistry of semipermeable membranes and their use as electrodes. The study of the electrode and ion-exchange properties of glass membranes and the successful application of the glass electrode to the determination of pH gave an impetus to the production of reversible electrodes made of other ion-exchange materials. For this purpose use was made of various minerals, clays, collodion, cellulose, and other substances capable in various degrees of exchanging ions. Since 1949 ion-exchange resins have come to be used for the preparation

of selective membranes, and of electrodes which are reversible with respect to a large number of cations and anions.

The present review discusses work on the theory of membrane potentials and the use of ion-exchange membranes made of mineral and organic exchangers as reversible electrodes with special emphasis on membranes made of ion-exchange resins, which are the most promising for practical application.

II. THEORIES OF MEMBRANE POTENTIALS

The first serious attempt at a theory of membrane processes was made by Michaelis[9,10] who visualised a membrane as a capillary structure penetrated by pores of various diameters. Owing to the unequal sizes of pores, molecules, and ions, the membrane acts as a sieve, stopping some ions and molecules and allowing others to pass through. The smaller the pores the greater is the part played by fields of force due to electrical charge, adhesion, and surface tension at the pore surfaces. The most important is the field due to the electric charge produced by the adsorption of ions on the pore walls, forming an electrical double layer which affects the mobility of the ions in the pores of the membrane.

The magnitude of the e.m.f. arising at the boundary between two electrolyte solutions separated by a membrane is expressed by Michaelis by an equation analogous to that deduced by Nernst for the diffusion potential between two electrolyte solutions

$$E = \frac{U_c - U_a}{U_c + U_a} \frac{RT}{ZF} \ln \frac{C_1}{C_2} , \qquad (1)$$

$$E = \frac{RT}{ZF} \ln \frac{U_{c_1} + U_a}{U_{c_2} + U_a} . \qquad (2)$$

Eqn. (1) relates to the case in which the membrane separates solutions of the same electrolyte at concentrations C_1 and C_2. Eqn. (2) is valid for the case in which the membrane separates solutions of different electrolytes at the same concentration (the electrolytes have the same anions but different cations).

In Eqns. (1) and (2) the symbols U_c and U_a denote the mobilities of cation and anion in the membrane, which are assumed to be independent of the concentration. From Eqn. (1) the ratio of the mobilities of cation and anion in the membrane can be calculated, and from Eqn. (2) the mobility ratio for two cations in the membrane if the mobility of the anion is put equal to zero.

The Michaelis theory played an important part in the electrochemistry of membrane phenomena. However, its fundamental equations (1) and (2) are approximate and the theory takes no account of interaction between solutes and the membrane material. The main concept of this theory – the link between the capillary and the electrical properties of membranes – has been further developed in papers by foreign and especially by Soviet scientists. The school of I.I. Zhukov at Leningrad University has carried out a large programme of work on the electrochemical properties of capillary systems, mainly membranes used in electrodialysis[11].

An important contribution to the electrochemistry of membrane processes taking into account their ion-exchange nature was made by the theory of fixed charges put forward independently by Teorell[12,13] and by Meyer and Sievers[14,15]. This theory is based on the view that organic membranes contain a number of dissociating ion-exchange groups, for example carboxyl or amino groups, which are strongly bound to the macromolecule. The immobile, fixed charges resulting from dissociation of these groups are balanced by an equivalent quantity of free, mobile ions of opposite sign. At the membrane–solution interface a Donnan equilibrium is established corresponding to the condition:

$$y(y + A) = C^2 , \qquad (3)$$

where y is the concentration of electrolyte which has penetrated into the membrane, and is equal to the concentration of ions of the electrolyte having the same sign as the fixed ions; A is the concentration of fixed ions in the membrane, expressed as the number of ionised groups per unit volume of water contained in the pores of the membrane; C is the concentration of electrolyte in the external solution; and $(y + A)$ is the concentration in the membrane of ions of opposite charge to the fixed ions.

The Donnan equilibrium results in the establishment at the membrane–solution interface of a potential termed the "Donnan potential":

$$E_{\text{Don}} = \frac{RT}{F} \ln \frac{C}{y + A} . \qquad (4)$$

The authors of the theory of fixed charges deduced an equation for the potential of a membrane separating two solutions of a uni-univalent electrolyte at concentrations C_1 and C_2. They assumed the electrolyte solution to be completely dissociated and ideal both inside and outside the membrane, and the concentration of fixed ions in the membrane to be constant. They regard the potential of the membrane as the sum of two Donnan potentials at the membrane–solution interfaces and a diffusion potential within the membrane. Expressing this last potential by means of the Henderson equation, they give the following expression for the concentration membrane potential:

$$E = E_{1\text{Don}} - E_{2\text{Don}} + E_{\text{diff}} = \frac{RT}{F} \left[u \ln \frac{x_2 + Au}{x_1 + Au} + {}^1/_2 \ln \frac{(x_1 + A)(x_2 - A)}{(x_1 - A)(x_2 + A)} \right],$$
$$u = \frac{U_c - U_a}{U_c + U_a}, \quad x = \sqrt{4C^2 + A^2} . \qquad (5)$$

