THE ELECTROCHEMICAL PROPERTIES OF AN ION-EXCHANGE MEMBRANE

DISSERTATION

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I. INTRODUCTION

Membranes are important in physical and biological chemistry due to their two-fold character. 1. They are barriers which selectively influence the transportation and exchange of the various molecular and ionic species contained in solutions in the two compartments which are separated by the membrane. 2. Since they are barriers they act as physicochemical machines which regulate the flow of energy in processes which occur across their thickness. In doing this, they transform various forms of energy into others; for instance, osmotic energy into electrical energy. The study of membranes and their role in living matter is thus a broad field with many facets. The paper which follows will be limited to only one of the many membrane types,--the ion-exchange membrane.

Ion exchange membranes form a special class in the much larger general field of membranes and their activities. Membranes of ion exchange character have been under investigation by physical chemists and biochemists for many decades. During this time practically all the fundamental electrochemical membrane phenomena were thought to have been described and explained. After the ion exchange nature of the membranes was realized new work was started based on the true fundamental physical mechanism. It was some years, however, before membranes were prepared from commercial type ion exchange materials. Study of membranes of this material has made it apparent that these materials in turn form a special sub-class in the larger class of ion-exchange membranes.

The literature contains much information concerning the possible or probable role of membranes in many in vivo processes which involve electrolytes. The experimental data in this field are in an extremely unsatisfactory state, primarily because of the formerly prevailing lack of adequate membranes (1). Ion exchange resins, because of their high charge density per unit area and their low inherent porosity, are a very promising material for the preparation of permselective membranes which will overcome the difficulties of the past. Such membranes may be expected to have a high capacity and a very low resistance; that is, a very high permeability for the critical ions.

Wyllie and Patnode (2) used ion-exchange membranes as an electrode for the determination of electromotive force produced by a concentration cell. This use is analogous to the use of the glass electrode for the measurement of H^+ activity. In the investigation to be reported in the present paper Amberplex C-1 membrane will be used as an electrode in order to determine the electromotive force developed by a concentration cell of various monovalent and divalent cations free from foreign agents, and also in the presence of a protein. From these measurements may be calculated the relative activities of the cations under the experimental conditions.

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(1) Sollner, K., Annals of the New York Academy of Sciences, 57, Art. 3, 177-203 (1953)

(2) Wyllie, M. R. J. and Patnode, H. W., Journal of Physical and Colloid Chemistry, 54, 204 (1950)

This research represents a continuation of extensive previous researches on permselective membranes of biological origin, of clay, and of collodian.

The results may help to clarify ion-exchange reactions in addition to obtaining information concerning the behavior of various ions, and to determine the usefullness of C-1 membrane material as an ideal membrane. It was hoped as well to further the possibility of developing a specialized electrode which in turn might contribute to a more complete understanding of membranes in general and, more specifically of biological membranes.

II. REVIEW OF LITERATURE

The Origin and Early Development of Ideas Concerning the Action of Ion-Exchange

The treatment of water by natural ion exchange materials is mentioned as long ago as the time of ancient Greece (3) when sand filters were used for the purification of sea water. Clays were studied by Sir Humphry Davy (3) and others in the early nineteenth century as a means of removing components of manure liquors.

Although Liebig, Fuchs (4) and others also made observations of the exchange abilities of soils, it is generally conceeded that Thompson (5) and Way (6), two English Agricultural chemists, were the first to recognize the ion-exchange phenomenon. Between the years 1848 and 1854, Thompson and Way observed the following:

1. Certain clays would exchange calcium for ammonium ions when treated with ammonium sulfate or ammonium carbonate.
2. An equivalent amount of calcium was released for the ammonium ions exchanged.
3. Some ions were not exchanged as easily as others.

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(3) Patten, H. E., and Waggaman, C., U. S. Department Agriculture Bureau of Soils, Bulletin 52 (1908)

(4) Liebig, J. van, American Chem. Pharm., 94,373, (1855)

(5) Thompson, H. S., Journal of the Royal Agriculture Society of England, 11, 58 (1850)

(6) Way, J. T., Journal of the Royal Agricultural Society of England, 11,313 (1850)

4. The amount of exchange increased with concentration, reaching a limiting value.
5. The aluminum silicates present in the clays were responsible for the exchange of the ions.
6. The temperature coefficient for the rate of exchange was too low for the exchange to be a true chemical reaction.
7. The ion exchange differed from a true adsorption.
8. Heating the clays destroyed their ability to exchange ions.

Thus, the fundamentals of ion exchange were recognized at the middle of the nineteenth century. Numerous European investigators continued this work but it was almost a quarter of a century later that the next contribution of value was made. Lemberg (7) found that the mineral leucite ($K_2O \cdot Al_2O_3 \cdot 4\ SiO_2$) could be transformed into analcite ($Na_2O \cdot Al_2O_3 \cdot 4\ SiO_2 \cdot 2H_2O$) by washing it with a solution of sodium chloride. He also found that analcite could be transformed into leucite by treating with a solution of leucite. Thus, the reversibility of the exchange process was established.

By the time this milestone had been passed it became apparent that two theories concerning the mechanism of ion exchange had become deeply rooted. One was the original theory of chemical action with the exchange of one ion for a different ion. The other was that of Liebig and his students. This theory maintained that each clay particle was honey-combed with capillaries and the exchange took place in these capillaries and thus was physical in nature.

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(7) Lemberg, E. Z deut. geol. Ges., 28, 519 (1876)

This controversy served to stimulate investigation into the field of ion-exchange. The fruit of these studies by the various investigators established the following important points:

1. The natural mineral complexes of the clays and soils were primarily responsible for their ion-exchange capacities. Thus, the capacities of various clays can vary as widely as the composition.
2. The order of replacement of such ions as calcium, magnesium, ammonium, potassium, and sodium in the soil was determined.

This, then, was the state of knowledge concerning the action of ion exchange at the turn of the century. About this time Gans (8) began his studies and developed the first industrial uses for ion-exchangers. He used both natural and synthetic aluminum silicates for water softening and treating syrups in sugar refineries.

A short time later Wiegner (9, 10) began a series of investigations concerned with the colloid chemistry of ion-exchange. He concluded that each particle of ion-exchange material was surrounded by an electrical double layer similar to that which is used to explain the stability of colloidal solutions. The inner layer next to the ion-exchange particle was composed of adsorbed anions. The outer

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(8) Gans, R., U. S. Patents 914,405 (March 9, 1909)
943,535 (December 14, 1909)
1,131,503 (March 9, 1915)

(9) Wiegner, G., Journal of the Society of Chemical Industry, 50,65-71 (1931)

(10) Wiegner, G., Journal of the Society of Chemical Industry, 50, 105-112 (1931)

layer was a diffuse double layer of cations which were attracted by the negatively charged anions.

About the time Wiegner was reaching his conclusions Pauling (11, 12, 13) and Bragg (14, 15) began publishing their work on the crystal structure of micas and clays. This work showed that these complex minerals, alumino silicates, have a crystal structure of such a type that the SiO_4 and AlO_4 tetrahedra share corners, leaving large "holes" in the crystal structure. This open frame work type of crystal structure combined with relatively low binding energies permit the migration into and out of the structure of both the ions of the solution and the ions of the mineral, providing the two have similar charges. Thus, for the first time ion-exchange theory was on firm ground.

By 1930 a considerable number of materials had been evaluated for their ion exchange properties. Among these were wool, coals, cellulose, horn and various other protein materials. These were found to have ion-exchange properties due to free amino and carboxyl groups (16). But the most significant advance up to this time was the use of sulfonated carbonaceous materials as ion-exchangers (17,18).

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(11) Pauling, L., Journal of the American Chemical Society, 49, 765-790 (1927)

(12) Pauling, L., Nature of the Chemical Bond, Cornell University Press, 1944.

(13) Pauling, L., Proceedings of the National Acadamy of Science, 12, 123 (1930)

(14) Bragg, W. L., Z. Krist., 74, 237 (1930)

(15) Bragg, W. L., Atomic Structure of Minerals, Cornell University Press, 1937

(16) Adams, R. S., Journal of the American Leather Chemists Association, 41,12,552-73 (December 1946)

(17) Broderick, S. J. and Bogard, D. V., U. S. Bureau of Mines Report of Investigations No. 3559 (1941)

(18) Liebknecht, O., U. S. Patent 2,206,007, June 23, 1940

The work of Gans (19) had been carried on and fully exploited by a number of groups over the intervening time. By the third decade of the twentieth century it became apparent that natural ion-exchange materials had definite limitations. Therefore, the announcement in 1935 by Adams and Holmes (20) that certain synthetic resins were capable of exchanging ions was greeted with much interest.

Present Status of Knowledge Concerning Synthetic Ion-Exchange Materials

The synthetic materials fall into two general classes. The cation exchangers which will exchange ions with a positive ionic charge and the anion exchangers which will exchange ions with a negative ionic charge. The synthetics can be further classified as to their origin:

1. Sulfonated carbonaceous materials which are cation exchangers.
2. Synthetic resins which may be either cation or anion exchangers.