The subscripts 1 and 2 relate here to two solutions having concentrations C_1 and C_2. From the point of view of the theory of fixed charges, the main characteristics of the membranes are the quantity A, which the authors term the "selectivity constant", and the ratio of the mobilities of cation and anion in the membrane (U_c/U_a). Both characteristics are assumed to be independent of the concentration of the solutions. Meyer and Sievers[14,15] suggested a graphical method for calculating A and (U_c/U_a) from the dependence of the membrane potential on the concentration of the solution. If the selectivity constant or the concentration of fixed ions $A \ll C_1$ and C_2, it can be neglected in Eqn. (5), which simplifies to

$$E = \frac{U_c - U_a}{U_c + U_a} \frac{RT}{F} \ln \frac{C_2}{C_1} . \qquad (6)$$

Eqn. (6) is the equation for the diffusion potential. If $A \gg C_1$ and C_2, Eqn. (5) yields the usual Nernst expression for the e.m.f. of a concentration cell:

$$E = \frac{RT}{F} \ln \frac{C_2}{C_1} . \qquad (7)$$

This last equation corresponds to the case in which the membrane is permeable only to ions of one sign, and can be regarded as an electrode which is reversible with respect to these ions.

Thus the concentration of fixed ions is important when it is comparable with the concentration of the external solution. When $C \gg A$, the potential is determined by the ratio of the external concentrations and the ratio of the ionic mobilities in the membrane; when $C \ll A$, only the ratio of external concentrations is significant.

The theory of fixed charges constituted a major advance in understanding the nature of membrane phenomena. It indicated a method for preparing membranes of high electrochemical activity, by showing that the selectivity of the membrane with respect to ions of a given sign is determined primarily by the concentration of dissociated ion-exchange groups in the membrane. However, this theory is approximate in character, and can represent real processes only in the few cases in which A and U_c/U_a remain constant.

Even in the early papers in which the theory of fixed charges was analysed and criticised, it was concluded[16-19] that the theory gives only the qualitative dependence of membrane potentials on concentration. A weakness of the theory is the neglect of the interaction of ions in solution and in the membrane. Meyer and Bernfeld[15] attempted to allow for this interaction by replacing A by the quotient $A/(l_a + l_c)^{\frac{1}{2}}$, where l_a and l_c are the partition coefficients of anions and cations between solution and ion exchanger, *i.e.* the actual ratio of the ionic activity coefficients in the external solution and in the membrane.

Marshall[20] replaced ionic concentrations in Eqn.(5) by activities in the external solutions and in the membrane. Instead of the quantity A he used the concept of the mean activity of the mobile ions inside the membrane, the charge on which was balanced by that on the fixed ions in the membrane. Manecke and Bonhoeffer[21,22] also employed the concept of a mean activity coefficient of the mobile ions in the membrane ($f_\pm$), and expressed the Donnan equilibrium by the equation

$$a^2 = C_+C_-f_\pm^2 = C_-(C_- - A)\times f_\pm^2 \ , \qquad (8)$$

where a is the mean activity of the electrolyte in the solution, C_+ and C_- are the concentrations of mobile ions in the membrane, and A is the concentration of fixed ions.

The development of synthetic ion-exchange resins provided ample opportunities for the preparation of ion-exchange membranes having a high concentration of fixed ions (with a large exchange capacity). Such membranes were used to test the Teorell–Meyer–Sievers theory more rigorously. This test could be carried out by comparing values of A and U_c/U_a given by the Meyer–Sievers graphical method with the same quantities determined by other methods (A analytically, U_c/U_a by a radioactive tracer method).

Bonhoeffer *et al.*[23,24] tested the applicability of the theory of fixed charges to resins of different acid strengths. They showed that the theory is consistent with the behaviour of a strongly acid cation exchanger, but in the cases of a weakly acidic cation exchanger and a weakly basic anion exchanger, one of the chief premises of the theory – the constancy of A – is not satisfied. These workers considered that this was due to the change in swelling properties and in the number of dissociated groups in the membrane with variation in the pH.

Helfferich[25] studied the variation of A with concentration for a strongly basic anion exchanger, and concluded that this quantity cannot be regarded as constant even after the introduction of corrections ($f_\pm$ or l), especially at high concentrations. Direct determinations of ionic mobilities in the membrane showed that these vary little with concentration, so that the divergence between theory and experiment can be explained primarily by different types of complicated ionic interactions within the membrane, which depend substantially on concentration.

Summarising the discussion of the theory of fixed charges, we can say that this theory is only qualitatively or, in a few cases, semi-quantitatively consistent with experiment. In spite of all the corrections and refinements which several workers have tried to introduce into the equation for membrane potentials, no rigorous calculation can be made of the e.m.f. of cells containing different types of membranes and different electrolytes. Membrane processes are in general very complicated. A theoretical consideration of these processes must take account of the transfer of solvent (the swelling properties of the exchanger), interaction between ions in solution and with the material of the membrane, and also kinetic factors in the exchange and transport of ions.