The sulfonated carbonaceous cation exchangers are prepared by treating materials as coal, peat, wood, lignite, etc., with fuming sulfuric acid and/or chlorosulfonic acid. This reaction gives rise to sulfonic acid exchangers known as sulfonated coals or carbonaceous

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(19) Gans, R., U. S. Patents 914,405 (March 9, 1909)
943,535 (Dec. 14, 1909)
1,131,503 (March 9, 1915)

(20) Adams, B. A. and Holmes, E. L., Journal of the Society of Chemical Industry, 54, 1-6 T (1935)

zeolites (21, 22). In 1935 Adams and Holmes (23, 24) found that phenolformaldehyde resins exhibited ion-exchange properties. These resins were prepared by the condensation of phenols with formaldehyde. The ion exchange took place at the phenolic groups of the resin. This initial development has since been followed by the appearance of a large and varied group of synthetic ion-exchange materials.

Basic Considerations Concerning Ion-Exchange Structure

Ion exchange resins are high molecular weight polymers which contain mobile ionic groups as a part of their structure. The anion exchangers contain amine groups and an equal quantity of anions. The cation exchangers contain phenolic, carboxylic, sulfonic, or phosphoric groups and an equal quantity of cations. Therefore, to prepare an ion-exchange resin, it is necessary to prepare a polymer with many cross linking bonds so that the whole is a macro three dimensional polymer. This polymer must of necessity have certain qualifications.

1. It must permit the diffusion of ions through its structure at a relatively fast rate.
2. It must have a negligible solubility in the solvents in which it is to be used and over a large pH range.

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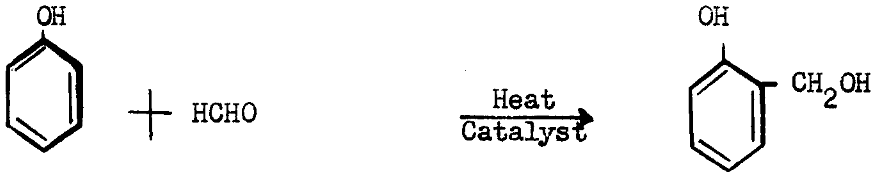
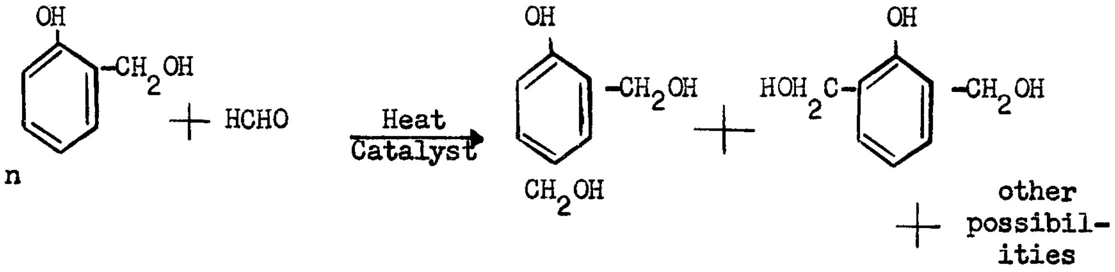
(21) Broderick, S. J., and Bogard, D., U. S. Bureau of Mines Report of Investigations No. 3559 (1941)
(22) Liebknecht, O., U. S. Patent 2,206,007 June 23, 1940
(23) Adams, B. A., and Holmes, E. L., Journal of the Society of Chemical Industry, 54, 1-6T (1935)
(24) Adams, R. S., Journal of the American Leather Chemists Association, 41, 12, 552-73 (December 1946)

3. It must have a sufficient number of ionic exchange groups per unit volume to make its use practical.
4. The resin must be resistant to both chemical and physical degradation.
5. It should be relatively stable to heat.
6. It should not swell greatly while in use.

These conditions are well characterized in the thermosetting resins of the phenolformaldehyde type. The most simple of these is formed from phenol and formaldehyde as follows: (25)



This intermediate may continue to react as:



Thus giving rise to other intermediates which may then react to form a polymer as:

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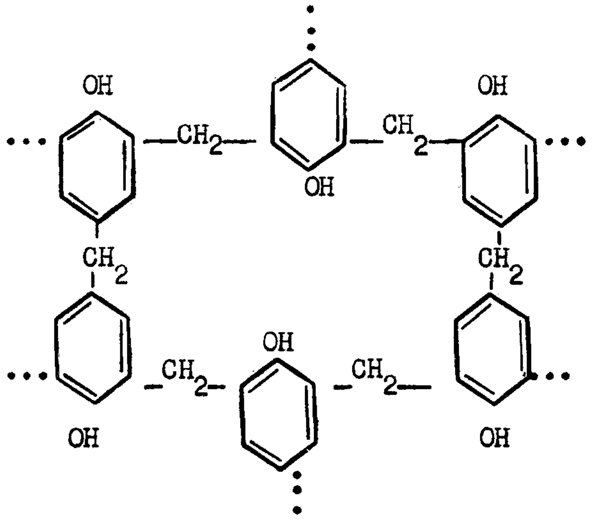
(25) Fieser, L. F., and Fieser, M., Organic Chemistry, D. C. Heath and Company, Boston 1944



In preparing a resin the ionic groups may be attached to the ring of the monomer or the groups may be introduced into the polymer after polymerization. The method to be followed may depend on the final use of the plastic. Cation exchange resins have been prepared containing -OH, -SH, $-SO_3H$, -COOH, $-CH_2SO_3H$ and other groups (26, 27, 28, 29, 30).

Anion exchangers may be prepared in a similar way, i.e., the formation of a resin by the polymerization of an aromatic amine and

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(26) Bauman, W. C., Skidmore, J. R., and Osmun, R. H., Industrial and Engineering Chemistry, 40, 1350-55 (1948)

(27) Bauman, W. C., "Ion-Exchange Resins of Stable Granular Form" U. S. Patent 2,466,675 April 12, 1949

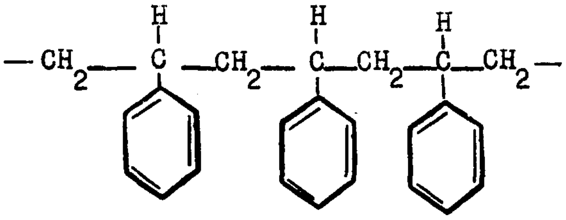
(28) Kressman, T. R. E. "Improvements Relating to Cation Exchange Resins", British Patent 618,251 February 18, 1949

(29) Kunin, Robert and Barry, R. E., Industrial and Engineering Chemistry 41, 1269-1272 (1949)

(30) Nachod, F. C. and Wood, W., "Cation-Exchange Materials" U. S. Patent 2,469,472 May 10, 1949

formaldehyde. In this case the exchange groups may be $-NH_2$, $-NHR$, $-NR_2$, and similar groups (31, 32, 33, 34, 35).

Also, a type of resin for cation exchange has been produced, based on a vinyl type polymerization. In this, styrene polymerizes to form a polymer with the possible linear structure:



The rapid development of the knowledge of the structure and properties of synthetic ion exchange resins still continues. According to present day manufacturers, this knowledge has now reached the point where it may be said that it is possible to design a specific ion-exchange resin to meet the requirements of almost any process requiring a given separation of ionic constituents.

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(31) Adams, B. A., and Holmes, E. L., Journal of the Society of Chemical Industry, 54, 1-6T (1935)

(32) Buckley, Gerard, D., and Ray, Neil H., "Anion Exchange Resin" British Patent, 615,363, January 5, 1949

(33) Dudley, James R., "Anion Exchange Resins" U. S. Patent, 2,467,523, April 19, 1949

(34) Lundberg, L. A., "Anion Active Resins Prepared from Alkylene Polyamines and Hydroxy Substituted Aliphatic Polyhalides" U. S. Patent 2,469,963 May 10, 1949

(35) Societe l'auxilliarie des chemins de fer et de l'industrie, British Patent 632,936 December 5, 1949

Exchange Resin Preparation

Present cation exchange resins are of two major ionic types: 1. Those in which the group responsible for exchange action is a sulfonic group. 2. Those in which it is a carboxylic group. The sulfonic acid exchangers are of three types which will be considered in the order of their origin.

The first sulfonic acid cation exchangers were prepared by treating carbonaceous materials with sulfuric acid. It was soon found that the capacity of a material prepared in this manner was limited. Sulfur trioxide at 150°C. was substituted for sulfuric acid. The resulting material had a much higher ion exchange capacity, was more dense, and had better physical stability. Some time later sulfuric acid was used to sulfonate a polystyrene type polymer (36). This type of cation exchanger proved to be of high capacity also. The more recent cation exchangers however, have a "built in" sulfonic group. They are prepared by causing a phenol and an aldehyde to polymerize in the presence of a sulfonic acid. These exchangers, of which "Dowex 30" is an example, have very high capacity and exceptional stability.