The fundamental assumptions of the theory of fixed charges were developed and refined during 1951–1953 by Teorell[26-28] in his extended theory of fixed charges. He tried to consider the various properties of charged and neutral membranes, with and without a current passing through them, from a single viewpoint. Great attention was paid to mass transfer through membranes and to related processes. Teorell analysed these phenomena by applying to such processes the Nernst–Planck equation describing the distribution of ions in the case of free diffusion of univalent ions:

$$\Phi' = -U'C'\left(\frac{RT}{C'}\frac{dC'}{dx} \pm F\frac{d\varphi}{dx}\right) , \qquad (9)$$

where Φ' is the flux, *i.e.* the quantity of ions of a given type entering the membrane through unit surface in unit time, U' is the mobility of cation or anion, C' is the concentration of ions of the given type within the membrane, x is a space co-ordinate in the direction of motion of the ions through the membrane, φ is a potential depending on x, R is the gas constant, F the Faraday (positive for cations, negative for anions), and T the absolute temperature. By applying Eqn.(9) to various membrane processes, Teorell deduced a series of equations for calculating the conductivity, the spatial distribution of ions in the membrane, the potential, etc. In the generalised theory too, he considered the membrane potential to be the sum of two Donnan potentials and a diffusion potential, this last being calculated on the basis of a Planck distribution.

Teorell's generalised equation for membrane potential, like any equation containing a diffusion potential, can be approximately solved only for particular cases – when the membrane separates (1) two solutions of the same electrolyte at different activities, and (2) solutions of two different electrolytes of the same activity. The generalisation made by Teorell describes complex membrane phenomena and their interplay, and is therefore a fruitful approach. However, the value of his general equations is limited by the fact that they can be solved only in the simplest cases.

A theoretical examination of membrane phenomena has been made also in a series of papers by Schlögl and his

collaborators[29-35]. In these, membrane processes are regarded as non-equilibrium or, under certain conditions, as steady-state processes. Schlögl's work is mainly devoted to an investigation of charged membranes carrying a current, the diffusion of ions through a membrane, and the determination of membrane potentials and ionic mobilities in a membrane. Like Toerell, he uses the Nernst–Planck equation (9) for the ionic flux to calculate the diffusion potential within the membrane.

According to Schlögl, the membrane potential is the sum of a diffusion potential within the membrane and two Donnan potentials at the two phase boundaries:

$$E = \frac{RT}{F}\int_{I}^{II}\frac{U_-C_- - U_+C_+}{U_-C_- + U_+C_+}d\ln a + \frac{RT}{2F}\ln\frac{f_-^{I}f_+^{II}}{f_+^{I}f_-^{II}} \quad , \qquad (10)$$

where U and C are the mobilities and concentrations respectively of ions inside the membrane, a is the activity of the external electrolyte solution, and f_+ and f_- are the ionic activity coefficients of the external solution.

The last term in Eqn.(10) contains the activity coefficients of individual ions, which cannot be determined experimentally. However, in combination with appropriate terms which must appear in a real cell owing to the auxiliary electrodes, the last term does give measurable quantities. Eqn.(10) is based on the same Teorell–Meyer–Sievers ideas, but it takes account of the interaction between the ions and with the material of the membrane. In order to integrate Eqn.(10) the dependence of U_+C_+ and U_-C_- on the external concentrations must be known. In some cases this dependence can be evaluated experimentally, for example by a radioactive tracer method[29].

Membrane potentials are considered from rather different standpoints in papers by the Japanese investigators Nagasawa and Kobatake[36,37], in which the potentials of collodion, regenerated cellulose film, and parchment membranes, and of the glass electrode are discussed on the basis of Eyring's theory of reaction rates. The equation derived by Kobatake and Nagasawa for the membrane potential is

$$E = \frac{RT}{F}\left[d\ln\left(\frac{c_1}{c_2}\right) - \alpha\ln\left(\frac{c_1+\beta}{c_2+\beta}\right) + \left(\frac{U_+-U_-}{U_++U_-}\right)\ln\frac{c_1+\beta}{c_2+\beta}\right], \qquad (11)$$

where c_1 and c_2 are the concentrations of the electrolyte solutions separated by the membrane, α and β are constants depending on the nature of the membrane and the ionic mobilities, and U_+ and U_- are respectively the mobilities of cation and anion in the membrane.

With a small charge on the membrane and in concentrated solutions Eqn.(11) simplifies to the usual equation for the diffusion potential, analogous to Eqn.(6). In dilute solutions and for dense membranes Eqn.(11) can be written in the form

$$E = \alpha\frac{RT}{F}\ln\frac{c_1}{c_2} \quad , \qquad (12)$$

where α is a function of the charge and the ionic mobilities in the membrane. For a glass electrode and membranes of ideal selectivity, $\alpha = 1$.

In 1953 Scatchard[38] published a paper in which membrane potentials were regarded from the viewpoint of the general thermodynamic relationships for the e.m.f.'s of voltaic cells with transport. His equation for the e.m.f. of a voltaic cell containing a membrane is

$$E\left(\frac{F}{RT}\right) = E_{0\alpha}\frac{F}{RT} - \sum_i \nu_{i\alpha}d\ln a_{i\alpha} - \int_{\alpha}^{\omega}\sum t_{i\alpha}d\ln a_i - \qquad (13)$$

$$- \sum_i \nu_{i\omega}\ln a_{i\omega} - E_{0\omega}\frac{F}{RT} \quad ,$$

where $E_{0\alpha}$ and $E_{0\omega}$ are the standard potentials of the two electrodes, $\nu_{i\alpha}$ and $\nu_{i\omega}$ are the numbers of moles of the i-th species formed at the corresponding electrodes by the passage of one Faraday, a_i is the activity of the i-th species, and t_i is the number of moles of substance i transported in the direction of the positive current by the passage of one Faraday.

The integral contains various transport numbers (t_i) of ions and neutral molecules, in particular of solvent molecules. Scatchard applies the general thermodynamic equation (13) to several cases, and makes careful allowance for the transport of solvent, which, like that of anions through a cation-exchange membrane, may lead to departures of the membrane from ideal behaviour. He examines the influence of hydrolysis (*i.e.* partial replacement of cations in a cation exchanger by hydrogen ions, and of anions in an anion exchanger by hydroxyl ions), diffusion, and other processes on the e.m.f. of a voltaic cell containing a membrane. He considers from the same viewpoint the bi-ionic potential, *i.e.* the potential difference obtained by separating solutions of two different electrolytes by means of an ion-exchange membrane. Scatchard comments that the Teorell–Meyer–Sievers method – division of the potential into two Donnan potentials and a diffusion potential – provides no opportunity for separating the main terms from the correction terms in the expression for the e.m.f. of a cell with a membrane, and that neglect of the transport of water, which in several cases is of considerable importance, is a shortcoming of previous theories. The transport of water was allowed for also in papers by Stewart and Graydon[39,40]. The equation which they derived for the membrane potential can be obtained by integrating Eqn.(13) under simplifying conditions.

A completely different approach to the electrical properties of semipermeable membranes was made by Staverman and Overbeek[41-44], who showed that in general membrane processes not far from thermodynamic equilibrium can be described by non-equilibrium thermodynamics, which is based on two principles – a linear law for the rate of approach of the system to a state of equilibrium, and Onsager's reciprocal relation. Investigations in which non-equilibrium thermodynamics is employed to explain membrane phenomena are still few[44-47], but definite progress may be expected from theories based on these ideas.

Work carried out in the Department of Physical Chemistry of Leningrad University on the electrode properties of ion-exchange membranes in pure and in mixed electrolyte solutions has used the ideas of Nikol'skii's ion-exchange theory of the glass electrode[48]. According to this theory, the electrode behaviour of a glass, as well as of an ion-exchange resin, which is selective to ions of one sign, depends on the composition of the solution and on the strength of bonding of the ions with the solid phase. This effect is determined by the magnitude of the equilibrium

constant (exchange constant K) for the exchange of A^+ and B^+ ions between the solid phase (s) and the solution (l):

$$B_l^+ + A_s^+ \rightleftarrows A_l^+ + B_s^+ , \qquad (14)$$

$$K = \frac{a_{A+l} \times a_{B+s}}{a_{A+s} \times a_{B+l}} .$$

The magnitude of the exchange constant defines the selectivity of the ion-exchange electrode with respect to one of the exchangeable ions. According to the ion--exchange theory, the electrode potential relative to a reference, *e.g.* calomel, electrode can be represented by the equation:

$$E = E^\circ + \frac{2.3RT}{ZF} \log(a_{A^+} + K a_{B^+}) , \qquad (15)$$

where a_{A^+} and a_{B^+} are the activities of A^+ and B^+ ions respectively in the solution. Belinskaya and Materova[49,50] have shown that, in spite of their substantial difference in physical and chemical properties, glass and organic ion--exchange resins possess similar electrode properties, since their electrode behaviour is governed by the exchange of ions between solid phase and solution. Thus it has been shown for resins of different acid strengths that the ability of the acidic group to undergo dissociation determines the selectivity towards hydrogen ions of electrodes made of these ion exchangers. The same is observed also with glasses having different exchange constants for hydrogen and metal ions[48]. This similarity confirms the applicability of the ideas of the ion-exchange theory of the glass electrode to resin membrane electrodes having ideal selectivity.

III. ELECTRODE PROPERTIES OF ION-EXCHANGE MEMBRANES

1. Mineral Membranes

In this section we shall discuss mineral membranes, which, like glass electrodes, may possess various electrode functions. The early workers in this field used various aluminosilicate minerals capable of ion exchange. Thus, for example, Tendeloo[51-53] chose the minerals muscovite and fluorite, and Marshall[54] selected apophyllite and chabazite. Such an electrode was prepared by attaching a polished plate of the mineral to a glass tube and soaking it in a solution of an appropriate electrolyte ($CaCl_2$, $BaCl_2$, KCl, etc.). These mineral membrane electrodes proved unsatisfactory. They had high resistances, and only roughly responded to a change in concentration of the corresponding cation. The use of clay materials for the preparation of electrodes seemed more promising. In 1941 Marshall and Bergman[20] worked out a method for preparing membranes from the colloidal fraction of electrodialysed clays (montmorillonite, beidellite). A suspension of the clay was poured on to a smooth surface and dried. The resulting film was attached to a glass tube, and an electrolyte solution of known concentration was poured over it. Such electrodes were investigated by measuring the e.m.f. of the following cell:

$$Hg \mid Hg_2Cl_2,\ KCl\ (sat.) \mid soln. \mid membrane \mid soln. \mid KCl\ (sat.),\ Hg_2Cl_2 \mid Hg .$$