The carboxylic ion-exchangers are also of the "built in" type. A typical example may be one in which resorcylic acid and formaldehyde are polymerized in an alkaline medium (37). The resulting resin

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(36) Bauman, W. C., Skidmore, J. R., and Comun, R. H., Industrial and Engineering Chemistry 40, 350 (1948)

(37) B. I. O. S. Report 621, Item 22 (1946)

has carboxylic groups available for exchange activity. This type of resin adequately meets all the requirements for an ion exchange material such as low swelling coefficient, high stability, high capacity, easy regeneration, etc.

Anion exchange resins are of one general type. These also may be termed the "built in" type of exchanger. An aromatic amine is polymerized with formaldehyde in an acid medium. The resulting resin has amino groups available for exchange activity. The anion exchangers may be classed as weak base or strong base, depending on the basicity of the amino groups which are available for exchange operations.

Mechanism of Ion Exchange Reactions

Ion exchange may be defined as the reversible exchange of ions between a liquid and a solid. Thus the mechanism of ion-exchange may be graphically shown. The exchange of calcium may be carried out by either a sodium or hydrogen ion, depending on the state of the exchanger.

$$2NaR + CaCl_2 \rightleftharpoons CaR_2 + 2NaCl$$

$$2HR + CaCl_2 \rightleftharpoons CaR_2 + 2HCl$$

R represents the cation exchanger. The active groups of the cation exchanger are: $-So_3H$, $-OH$, $-COOH$ and $-CH_2So_3H$. The depleted exchanger may be regenerated with NaCl. This may be represented:

$$CaR_2 + 2NaCl \rightleftharpoons 2NaR + CaCl_2$$

Cation exchangers operate with a finite rate which varies with the ions being exchanged. In aqueous solution at low concentrations and ordinary temperature, the extent of the exchange increases with increasing valency (38). In the case of ions of the same valence those of the higher atomic weights are taken and held in preference to those of smaller atomic weights (39).

Anion exchange mechanism is less certain than cation exchange. Two theoretical mechanisms have been advanced which are represented below:

1. Acid adsorption (40). The whole acid molecule is absorbed as: $RNH_2 + HCl \longrightarrow RNH_3Cl$
2. The conventional exchange mechanism:
    - a. $RNH_2 + HOH \rightleftharpoons RNH_3OH$
    - b. $HCl \rightleftharpoons H^+Cl^-$
    - a. + b. $RNH_3^+OH^- + H^+Cl^- \rightleftharpoons RNH_3Cl + H_2O$

The depleted resin may be regenerated with an alkali as sodium carbonate.

$$2RNH_3Cl + Na_2CO_3 \rightleftharpoons RNH_2 + 2NaCl + H_2O + CO_2$$

Kunin and Myers (41) found the general order for increasing exchange to be: hydroxide $>$ sulfate $>$ chromate $>$ citrate $>$ tartrate $>$ nitrate $>$

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(38) Walton, H. F., Journal of the Franklin Institute, 232, 305, (1941)

(39) Jaeger, F. M., Transactions of the Farady Society, 25, 320-345, (1925)

(40) Edwards, W. R., Jr., Schwartz, M. C., and Boudreaux, G., Industrial and Engineering Chemistry, 32, 1462 (1940)

(41) Kunin, R., and Myers, R. J., Journal of the American Chemical Society, 69, 3874, (1947)

arsenate $>$ phosphate $>$ molybdate $>$ acetate = iodide = bromide $>$ chloride $>$ fluoride.

Nachod and Wood (42) in studying the ion-exchange reaction velocity of various cation and anion exchangers at increasing temperatures, found that the reactions were second order, bimolecular reactions. The values could be calculated by using concentrations instead of activities. Anion exchange or acid adsorption rates were very much slower than the rate of cation exchange reactions. This suggests a different reaction mechanism for anion exchangers than for cation exchangers. It was concluded from temperature studies that the rate of exchange is more or less independent of temperature.

Later, Nachod and Wood (43) showed that the cation exchange capacity increases as a function of the charge of the cation; however, the monovalent ions exchange with faster rate than the divalent ions. Within a valency group, the ion in the lower part of the group, exchanges faster and has a higher equilibrium exchange. At the end of the group the differences are less pronounced. The variation of the rate constants among the cations is generally what one would expect from their respective diffusion rates. Other effects, as ionic charge, size and steric availability of the exchange position in the exchanger play a decided role. It was also shown

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(42) Nachod, F. C., and Wood, W., Journal of the American Chemical Society, 66, 1380 (1944)

(43) Nachod, F. C., and Wood, W., Journal of the American Chemical Society, 67,629 (1945)

that the equilibrium exchange for a series of ions in one group is a function of their size, the hydrated ionic radius or volume.

Applications of Synthetic Ion Exchange Resins

One of the first commercial applications of ion exchange was the use of zeolites in the softening of water. This application was proposed by Gans (44) in 1905 and patented by him sometime later. The present methods of water softening are very similar, except for the use of better exchange materials.

Harrison, Myers, and Herr (45) showed that synthetic ion-exchange resins could be used to produce water of a quality equal to that of U.S.P. distilled water.

Myers, et. al., (46, 47) showed that synthetic ion-exchange resins can be used to remove many ions from aqueous solution. Their work was concerned mainly with adsorption efficiency and regeneration conditions of Amberlites. They also demonstrated that the synthetic ion-exchange resins produced typical Freundlich adsorption isotherms when in contact with acid and salt solution.

Ions having similar analytical properties may be fractionated. The principles are similar to those in chromatographic analysis.

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(44) Gans, R., U. S. Patents 914,405 (March 9, 1909)
943,535 (December 14, 1909)
1,131,503 (March 9, 1915)

(45) Harrison, J. W. E., Myers, R. J., and Herr, D. S., American Pharmaceutical Association, Sci. Ed., 32: 121-128 (1943)

(46) Myers, R. J., Eastes, J. W., and Myers, F. J., Industrial and Engineering Chemistry 33, 697-706 (1941)

(47) Myers, R. J., and Eastes, J. W., Industrial and Engineering Chemistry, 33, 1203-1212 (1941)

However, several additional principles are involved in ion-exchange. The chromatogram is developed by displacing the adsorbed ions with a foreign ion of like charge. The two ions tend to separate into bands as the foreign ion replaces them because of differences in exchange potential. The sharpness of the separating boundries depends on (1) differences in exchange potential, (2) nature of elution agent, (3) length of column, (4) degree of column loading, (5) flow rate during development and (6) particle size.

The use of ion-exchange resins has given rise to many new techniques in the field of organic chemistry. Also, Winters and Kunin (48) have shown that by using several resins, it is possible to separate amino acids into their respective charge groups (acid, basic, neutral) and also to separate the basic amino acids into the three individual acids (arginine, lysine and histidine).

Separations based on differences in acidity and basicity have been shown by Kunin and McGarvey (49) to be feasible. Weak acids may be separated from stronger acids by passing through a bed of weakly basic, anion exchange resin, an exchanger not sufficiently basic to neutralize the weak acids. Likewise, bases may be separated by choosing the correct cation exchanger. Weakly basic alkaloids as strychnine and caffeine may be separated from the more

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(48) Winters, J. C., and Kunin, R., Industrial and Engineering Chemistry, 41, 460 (1949)

(49) Kunin, R., and McGarvey, F. X., Industrial and Engineering Chemistry, 41, 1265-8 (1949)

basic ones as quinine, brucine, and nicotine by means of a carboxylic exchanger.

Herr (50) separated thiamine from riboflavin by means of IR-100 resin. The vitamin was eluted with strong mineral acid.

Cohn (51, 52) using both anion and cation exchangers separated nucleic acids and related compounds.

Kunin and Barry (53) were able to adsorb and recover large molecules as insulin, urease, gelatin, and albumin. A special porous anion exchanger was necessary to effect this separation. Chinchona bark alkaloids have been recovered on a pilot plant scale (54,55).

McCready and Hassid (56) prepared glucose -1- phosphate and purified it by means of ion-exchange adsorbents.

Reid and Jones (57) used a mixture of a strong acid cation exchanger in the hydrogen form and a strong base acion exchanger to fractionate blood plasma proteins. This mixture removes the salts from a solution of blood serum proteins at room temperature and at

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(50) Herr, D. S., Journal of Industrial and Engineering Chemistry 37,631 (1945)
(51) Cohn, W. E., Journal of the American Chemical Society 71, 402 (1949)
(52) Cohn, W. E., Science 109, 377 (1948)
(53) Kunin, R., and Barry, R. E., Industrial and Engineering Chemistry 41, 1269 (1949)
(54) Applezweig, N., Journal of the American Chemical Society 66, 1990 (1944)
(55) Applezweig, N., and Ronzone, S., Industrial and Engineering Chemistry 38, 576 (1946)
(56) McCready, R. M., and Hassid, W. Z., Journal of the American Chemical Society 66, 560 (1944)
(57) Reid, A. F., and Jones, F., Industrial and Engineering Chemistry 43, 1074-1075 (1951)

constant pH. As the salts are removed, the various globulin fractions are precipitated.

Ion-exchange resins have also been studied as chemical therapeutic agents. Segal, et. al., (58) has employed a purified, highly divided anion exchanger as an antacid in peptic ulcer therapy.

An ion-exchange system has been used as artificial kidneys for animals in research studies (59). Cation exchanges have also been used as a means of removing sodium from the body in the treatment of edema and hypertension. Since ion-exchange resins are stable and are not absorbed by the body, this field of research appears to be most promising.

There are also many miscellaneous applications of ion-exchange resins. The mean atomic weight of rare earth mixtures has been determined as well as equilibrium constants and activity coefficients of various complexes.

Ion-exchange resins have been employed as catalysts for organic reactions since 1942. Cation exchangers have recently been employed in esterification reactions on a commercial scale (60); anion exchangers in the base form have been used experimentally for the

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(58) Segal, H. L., Friedman, H. A., Ellis, E. E., and Watson, J. S., The American Journal of Digestive Diseases 17, 293-296 (1950)

(59) Minhead, E. E., and Reid, A. F., Journal of Laboratory and Clinical Medicine 33, 841, (1948)

(60) Anon., Chemical Industries 61, 381, (1947)

mutarotation of glucose (61), and for the formation of nicotinamide from nitrile (62).

Levesque and Craig (63) have found that the rate of esterification of oleic acid with n-butanol varied with the external area of the resin particle. In catalytic applications the rates of the exchange and adsorption are of prime importance. Therefore, much of the work in catalytic ion-exchange chemistry has been done in this area.

Synthetic ion-exchange material has been made into membranes and used as membrane electrodes (64). By their use it is possible to determine the activities of many ions for which specific reversible electrodes do not exist or where conventional type electrodes involve considerable experimental difficulties. After a membrane has been saturated with critical ions, activity determinations can be made within a few minutes.

Suitable membranes for Gibbs-Donnan equilibrium have not been available in the past. Permselective membranes of synthetic ion-exchange material are ideal for this purpose (65).

Salts of pH sensitive organic acids may be converted into the free acid by membrane hydrolysis.

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(61) Jenny, H., Journal of Colloid Science 1, 33 (1946)
(62) Galat, A., Journal of the American Chemical Society 70, 3945 (1948)
(63) Levesque, C. L., and Craig, A. M., Industrial and Engineering Chemistry 40, 96 (1948)
(64) Sallner, K., Journal of the American Chemical Society 65, 2260 (1943)
(65) Sollner, K., and Sollner, H. P., Journal of the American Chemical Society 67, 346 (1945)

A series of alternating cation and anion exchange membranes separating alternate high and low electrolyte concentrations will form a battery. Such a battery with ten-fold concentration differentials can theoretically build up 59 millivolts per compartment or 5.9 volts per one hundred compartments. The same system may be reversed and employed, by means of electrical power to concentrate demineralized electrolyte solutions (66). The demineralization of sea water at an energy consumption as low as 20 Kw. Hr. per 1000 gallons has been reported (67) using a modified plan.

Nonelectrolytes may be separated by the simultaneous use of both electropositive and electronegative membranes in diffusion dialysis. Permselective membranes may make electrodialysis an economically feasible commercial process after it has been lying dormant for many years.

Sollner (68) has applied permselective membranes to many biological problems including the situation of a membrane composed of preferentially anion and preferentially cation permeable parts. He found that the permeability of such mosaic membranes could be precalculated quantitatively on the basis of purely electrical data with an error of less than ± 0.2 per cent.

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(66) Bauman, W. C., Anderson, R. E., and Wheaton, R. M., Annual Review of Physical Chemistry 3, 109-130 (1952)

(67) Ionics, Inc., Bulletin No. 1 Nepton Membranes, Revised ed. (1952), Ionies, Inc., Bulletin No. 2 Nepton, Membrane Demineralization, Revised Ed. (1952)

(68) Sollner, K., Annals of the New York Academy of Sciences, 57, Art 3, 177-203 (1953)

Theories of Ion-Exchange

From the time of the earliest papers on ion-exchange, theories were advanced to explain the mechanism of the phenomenon. As more and more exchange materials were investigated, and allied research threw new light on the process, the various theories were amended or abandoned. New theories were advanced until at present three major theories remain. These theories are: (a) the crystal lattice exchange theory, (b) the double layer theory, first preposed by Helmholtz, and (c) the Donnan membrane theory. These explanations are widely divergent in spite of the fact that they attempt to explain the same facts.

In considering these theories only ion exchange due to primary coulombic attractive forces will be considered. Attractive forces due to van der Waals forces, which may also contribute somewhat to ion exchange capacity in the form of physical adsorption, will not be considered. In all the proposed theories it is required that electrical neutrality be maintained between the exchange particle and the solution.

The Crystal Lattice Theory

The work of Bragg (69) and Pauling (70) on the crystal structure of natural ion-exchange silicates, together with the modern

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(69) Bragg, W. L., Z. Krist., 74, 237 (1930)

(70) Pauling, L., The National Academy of Science Proc., 12, 123, (1930)

concept of ionic solids has increased our understanding of ion exchange to a great extent. Born (71) considers the constituents of an ionic solid to be present as ions instead of molecules. A crystal of sodium chloride, therefore, is completely dissociated, consisting only of sodium ions and chloride ions. Each ion of the crystal is surrounded by a fixed number of ions of the opposite charge. The crystal is "held together" by coulombic forces which are dependent on the charges of the ions and the distance between the ions. Therefore, an ion at the surface of an ionic solid is less tightly held because it is subject to less attractive forces than one on the interior. Likewise, an ion at the corner of an ionic solid is less tightly held than a surface ion. When an ionic solid is placed in a highly polar medium as water, the coulombic forces holding the ion to the solid are reduced to such an extent that the corner ions are easily replaced by another ion in the solution. The surface ions are almost as easily replaced. The ease with which these ions may be replaced by another ion depends on (a) the nature of the forces binding the ion to the crystal, (b) the charge of the exchanging ion, (c) the relative sizes of the two ions, and (d) accessibility of the lattice ions. Thus, the corner ions will be the first to be exchanged, followed by the surface ions. In the case of a densely packed crystal lattice as the micas and feldspars the ion exchange will stop at this point. It is therefore necessary to finely divide

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(71) Born, M., Atomtheorie des festen Zustandes, Leipzig, 1923

materials of this type to give much surface with many corner and surface ion positions.

The natural silicates have an open type crystal lattice which permits cations from the interior to migrate to the surface of the ionic solid and ions of comparable size to migrate from the surface to the interior of the crystal structure. Ion-exchange minerals of this type need not be finely divided to have a high exchange capacity.

Some mineral exchangers also are capable of exchanging hydroxyl ions for other anions and thus are amphoteric in nature.

To determine, a priori, that an ion in a crystal lattice will exchange with another ion is difficult. The exchangeable ions occupy essential sites in the crystal lattice of the solid and therefore certain energy requirements must be met. The relative binding energies of the exchanging ions must not be too dissimilar or the ion either will not exchange or the replacement ion will be difficult to remove. However, the coulombic forces of the lattice must be satisfied. To date, very little consideration has been given to this problem in ion-exchange investigations.

Ion-exchange resins do not have the crystallinity which has been so prominent in the discussion up to this point. However, experimental results indicate a very similar exchange mechanism. While the ion-exchange resins are high molecular weight polymeric electrolytes experimental results show that the exchange ions apparently are free to migrate within the polymer thereby permitting exchange throughout the resin structure.

The Electrical Double Layer Theory

In 1853 Helmholtz (72) presented the idea that colloidal particles are stable in the colloidal state due to an electrical double layer existing at the solid-solution interface. This theory assumed that the double layer consisted of two discreet monoionic layers of opposite charge. One layer of which would be "sandwiched" between the colloid solid and the outer charge layer, touching each at their respective boundry plane.

The origin of this double layer lies in one or a combination of the following: (a) the preferential adsorption of one ion of an electrolyte in which the particle is suspended, (b) the direct ionization of some of the surface molecules, (c) the selective adsorption of H^+ or OH^- ions from water.

Gouy (73) modified the theory somewhat by assuming that the outer layer of ions is not a discreet layer one ion thick but rather a diffuse layer of ions that extends into the external liquid medium.

Stern (74) further modified the theory by assuming that part of the ions of the inner layer are free to move while part remain attached to the surface of the solid. The attached ions are held by electrostratic and physical forces which differ for each ion.