The measured value was compared with the e.m.f. calculated from the Nernst equation, in which concentrations had been replaced by the activities of the cations in the two solutions†:

$$E = \frac{RT}{ZF} \ln \frac{a'_+}{a''_+} . \qquad (16)$$

Marshall and his coworkers, and later Bose *et al.*, showed that clay mineral electrodes can be used to determine the activities of the following ions in pure dilute electrolyte solutions – K^+,[20,55] NH_4^+,[56] Na^+,[56,57] Mg^{2+},[55,58] Ca^{2+},[59,60] Mn^{2+},[61] Co^{2+},[61] Cu^{2+},[61] and Zn^{2+}.[61]

These workers applied to the experimental results the fundamental principles of the Teorell–Meyer–Sievers theory of fixed charges as modified by Marshall[62] to allow for the peculiarities of clay films.

Marshall's work showed that the electrode properties of clay membranes depend on the temperature to which the membranes have been heated, the nature of the clay, and the exchange cation. Heat-treatment (400°–600°) improves the mechanical properties of membranes, makes them more compact, and increases the charge per unit volume[57,63,64]. With the hydrogen form of montmorillonite, heat-treatment changes the selective properties of the membranes. Thus membranes heated above 450° are selective only towards singly charged ions, which enables the activity of such ions to be determined in the presence of ions carrying a double charge. The hydrogen form of montmorillonite heated at a lower temperature (up to 350°) is selective towards both types of ions. Membranes prepared from the potassium or the calcium form of montmorillonite are sensitive to both univalent and bivalent ions independently of the temperature of heat-treatment. Beidellite membranes react to a change in concentration of ions bearing one, two, or three charges.

Marshall proposed a method for determining ionic activities in mixed solutions based on the selective properties discovered in clay membranes[57-60,65-67]. The technique worked out for determining the activities of various ions was applied to the investigation of colloidal solutions and to obtaining titration curves for various clays[68-76].

Mineral electrodes possess several substantial defects, which limit their practical application. They have a high electrical resistance and low chemical and mechanical stability, and they act as reversible electrodes only within a very narrow range of concentrations, usually from 0.1–0.01 to 0.0001 N solutions for univalent cations, and from 0.01 to 0.0001 N for bivalent cations.

In 1948 Wyllie[77] was able to prepare membrane electrodes from fragments of shales. Such electrodes extended the range over which the electrode e.m.f. follows the change in sodium ion concentration roughly to 1 M NaCl.

2. Membranes Based on Some Organic Substances

Organic substances such as collodion, cellulose, proteins, etc. all possess weakly acidic or weakly basic properties and are able to exchange ions.

Collodion membranes were first studied in detail by Michaelis[9,10]. The so-called dried collodion membranes which he prepared, when placed between two different

† Activity coefficients of the individual ions were calculated on the assumption that $f_{K^+} = f_{Cl^-}$.

electrolyte solutions, give potentials close to the theoretical values, *i.e.* to those calculated from the Nernst equation for the potential of a reversible electrode.

A great deal of knowledge on the various properties of collodion and protamine membranes has been obtained by Sollner and his coworkers[78-80]. They have described methods for the preparation of the membranes[81-86], membrane potentials in various electrolyte solutions[87-90], the resistance of the membranes[91-93], and the Donnan membrane equilibrium[18,78,94,95].

Sollner's work has shown that oxidised collodion can yield membranes possessing a low resistance (from a few down to one hundredth ohm cm^{-2}) and giving potentials in dilute solutions (< 0.1 M) which are close to the theoretical values. According to his results[80], the selectivity of collodion membranes is maintained in K_2SO_4 solutions up to a concentration (on the two sides of the membrane) of 0.2/0.1 *N*, while in KCl this limit is at 0.04/0.02 *N*, in LiCl 0.02/0.01 *N*, and in HCl 0.004/0.01 *N*. In more concentrated solutions the membranes begin to lose their selectivity towards the cation and allow anions to pass through in considerable quantities.

Collodion membranes impregnated with protamine possess anion-exchange properties. Their selectivity towards anions is somewhat less than that of oxidised collodion membranes towards cations.

Sollner ascribes the appearance of potentials on collodion membranes to the presence in the matrix of the membrane of active groups capable of dissociating, *e.g.* carboxyl groups[78,80,96]. In his opinion the electrochemical activity is determined by the exchange capacity of the membrane. Collodion differs from substances which are normally called ion exchangers only in the small number of groups capable of dissociation.

Sollner and his coworkers were the first to suggest the use of collodion membranes as electrodes for measuring the activity of cations – K^+, Li^+,[93,97,98] Na^+, NH_4^+, Mg^{2+},[93,97] Ca^{2+}, Rb^+, Cs^+.[78,80] In Sollner's opinion, protamine membranes can be used as electrodes reversible with respect to anions – BO_3^-, I^-;[93] R^-, Cl^-, ClO_3^-, ClO_4^-, NO_3^-, IO_3^-; and $CH_3.COO^-$.[95-98]

Collodion membranes were successfully used by Carr[99-101] to determine the activity of calcium, sodium, and chloride ions in protein solutions. In 1953 Shafershtein and Bulgakova[102] reported the use of oxidised collodion membranes to determine the activity of potassium and sodium ions in protein solutions. They concluded that the membranes could not be used at pH < 4.5. They suppose that at low pH values the dissociation of carboxyl groups is suppressed and the surface charge on the membrane is thereby decreased, the membrane itself becoming permeable to anions. The pH value of 4.5 mentioned by Shafershtein and Bulgakova can apparently be regarded, by analogy with the behaviour of resins having feebly acid groups[49], as a limit down to which hydrogen ions do not affect the potential of a membrane functioning as a metal.