Thus the present electrical double layer theory is fundamentally that of Helmholtz with modifications by Gouy and Stern. Some

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(72) Helmholtz, H. von, Annals of Physical Chemistry, 7, 337-382 (1879)

(73) Gouy, M., Journal of Physics, 9, 457-468 (1910)

(74) Stern, O., Z. Elektrochemie, 30, 508-516 (1924)

workers in ion exchange research have taken this theory and applied it as a whole to explain the mechanism of ion exchange.

We may consider the concentration of the ions constituting the diffuse layer as varying continuously and depending upon the concentration and pH of the external solution. If the concentration of ions in the external solution is changed by the addition of a foreign ion, the equilibrium is upset and a new equilibrium is obtained. Some of the new ions will enter the diffuse layer, replacing some of the ions previously held in this layer. In order to maintain the law of electroneutrality, the change must be stoichiometric.

The crystal lattice theory assumes a fixed number of exchange sites, the maximum of which cannot be exceeded. In the double layer theory of exchange, however, the ion-exchange solid has a variable capacity that depends on the diffuse double layer. The diffuse double layer is dependent on both the concentration and pH. In some types of systems, both types of exchange may occur simultaneously.

Donnan Membrane Theory

The third explanation concerning the mechanism of ion exchange is a special case of Donnan's theory of membrane equilibria. This theory deals with the equilibria resulting when a membrane separates two electrolytes, one at least of which contains an ion that cannot diffuse through the membrane. If one starts with two completely ionized electrolytes, e. g., NaCl and NaR, separated by a membrane impermeable to the ion R, equilibrium will be established only when the product of the concentration of sodium and chloride ions has the same value on both sides of the membrane, thus:

$$[\mathrm{Na}^+]_1 \times [\mathrm{Cl}^-]_1 = [\mathrm{Na}^+]_2 \times [\mathrm{Cl}^-]_2$$

when $[\mathrm{Na}^+]_1$ and $[\mathrm{Cl}^-]_1$ are the concentrations of sodium and chloride ions on one side of the membrane and $[\mathrm{Na}^+]_2$ and $[\mathrm{Cl}^-]_2$ are corresponding concentrations on the opposite side of the membrane.

In order that the principle of electroneutrality be obeyed,

$$[\mathrm{Na}^+]_1 = [\mathrm{Cl}^-]_1 + [\mathrm{An}^-]_1 \quad \text{and} \quad [\mathrm{Na}^+]_2 = [\mathrm{Cl}^-]_2$$

$[\mathrm{Na}^+]_2\,[\mathrm{Cl}^-]_2 = [\mathrm{Cl}^-]_2^2$ and $[\mathrm{Na}^+]_1$ must be greater than $[\mathrm{Cl}^-]_1$ since $[\mathrm{Cl}^-]_2^2 = [\mathrm{Cl}^-]_1\,[\mathrm{Na}^+]_1$ then $[\mathrm{Cl}^-]_2 > [\mathrm{Cl}^-]_1$ i.e., The concentration of NaCl is greater on the side that is free of the non-diffusible ion.

When equilibrium is established, in solution 1, let:

$$X = [\mathrm{Na}^+] = [\mathrm{Cl}^-]$$

In solution 2, let:

$$Y = [\mathrm{Cl}^-]$$

$$Z = [\mathrm{R}^-]$$

$$\text{then } Y + Z = [\mathrm{Na}^+]$$

Since the product $[\mathrm{Na}^+] \times [\mathrm{Cl}^-]$ will be the same in both solutions at equilibrium, therefore:

$$X^2 = Y\,(Y + Z)$$

If a second cation K^+ is added to the system, the following must be obeyed:

$$[\mathrm{Na}^+]_1\,[\mathrm{Cl}^-]_1 = [\mathrm{Na}^+]_2\,[\mathrm{Cl}^-]_2$$

and $$[K^+]_1 [Cl^-]_1 = [K^+]_2 [Cl^-]_2$$

Dividing the two equations

$$\frac{[Na^+]_1}{[K^+]_1} = \frac{[Na^+]_2}{[K^+]_2}$$

This indicates that an exchange of ions must take place until the concentration ratios are equal in both phases.

In order to extend this theory of membrane equilibria to the mechanism of ion-exchange certain assumptions must be made. It must be assumed that the colloidal micelle, to which the exchangeable ion is attached, is the nondiffusible ion. While no membrane is present in ion-exchange equilibria, the interface between the solid and liquid phases may be considered as a membrane. The exchange of ions in living cells and across cellophane or parchment membranes has been found to follow the Donnan theory. If all the ions are capable of diffusion, as in an ionic solid, the Donnan theory cannot be applied. However, it can be applied to most conventional ion-exchange materials because one ion is always a high polymeric nondiffusible ion.

The three ion-exchange theories are similar in that the exchange site is an ionic grouping capable of forming an electrostatic bond with an ion of opposite charge. They differ in the position and origin of the exchange site.

Literature on Ion-Exchange Resin Membrane Electrodes

If a semipermeable membrane separates two solutions of different concentration of the same electrolyte, an electromotive force arises that is different in most cases from the liquid junction potential that would arise between the same two solutions on free diffusion, that is, in the absence of a membrane. The electromotive forces arising from such arrangements is referred to as concentration potentials.

The first extensive study of such potentials was carried out by Michaelis (75) with collodion membranes. Since this early work, Sollner (76) and his co-workers have tirelessly extended this work. Haber and Klemensiewiez (77) observed that the potential difference between two solutions separated by a glass plate depended on their hydrogen-ion concentrations. This work resulted in the employment, some years later (78), of a glass electrode as a hydrogen-ion indicator.

It has been assumed that the glass membrane of the glass electrode functioned primarily as a semipermeable membrane (79) and thus in the case of hydrogen acts as a hydrogen electrode. It is a logical step to replace the glass membrane with an ion-exchange material.

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(75) Michaelis, L., Colloid Symposium Monograph 5, 135 (1927)

(76) Sollner, K., Annals of the New York Academy of Sciences 57, Art 3, 177-203 (1953)

(77) Haber and Klemensiewiez, Z. physikal Chem., 67, 385 (1909)

(78) Hughes, W. S., Journal of the American Chemical Society 44, 2860 (1922)

(79) Dole, M., The Glass Electrode, John Wiley and Sons, Inc., New York, 1941

The ion-exchange material could then be saturated with the desired cation or anion and may function as a selective electrode for that particular ion. For example, a membrane may be saturated with Na^+ and may then act as a sodium electrode when in an electrolytic solution. Efforts to do this have met with only limited success (80, 81).

The conception of membranes as ion exchange bodies leads to the fixed charge theory of electrical membrane behavior. This theory was first presented by Teorell (82) and later in greater detail by Meyer and Sievers (83, 84). According to this theory each membrane is permeated with many pores, the walls of which carry a definite number of potentially dissociable groups. In the case of electronegative membranes these groups are anionic (acidic) groups, such as the carboxyl groups. In the case of electropositive membranes these groups are cationic (basic) groups, such as amino groups. These dissociable groups are an integral invariable part of the membrane structure. Their number is independent of the nature or concentration of the adjacent electrolyte solutions. The counter ions of the fixed charge wall groups and any other

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(80) Tendaloo, H. J. C., Journal of Biological Chemistry, 113, 333 (1936)
(81) Anderson, R. S., Journal of Biological Chemistry, 115, 323 (1936)
(82) Teorell, T., Transactions of the Faraday Society, 33, 1054 (1937)
(83) Meyer, K. H. and Sievers, J. F., Helvetica Chemica Acta, 19, 649, (1936)
(84) Meyer, K. H., Transactions of the Faraday Society, 33, 1073 (1937)

non-exchangable electrolyte that may be present, carry any current which flows across the membrane. The concentration of the nonexchangable electrolytes is determined by a Donnan equilibrium existing between the electrolytic pore structure of the membrane and the adjacent outside electrolyte solution, the fixed wall groups being the nondiffusible ions. In a concentration cell, a Donnan equilibrium is set up between each solution and its adjacent side of the membrane with a corresponding concentration drop across the membrane. The concentration potential is considered to be the algebraic sum of the two Donnan potentials plus the liquid junction potential within the pores.

Zeolite membranes prepared by Marshall (85) conformed to the Teorell-Meyer-Sievers theory. Marshall prepared clay membrane electrodes from a variety of clays. Each clay was found to have its own individual properties. Wyoming and Arizona bentonite clays were found to have selective properties in that they would respond only to monovalent ions (86).

Wyllie and Patnode (87) prepared membranes from ion exchange resins by grinding the granular amberlite IR-100-Na resin with polymerized methyl methacrylate and molding the membrane in metallographic press. Excellent agreement with theoretical values were obtained in

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(85) Marshall, C. E., Journal of Physical Chemistry, 43, 1155 (1939)
(86) Marshall, C. E., Journal of Physical and Collodial Chemistry, 52, 1284 (1948)
(87) Wyllie, M. R. J. and Patnode, H. W., Journal of Physic and Colloid Chemistry, 54, 204 (1950)

sodium as high as four molar. They also prepared membranes using polystyrene as the bonding agent, and membranes constructed from shale plates.

Kressman (88) prepared ion-exchange materials in the form of sheets and rods. Membranes were prepared from these sheets of ion-exchange resin. In addition he formed electrode membranes from ion-exchange material supported on sintered glass. No details of the electro-chemical behavior of these membranes were given.

Schindewolf and Bonhaeffer (89) prepared membranes from phenol-formaldehyde resins to study the dissociation of polyphosphate salts of barium chloride, sodium chloride, and hydrochloric acid. Hydrochloric acid solutions gave potentials which were in agreement with the Nernst equation for concentration cells up to concentrations nearly equal to one normal, sodium chloride to one-tenth normal and barium chloride to three-hundredths molar. Poor results were obtained with very dilute solutions in the order of 5×10^{-4}.

Browne (90) prepared membranes from several ion-exchange resins, using methyl methacrylate as a binder, and studied their behavior in solutions of the chlorides of some alkali metals. He reported that amberlite IR-120 gave the best electrodes for cation sensitive membranes and that the membranes obeyed the Teorell-Meyer-Sievers theory fairly well.

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(88) Kressman, T. R. E., Nature, 165, 568 (1954)
(89) Schindewolf, H., and Bonhaeffer, K. G., Zeitschrift fur Elektrochemie, 57, 216 (1953)
(90) Browne, J. W., M. S. Thesis, University of Missouri, 1951

Winger, Bodoner, and Kunin (91) described membranes prepared from a commercial product of the Rohm and Hass Company. These materials are amberplex C-1, a cation exchanger, and amberplex A-1, an anion exchanger. The electrochemical behavior of these membranes was studied in potassium chloride solutions.

Juda, et. al., (92) determined the transport number of the sodium ion for several types of ion-exchange membranes. The conductances of the exchange resins were also studied. In this study the membranes were considered as solid electrolytes.

The mobilities of sodium and bromide ions in membranes were measured by Schlogel (93).

Bergin and Heyn (94) used membranes which were sintered glass impregnated with an ion-exchange resin to determine potentials of liquid ammonia, alcohol, and water solutions. The results were good when compared to theoretical values.

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(91) Winger, A. G., Bodoner, G. W., and Kunin, R., Journal of the Electrochemical Society, 100, 178 (1943)

(92) Juda, W., Rosenberg, N. W., Morinsky, J. A., and Kasper, A. A., Journal of the American Chemical Society, 74,3736 (1952)

(93) Schlogel, R., Zeitschrift fer Elektrochemie, 57,195 (1953)

(94) Bergin, M. J. and Heyn, Arno H. A., Journal of the American Chemical Society, 76, 4765-4769 (1954)

III. THEORY OF ION-EXCHANGE MEMBRANE ELECTRODES

Membranes may be divided into two classes, "homogeneous phase membranes" and "porous membranes". The homogeneous phase (oil membranes) function by means of "selective differential solubility". Materials which are oil soluble can penetrate and cross it. Porus membranes act as sieves which screen out the various particles according to size, and to some extent according to different adsorbabilities. In the case of ions the sign and magnitude of their charge is also a governing factor. Membranes of "ion exchange character" fall into the porous membrane class.

Porous membranes can be further classified according to their pore size. Large pore size membranes, as exemplified by dializing membranes, and small pore size membranes. The small pore membranes have been termed "molecular sieve" or "ion sieve" membranes. The pores of these membranes are so small that different low weight molecules and ions are retarded to different degrees in passage or are stopped altogether. Membranes of both porosities are found in living organisms and are therefore of prime interest.

It has been previously noted that a potential would develop across a semi-permeable membrane separating two solutions of different ion concentration. The sign and magnitude of the potential depends on the concentrations and the concentration ratio of the electrolyte in the two adjacent solutions, the nature of the electrolyte and the nature of the membrane.

Highly porous membranes give potentials which are not much different from their corresponding liquid junction potentials in sign and magnitude. This is to be expected since the membrane does little to change the character of the liquid junction.

One fundamental fact may be presented in the electrochemistry of porous membranes. The electrokinetic charge on the membrane governs the deviation of the concentration potential from the liquid junction potential. With electropositive membranes, the dilute solution is more negative than on free diffusion. With electronegative membranes, the dilute solution is more positive than on free diffusion. Thus, it may be concluded that electronegative membranes are preferentially cation permeable and electropositive membranes are preferentially anion permeable.

While the liquid junction potential represents one potential limit, the other potential limit is represented by the potential which would result if the two solutions were connected to each other through a pair of reversible electrodes, specific for either cations or anions, as this case may be. The theoretical value of this arrangement is often called the "thermodynamically possible maximum value". This concentration potential value is often closely approached by some membranes of very low porosity, that is, small pore diameter.

The origin of the concentration potentials across porous membranes may be found in the assumption that transportation of electricity across these membranes is divided between the anions and cations in a proportion which is different from the ratio of transference numbers in a like free solution (95, 96).

Previously it was concluded that electronegative membranes are preferentially cation permeable, and electropositive membranes are preferentially anion permeable. Therefore, cations would carry a greater portion of the current that is transported across an electronegative membrane. Thus, in the electronegative membranes the transference numbers of the cations in the membrane pores (T_+) is larger than the cation transference numbers in a comparable free solution. The opposite is true in an electropositive membrane.

By the use of a modified Nernst equation we may correlate membrane concentration potential (ϵ) and the membrane transference numbers (T_+, T_-).

$$\epsilon = \frac{T_+ - T_-}{T_+ + T_-} \quad \frac{RT}{F} \quad \ln \frac{a_\pm^{(2)}}{a_\pm^{(1)}} \qquad (1)$$

$a_\pm^{(1)}$ and $a_\pm^{(2)}$ are the activities of the electrolyte in the two solutions. The sum of T_+ and T_- are by definition unity. If an electropositive membrane is permeable to anions exclusively and

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(95) Michaelis, L., Bulletin of the National Research Council, U. S. 69, 119 (1929)

(96) Michaelis, L., Colloid Symposium Monograph 5, 135 (1927)

therefore impermeable to cations, the transference number of the anion τ_- is 1 and the transference number of the cation τ_+ is 0. Likewise, if an electronegative membrane is exclusively permeable to cations the cation transference number τ_+ is 1, etc. A membrane which is permeable only to the cation or anion is said to be a "membrane of ideal ionic selectivity".

The source of the electrokinetic charge on the membranes as well as their electromotive action has been clearly understood for several decades. Ideally the membrane is composed of many pores which penetrate the membrane from one side to the other. The ion-exchange material is a definite chemical compound with an established percentage or ratio of dissociable groups. Thus the pore or channel through the membrane will have a number of removable ions which depends on the diameter of the pore. For every ion which is able to move or migrate there remains a fixed counter ion. Thus, the fixed ions form the inner part of an electrical double layer, the movable ions being the outer part. This fixed wall charge does not participate in the transportation of electricity. The movable, or dissociable ions, as well as their counterparts from the solution which momentorily take their place, transport the electricity across the membrane.

The membrane therefore will have an over all charge of the same sign as that of the fixed non-dissociable ion. Ions of the same sign of charge which approach the membrane will be repulsed by it and thus prevented from entering the pores. Therefore, no ions of the same sign as the membrane can cross the membrane. This model represents a membrane of ideal ionic selectivity which is only theoretically possible.

In practice ions of both signs cross the membrane; their ratio being affected by other factors as well as the above. The ionic selectivity of a membrane decreases if the concentration of the adjacent electrolyte solutions is increased. With an increased number of ions adjacent to the membrane more electrolyte enters the pores thereby decreasing the specific influence of the membrane.

Polyvalent ions with a charge of the same sign as the membrane are more restricted in penetrating the membrane than univalent ions due to size and greater repulsion.

All the pores permeating the membrane are not of the same size. Thus all membranes are heteroporous, a "mosaic" of wide and narrow channels (97).

The sum of these factors, each contributing in its way, lead to the observed behavior of the membranes and the deviation from the ideal membrane.

The Teorell-Meyer-Sievers (98, 99) theory correlates quantitatively the previously outlined theory concerning porous membranes. This theory considers that the membrane consists of a framework

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(97) Zsigmondy, R., Kolloidchemie, 5th edition 1, 61 (1925) Leipzig
(98) Teorell, T., Transactions of the Faraday Society, 33, 1054 (1937)
(99) Meyer, K. H. and Sievers, J. E., Helvetica Chemica Acta, 19, 649 (1936)

with a fixed electrostatic charge. The magnitude of this charge varies for each membrane. This characteristic of individual membranes is called the selectivity constant with the symbol A. Negatively charged membranes are permeable to cations and sensitive to cations only.