Hirsch[103-105] has studied the effect of pH on the potentials of membranes made of oxidised cellulose film and of cellulose with a constant ratio of the salt concentration on the two sides of the membrane (0.03/0.003 M KCl or NaCl). Hirsch correctly attempts to find a link between the rise in potential with increase in pH and the exchange properties of the membrane material. However, the method proposed for calculating the dissociation constant of the acidic groups of the membranes from the curves relating membrane potential and pH cannot be regarded as correct, since the membrane potential is determined not only by the pH but also by the activity of the metallic ions.

3. Membranes Made of Ion-Exchange Resins

Ion-exchange membranes can be of two types depending on the methods of preparation – (1) homogeneous, consisting solely of the ion-exchange material, and (2) heterogeneous, which contain an inert binder in addition to the ion exchanger.

Homogeneous membranes are usually obtained in the synthesis of the resin, by completing resinification in special moulds. To confer mechanical strength on them, the membranes are sometimes poured on to various supports, networks of non-conducting inert materials. Homogeneous membranes have been prepared from strongly acid cation exchangers[106-113], weakly acid cation exchangers[114-116], strongly basic anion exchangers[21,25,116,117], and weakly basic anion exchangers[118].

Heterogeneous membranes can in principle be prepared from any resins by varying the nature of the binder and the resin content of the membrane. Among substances which can be employed as binders are polystyrene, poly(methyl methacrylate), polyethylene, poly(vinyl chloride), paraffin wax, collodion, rubber, various cements, etc.

Several methods exist for preparing heterogeneous membranes: (1) compressing[118] a mixture of the finely powdered resin and binder under pressure[110,119-131]; (2) milling an inert binder with the powdered resin[110,132-135]; (3) casting the membranes from solution or from a melt of the binder containing the powdered ion-exchange resin[49,128,136-141] or a polyelectrolyte type of material[80,137,142]; (4) treatment of inert membranes with the aim of conferring ion-exchange properties on them by adsorption, *e.g.* of dissolved sulphonated polystyrene with collodion[80,137,142], the sulphonation of polystyrene[135,143], etc.‡; (5) binding the swollen resin with Portland cement[119]. Descriptions of the methods for preparing various homogeneous and heterogeneous membranes can be found also in several review papers[144,145] and monographs[146-149].

Homogeneous membranes will obviously possess a lower resistance than non-homogeneous membranes prepared from the same resin. On the other hand, the mechanical strength of the latter is greater, since a wide selection of binders of great strength is available for their preparation, and the resin content of the membrane can be varied. Extensive information on the physical properties of membranes, mainly used in electrodialysis, is given in papers by Winger *et al.*[150], Trostyanskaya[133], Spiegler[110], and Osborn[149].

The first papers on the electrode properties of ion-exchange resin membranes appeared during 1949–1950. Kressman and Kitchener[120,151], Juda and McRae[152], and Wyllie and Patnode[121] described methods for making resin membranes and discussed the possibility of using such membranes as reversible electrodes for activity measurements in electrolyte solutions.

The materials chosen for investigation were cation exchangers possessing a considerable exchange cpacity or

‡ Membranes obtained by this method may be regarded as either homogeneous or non-homogeneous.

a high concentration of fixed ions. These resins should, according to the Teorell–Meyer–Sievers theory, ensure that the membranes are highly selective towards cations. Wyllie and Patnode[121] made a detailed study of the electrode properties of Amberlite IR-1, Zeocarb, and Amberlite IR-100 membranes in NaCl solutions (the membranes were prepared by pressing a mixture of the powdered resin and polystyrene or methyl methacrylate). Although these workers measured the membrane potentials by means of voltaic cells with transport, for which no exact calculation can be made of the theoretical e.m.f. values, the measured membrane potentials confirmed the high selectivity of the membranes, which was maintained up to a comparatively high concentration of NaCl. Such results have not been obtained with any of the mineral or clay membranes studied up to the present. The simplicity of preparation, high electrochemical activity (selectivity towards anions or cations), comparatively low resistance, and the mechanical strength of resin electrodes have attracted the attention of many investigators.

During recent years resin membranes have been used as reversible electrodes to determine the activity of various electrolytes. Papers in which ion-exchange resin electrodes have been studied are listed, for convenience of classification, in the Table.

TABLE. Papers on the electrode properties of ion-exchange resin membranes.