The selectivity constant is assumed to be the cause of a Donnan potential originating at each membrane face and it is given units of concentration. It is also assumed that a liquid junction potential is set up inside the membrane and the corresponding potential calculated by means of the Henderson equation. The selectivity constant "A" may be considered as the thermodynamic activity of the ionized sites within the membrane. In the case of a cation sensitive membrane, the equation for the potential reduces to the following:

$$E = \frac{RT}{F}\left[U\ln\frac{\left(\frac{4a_2^2}{A^2}+1\right)^{\frac{1}{2}}+U}{\left(\frac{4a_1^2}{A^2}+1\right)^{\frac{1}{2}}+U} + \frac{1}{2}\ln\left(\frac{\left(\frac{4a_2^2}{A^2}+1\right)^{\frac{1}{2}}+1}{\left(\frac{4a_1^2}{A^2}+1\right)^{\frac{1}{2}}-1}\right)\left(\frac{\left(\frac{4a_2^2}{A^2}+1\right)^{\frac{1}{2}}-1}{\left(\frac{4a_2^2}{A^2}+1\right)^{\frac{1}{2}}+1}\right)\right]$$

$$\text{Where}\quad U = \frac{U_c - U_a}{U_c + U_a} \qquad (2)$$

The quantities a_1 and a_2 are the respective activities of the cation on the two sides of the membrane and Uc and Ua are the mobilities of the cation and anion respectively.

When the quantity "A" is large compared to a_1 and a_2 the equation reduces to the Nernst equation for concentration cells:

$$E_o = \frac{RT}{nF}\ln\frac{a_2}{a_1} \qquad (3)$$

When a_1 and a_2 are large compared to "A" the equation reduces to that of a simple liquid junction between two solutions of an electrolyte of different concentration.

$$E = U\frac{RT}{F} \ln \frac{a_2}{a_1} = (t^+ - t^-)\frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (4)$$

where t^+ and t^- are the respective transference numbers of cation and anion. This latter expression which was derived for any liquid junction between two solutions may be applied to a membrane boundary. The transference numbers will be those within the membrane.

$$E = (t_+ - t_-)\frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (5)$$

Since $t_- = 1 - t_+$, equation 5 may be written for the cation:

$$E = (2t_+ - 1)\frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (6)$$

From equation 4 it may be seen that as the membrane becomes selective for cations to the exclusion of anions the transference number of the cation in the membrane approaches one and the equation becomes the Nernst potential equation (3). This is the maximum possible voltage, E_o. Dividing equation 6 by 3 we obtain:

$$E/E_o = 2t_+ - 1 \qquad (7)$$

$$\text{or} \quad t_+ = \frac{E + E_o}{2E_o} \qquad (8)$$

Thus the average transference number of the cation in the membrane may be defined.

A value known as permselectivity of a membrane may be expressed in terms of the transference numbers.

$$P = \frac{t_{+}-t_{o}}{1-t_{o}} \tag{9}$$

t_o is the transference number of the ion in free solution. The perselectivity is a measure of the degree to which a membrane singles out the cation or anion in the development of the membrane potential.

For a particular membrane the measured potential is determined by the selectivity constant "A" and by the mobility ratio Uc/Ua within the membrane. The two quantities may be calculated when the activities of the salts in solution are known, or they may be determined graphically as described by Marshall (100).

If the solution in which measurements are to be made contains more than one type of cation or anion, the activities of both can be determined if the activity of one of the ions can be determined by an independent method. The equation necessary to calculate the activity of such a mixture may be derived from the Henderson equation for liquid junction potentials. In the case of a solution of a potassium salt and hydrogen ion the equation is:

$$\text{EMF} = \frac{RT}{F} \ln \left[\frac{a_{k_1^+}}{a_{k_2^+}} - \frac{U_{H^+}}{U_{k^+}} \quad a_{H^+} \right] \tag{7}$$

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(100) Marshall, C. E., Journal of Physical and Collodial Chemistry, 58, 1284, (1948)

Where $a_{k_1^+}$ and $a_{k_2^+}$ are the known and unknown activities of potassium, a_{H^+} is the activity of the hydrogen ion and U_{H^+}/U_{k^+} is the mobility ratio of hydrogen and potassium. The mobility ratio is determined for known solutions and, as the activity of the hydrogen ion may be determined with the glass electrode, the activity of potassium may be calculated. If, however, the activity of one of the cations cannot be determined by an independent method, then approximations must be used and an approximate answer will result. The principle is the same for anions. The expressions for multivalent ions do not have ready solutions and a process of successive approximations must be used.

Marshall (101) found that clay membranes gave potentials considerably lower than predicted by the Teorell-Meyer-Sievers theory if sample liquid junctions were formed. The internal liquid junction was dropped from the equation and the membrane was considered to have exchange properties for cations and to behave in a reversible manner. For simple systems the equation reduces to the sum of two Donnan potentials. The heat effect of the reaction will be equal to the difference between the bonding energies of the ions involved. If the same ion is on both sides of the membrane the difference is zero. If the ions differ the potential may be written:

$$\mathrm{EMF} = \frac{4.185}{F}(H_1 - H_2) + \frac{RT}{F} \ln \frac{a_1}{a_2} \qquad (8)$$

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(101) Marshall, C. E., Journal of Physical and Collodial Chemistry, 52, 1284 (1948)

where H_1 and H_2 are the bonding energies and a_1 and a_2 the activities of the two ions involved. The quantity $\frac{4.185}{F}(H_1 - H_2)$ is equal to $\frac{RT}{F} \ln \frac{U1}{U_2}$ and the concept of a heat effect replaces that of the mobility ratio when solutions of two ions are considered.

The theory of absolute reaction rates has been applied to the calculation of membrane potentials by Nogasawa and Kobatake (102). They considered that the membrane acted as a bundle of small cylinders and the diffusion of ions through the membrane was used as a basis for the derivation of a theoretical equation. While the theory is applicable to other types of membranes it was applied to the glass electrode only.

Scatchard (103) developed equations for membrane action from the general equation for an electromotive cell with transference. The deviation from ideal behavior was ascribed to the transfer of water through the membrane; the resulting equation reduces to that of the Teorell-Meyer-Sievers theory when the same simplifying assumptions are made. In all cases the necessary assumption is made that mean activity coefficients may be used in calculating the theoretical potentials.

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(102) Nogasawa, M., and Kabatake, Y., Journal of Physical Chemistry, 56, 1017 (1952)

(103) Scatchard, G., Journal of the American Chemical Society, 75, 2883 (1953)

IV. EXPERIMENTAL PROCEDURE

Basic Considerations

The measurement of membrane concentration potentials consists of the determination of the electromotive force which arises in the series C_2/ membrane/ C_1, the EMF sign being that of C_1 the more dilute solution. The complete measurement chain consists of saturated calomel electrode/ saturated potassium chloride/ saturated potassium chloride agar bridge/ electrolyte C_2/ membrane/ electrolyte C_1/ saturated potassium chloride agar bridge/ saturated potassium chloride/ saturated calomel electrode.

Ion-exchange membranes in such concentration chains will reach a final stable concentration potential, in a reasonable time, only if their movable ions are the same as those contained in the adjacent solutions. Therefore, it is necessary to saturate the membrane by ion-exchange with the particular ion under consideration before the measurement chain is set up. When a membrane previously saturated with the desired ion is placed in such a concentration chain, its electromotive response is almost immediately at its maximum and is reproducible.

This final concentration potential is a function of the nature of the membrane and the nature of the electrolyte, as well as the concentration ratio and the absolute concentration of the electrolyte in solution.

The maximum electromotive force would occur if the membrane behaved, under a given set of conditions, as an ideal membrane for the reversible transfer of the desired ion. The calculation of the maximum potential is based on the Nernst equation:

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1}$$

Where E is the maximum potential, R is the gas constant 8.315 joules per degree, T is the temperature in degrees absolute, n is the valence of the ion, F is Faraday's constant 96,494 coulombs, and a_1 and a_2 are the ionic activities of the dilute and concentrated solutions respectively. Previous reports appear to show that in the case of univalent ions in dilute solutions the electromotive force can be determined with considerable accuracy. In the case of divalent ions it appears that the results may contain some small inherent error which is insignificant when compared to the reproducibility of experimental data.

In dilute solutions ion-exchange resin membranes are almost completely permselective, thus excluding the ion of opposite charge. As the concentration of the solutions increase, both cations and anions enter the membrane and participate in the transport of current across the membrane, thus its permselectivity decreases with increasing electrolyte concentrations.

In the past cation exchange membranes have been of a weakly acidic nature which made the membranes sensitive to pH and reduced the ion selectivity at higher solution concentration. It was thought that since Amberplex C-1 membrane material is a strong sulfonic acid type, the response of this material should be good at higher concentrations and especially in slightly acidic solutions. Amberplex C-1 material was therefore selected for the study reported in this paper.