Electrode function	Electrolyte	Reference	Electrode function	Electrolyte	Reference
H^+	HCl	42,121,124,128,137, 142,143,154–157	NH_4^+	NH_4OH NH_4Cl $(NH_4)_2SO_4$	153 154 154
	H_2SO_4, H_3PO_4	154,155,156	Li^+	LiCl	124,126,156
	HNO_3	155	Ag^+	$AgNO_3$	156
	β-naphthol-sulphonic acid	154	Ca^{2+}	$CaCl_2$	126,156
			Mg^{2+}	$MgCl_2$	126
Na^+	NaCl	42,109,111,121,123, 124,128,153,154,156, 158,159,160	Ba^{2+}	$BaCl_2$	111,124,131,153,162
			Zn^{2+}	$ZnSO_4$	164
	Na_2SO_4	123,156,158	Cd^{2+}	$CdCl_2$ $CdSO_4$	124 164
	$NaNO_3$ Na_2SO_4 CH_3COONa $C_7H_5O_3Na$	158	Cu^{2+}	$CuSO_4$	124
			Mn^{2+}	$MnSO_4$	164
			Cl^-	NaCl	122,127,155,156
	sodium poly (vinyl sulphate)	158		KCl HCl	127,141,145,148,155
	sodium polyacrylate	161		$BaCl_2$ $MgCl_2$	155 127
K^+	KCl	21,111,115,123, 137,139,140,142,154, 156,157,162	Br^-	KBr	129
			NO_3^-	KNO_3	129
			CH_3COO^-	CH_3COONa	155
	K_2SO_4 $K_4Fe(CN)_6$	154 154	SO_4^{2-}	H_2SO_4 Na_2SO_4	128 122,127
	potassium polyacrylate	161		K_2SO_4 $MgSO_4$	127 127
			PO_4^{3-}	$NaHPO_4$ H_3PO_4	127 127

Special mention must be made of the work of Bergin and Heyn[163], which showed that cation-exchange membranes can be used to measure the activity of (NH_4^+) cations in alcoholic and aqueous–alcoholic solutions. In addition, measurements of membrane potentials have been made in several researches having quite different aims – determination of ionic transport numbers through the membrane from the e.m.f. of a voltaic cell[108,116–168], determination of concentration of fixed ions by the Meyer–Sievers graphical method[23,24], and determination of the selectivity characteristics of membranes[120,138,150,167]. Information about the electrode properties of membranes can be obtained also from the results in these papers.

The following methods are used to measure the activity or concentration in pure electrolyte solutions by means of membrane electrodes:

a) Calculation from theoretical equation. For this purpose we set up a voltaic cell without transport, of the type

$$\mathrm{Ag}\,|\,\mathrm{AgCl},\quad \underset{a_1}{MCl_n}\,|\,\text{membrane}\,|\,\underset{a_2}{MCl_n},\quad \mathrm{AgCl}\,|\,\mathrm{Ag}, \qquad \text{(I)}$$

where $n = 1, 2, \ldots$; or a cell with transport

$$\mathrm{Hg}\,|\,Hg_2Cl_2, \mathrm{KCl\ (saturated)}\,|\,M_mX_n\,|\,\text{membrane}\,|\,M_mX_n\,|\,\mathrm{KCl\ (saturated)}, Hg_2Cl_2\,|\,\mathrm{Hg}. \qquad \text{(II)}$$

From the measured e.m.f. and the known activity of one of the solutions, the unknown activity is calculated using the equation for the appropriate voltaic cell:

$$E_I = \frac{\nu RT}{ZF} 2.3 \log \frac{a_{\pm}^{(2)}}{a_{\pm}^{(1)}}, \qquad (17)$$

or

$$E_{II} = E_{II}^0 + \frac{RT}{ZF} 2.3 \log a_i \approx E_{II}^0 + \frac{RT}{ZF} 2.3 \log a_{\pm}, \qquad (18)$$

where E_{II}^0 is a constant term in the e.m.f. of the voltaic cell, ν the number of ions into which a molecule of the electrolyte dissociates, Z the valency of the cation with respect to which the membrane is reversible, $a_{\pm}$ the mean activity of the electrolyte, and a_i the activity of the ion with respect to which the membrane is reversible.

The use of voltaic cells without transport enables the determination of activity to be thermodynamically more rigorous than that of cells with transport.

b) Calculation from calibration curve. If the electrode behaviour of the membrane is not theoretical, activities can be determined by means of a calibration curve obtained with solutions of known activity, as is done, for example, in work with glass electrodes.

c) Titration to zero membrane potential. In a voltaic cell of type I or II (having two identical auxiliary electrodes) the membrane is used to separate the electrolyte solution of unknown concentration from a definite quantity of water (or of a dilute solution of the electrolyte of known concentration). To the water is then added a standard, more concentrated solution of the same electrolyte until the e.m.f. becomes zero. The unknown concentration can be calculated from the volume of the standard solution used in the titration.

d) Potentiometric titration. This can be an acid–base or a precipitation titration, the ion-exchange resin electrodes serving as indicator electrodes reversible with respect to cations or to anions.

Such indicator electrodes have been widely used by Sinha [122,130] and later by Parsons [169] for the titration of hydrochloric acid with caustic soda, of sodium chloride with silver nitrate, potassium sulphate with barium chloride and barium acetate [122,130], and sodium sulphate and sulphuric acid with barium acetate [169].

In the first method the activity can be calculated only with membranes whose electrode behaviour is theoretical. Such membranes have been obtained from many strongly acidic resins [21,42,121,142,153,154,156,157,165] and from some feebly acidic resins containing carboxyl groups [42,123,156]. The other three methods are applicable both to electrodes which behave theoretically and those whose behaviour diverges somewhat from the theoretical.

The range of concentrations over which membrane electrodes can be used in pure electrolyte solutions depends on the nature of the membrane and of the electrolyte. At very low and high electrolyte concentrations there are departures from the linear relation between the potential of the membrane electrode and the logarithm of the mean electrolyte activity. According to the data of Schindewolf and Bonhoeffer [153] and of Kressman [154] deviations in dilute solutions begin at concentrations of $5 \times 10^{-4}-10^{-5}$ M, and are explained by the chemical instability of the material of the vessels used for the potential measurements. In concentrated solutions the potential differs from the theoretical value for all membranes [109,114,137,153,154,156]. The electrode behaviour of cation-exchange resin membranes is maintained up to higher concentrations in solutions of acids than in salt solutions – HCl up to 1–4 M, [153-156] H_2SO_4 up to pH = 0 [154] and 4.48 M, [156] and H_3PO_4 up to pH = 0.[156] With electrodes reversible with respect to doubly charged ions the range within which a linear relationship between E and $\log a_{\pm}$ is obeyed is smaller in uni-bivalent electrolytes [126,131,153] than in uni-univalent electrolytes.

The anionic behaviour of resin membranes has been less thoroughly studied than their cationic behaviour. Available results indicate that the membranes function as electrodes up to higher concentrations in solutions of uni-bivalent electrolytes than in those of uni-univalent electrolytes.

Deviations of the membrane potential from the theoretical value corresponding to the equation for the e.m.f. of a concentration cell with reversible electrodes may be primarily determined, at high electrolyte concentrations, by diffusion of the ion of the same sign as the membrane (Donnan sorption) and by transport of the solvent.

The behaviour of membrane electrodes in mixed electrolyte solutions is of great interest, but there are few papers on this topic, and they are almost all concerned with electrodes made of strongly acidic resins. Thus Manecke [21] investigated the behaviour of membranes made of a phenolsulphonic cation-exchange resin in mixed solutions of sodium and potassium chlorides, and concluded that such membranes are not specific with respect to the individual cations, their use requiring preliminary calibration of the electrodes in mixed solutions of known concentration.

Schindewolf and Bonhoeffer [153] have shown that the potentials of sodium electrodes based on a phenolsulphonic cation-exchange resin, with sodium chloride concentrations on the two sides of the membrane of $10^{-2}\,N/10^{-3}\,N$, are independent of pH only within the pH range 5–8. In a study of the electrode behaviour of sodium membranes from a sulphonated cation-exchange resin, Kressman [154], found the membrane potentials in 0.01 M sodium chloride solution to be independent of the hydrogen-ion concentration over the range pH 4–10. In the case of hydrogen membrane electrodes he showed [154] that the potassium ion affects the membrane potential when its concentration exceeds that of the hydrogen ions by a factor of 2.5. Kressman is inclined to explain the observed slight selectivity of sulphonated cation-exchange resin membranes towards the hydrogen ion by the greater mobility of the latter in the membrane as compared with the potassium and sodium ions.

Kahlweit [157] used membrane electrodes made of a phenolsulphonic resin to study the effect of additions of various acids on the activity coefficients of hydrochloric acid, and of additions of salts on those of potassium chloride. In isolated cases he obtained results close to published values, *e.g.* for the $HCl-HClO_4$ system.

Thus sulphonated resin electrodes exhibit no appreciable selectivity towards any cations. To obtain specific electrodes it was of interest to investigate the electrode behaviour of membranes made of selective resins.

Woerman *et al.* [138] studied the electrode properties of a resin which was selective towards potassium ions, owing to the presence in the resin of groups able to form a sparingly soluble compound with such ions. Electrodes made of this resin did not, however, exhibit the expected selectivity towards potassium ions. This was explained by the stable bonding of these ions making it possible for other ions to diffuse into the membrane. This conclusion was supported by independent measurements of the mobilities of potassium and sodium ions in the membrane. Since these results were obtained with only one resin, and no data were given for the behaviour of the membrane in pure solutions, the conclusions in this paper cannot be generalised to other possible cases of selective membrane electrodes.

More positive results are given in papers on the electrode properties of membranes made of resins containing active groups of different acid strengths [49,50]. Membranes from weakly acidic resins were shown to possess considerable selectivity towards hydrogen ions compared with sodium ions. Within certain limits, electrodes made of these resins enable pH measurements to be made in solutions of complicated composition. The ion-exchange character of membrane electrodes and their analogy with glass electrodes suggest that, with a correct choice of resin, electrodes might be obtained having the same high selectivity towards individual ions as that possessed, for example, by the glass electrode. The problem of increasing the selectivity of resin electrodes is bound up with the synthesis of special resins and with a detailed study of ionic mobilities in the resin phase. The production of selective electrodes will permit the solution of many practical problems of potentiometric pH control and of the determination of ionic activities in mixed electrolyte solutions.

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Department of Physical Chemistry,
Leningrad State University