Electrode Preparation and Potential Measurements

Amberplex C-1 sheets were cut into circular discs about 0.75 inches in diameter and were cemented to glass tubes 2.5 inches long and 0.6 inches inside diameter, giving the electrode an exterior surface area of about 0.28 square inches. The cement used was Cenco Sealstix thermosetting sealing material. It was originally planned to use membranes having an outside area of one square inch, however excessive swelling of the membrane during the preliminary conditioning of the membrane made this size impractical. These tubes with the membrane sealed in place served as the inner half of the concentration cell. They were inserted in a rubber holder ring and were used in conjunction with a two hundred and fifty milliliter beaker and two commercial calomel electrodes as shown in Figure 1.

Each membrane was soaked in a saturated solution of the electrolyte in question until any asymmetry potential present had disappeared. The term asymmetry potential refers to that potential which is observed when both electrodes are immersed in a solution, or solutions of equal concentration. The disappearance of asymmetry potential was taken as an indication that ion exchange between the saturated solution and the membrane had reached equilibrium; that is, that all the replaceable sites had been filled with the desired cation and therefore the membrane was homogeneous as far as the cation in question was concerned.

A solution of known activity of the desired electrolyte was placed on each side of the membrane and the potential across the membrane was measured. Several charges of solutions were necessary before reproducible values were obtained. All of the potential measurements were made with a Leeds and Northrup type K potentiometer at a room temperature of 25 C. The galvanometer was a Pfaltz and Bauer multiple mirror type. The solutions used were prepared from analytical reagent grade salts of the metallic chloride using deionized water having a conductivity of 2×10^{-6} ohm^{-1} cm.^{-1} The activity coefficients used were obtained from Latimer (104). All solutions of salts were prepared as follows where practical. The salt was dried at 100°C over night and the calculated amount weighed and added to 1000 grams of deionized water. In cases where this was not practical a stock solution was prepared. The cation concentration of this solution was determined by quantitative analysis. The desired solution concentrations were prepared by proper dilution from these stock solutions.

Because of damage in preparation due to swelling, mechanical damages and other causes, only about twenty-five per cent of the membranes tested were usable. After eliminating membranes with

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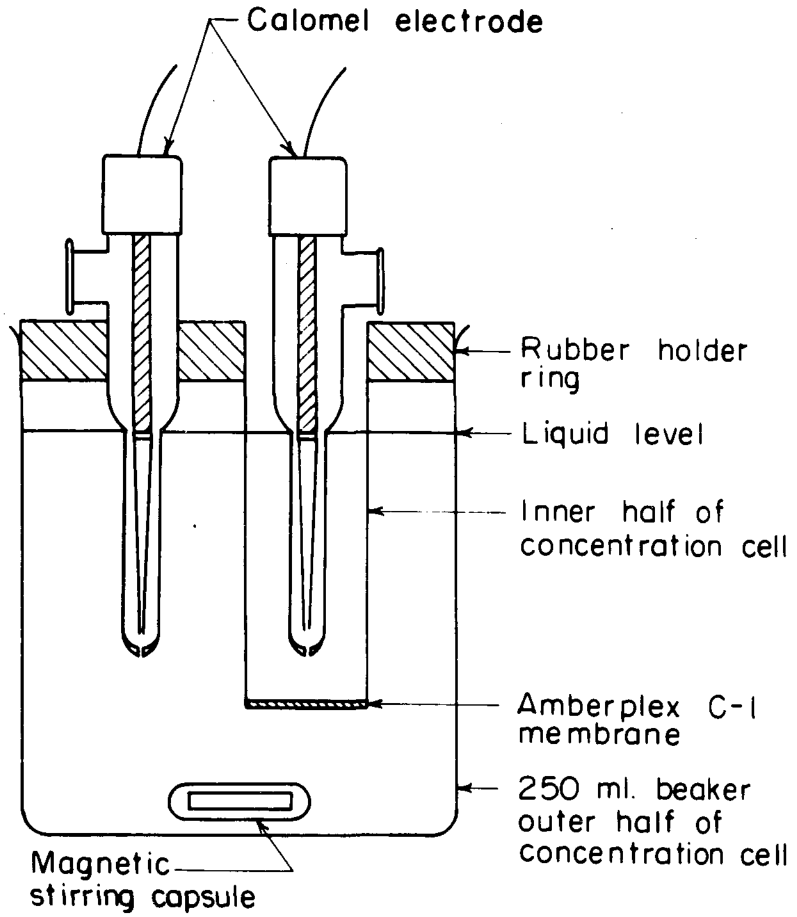
(104) Latimer, W. M., Oxidation Potentials, New York, Prentice-Hall, Inc., 1938



$$\underbrace{\text{Hg} \mid \text{Hg}_2\text{Cl}_2 \mid \begin{matrix}\text{Saturated}\\ \text{KCl}\end{matrix}}_{\text{Calomel Cell}} \Bigg| \begin{matrix}\text{Salt}\\ \text{Solution } a_1\end{matrix} \overset{\text{Membrane}}{\Bigg\|} \begin{matrix}\text{Salt}\\ \text{Solution } a_2\end{matrix} \Bigg| \underbrace{\begin{matrix}\text{Saturated}\\ \text{KCl}\end{matrix} \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg}}_{\text{Calomel Cell}}$$

Fig. 1. The cell used in measuring concentration potentials.

obvious leaks, cracks etc., ten membranes for each cation were characterized. From this number, four were selected with which to make the experimental measurements. The results of these characterization determinations may be seen in Table I. The activities of the solutions used were .003 and .009. Tables II through XI give the data for the preparation of the standard solutions of the various salts.

The following procedure was used to obtain the potential measurements. The membrane, which had been previously mounted and soaked in a saturated solution of the desired cation chloride, was mounted as shown in Figure 1.

The solutions of the electrolytes were prepared in order that the activity ratio, of one to the other would be three to one or multiples of three to one. This ratio was chosen because a significant EMF was developed and still the EMF was not so large that it was difficult to measure with the available instruments. Solutions of the desired activities of a given salt were then placed in the inner and outer compartments of the cell. It was necessary to change these solutions several times before a maximum voltage was reached. The cells apparently reached equilibrium very quickly as a constant voltage was relatively easy to obtain with little drifting. The next reading was obtained by discarding one of the solutions and replacing it with the next activity in line.

Table I

Characterization of Membranes using Concentration Cell
Having Activities of .003 and .009
EMF Measurements with Membranes Saturated with Various
Cations from the Metallic Chlorides.

Salt	Membrane Number										Theory*
Used	1	2	3	4	5	6	7	8	9	10	EMF
NH_4Cl	29.1	25.7	21.5	23.4	19.9	28.0	28.0	25.9	24.0	27.9	28.2
KCl	28.6	25.7	24.2	28.0	26.0	24.0	22.8	26.0	21.3	26.6	28.2
NaCl	24.1	27.1	27.3	21.0	28.7	19.4	24.1	26.4	23.0	24.7	28.2
LiCl	25.9	28.2	28.6	22.1	25.7	26.3	22.3	28.7	20.2	19.9	28.2
$BaCl_2$	14.0	11.1	10.1	8.6	12.2	8.1	13.5	15.0	10.6	14.5	14.1
$CaCl_2$	15.1	12.0	9.0	11.5	13.5	14.0	15.7	10.4	11.3	14.1	14.1
$MgCl_2$	10.1	13.3	12.6	13.1	8.4	13.7	11.6	7.7	11.7	10.4	14.1
$FeCl_2$	14.3	12.6	14.5	16.1	13.9	7.8	10.6	11.8	13.2	9.6	14.1
$CuCl_2$	13.9	8.2	12.2	13.8	10.2	9.3	8.2	10.3	12.8	11.7	14.1
$ZnCl_2$	13.6	10.7	11.5	10.5	13.3	14.2	11.3	13.4	10.6	14.0	14.1

* Maximum potential according to theoretical Nernst equation.

Table II

Data for the Preparation of the Standard Solutions of Ammonium Chloride

Activity of NH_4Cl	Molality of NH_4Cl	Activity * Coefficient
0.001	0.00105	.961
0.003	0.00322	.933
0.009	0.01020	.886
0.027	0.03260	.828
0.081	0.10700	.759
0.243	0.35800	.680

* Temperature of 25°C.

Table III

Data for the Preparation of the Standard Solutions of Lithium Chloride

Activity of LiCl	Molality of LiCl	Activity * Coefficient
0.001	0.00104	.963
0.003	0.00319	.939
0.009	0.01000	.896
0.027	0.03170	.851
0.081	0.10200	.795
0.243	0.32600	.747

* Temperature of 25°C.

Table IV

Data for the Preparation of the Standard Solutions of Potassium Chloride

Activity of KCl	Molality of KCl	Activity * Coefficient
0.001	0.00104	.965
0.003	0.00318	.944
0.009	0.00993	.906
0.027	0.03120	.864
0.081	0.10300	.787
0.243	0.34200	.709

* Temperature of 25°C.

Table V

Data for the Preparation of the Standard Solutions of Sodium Chloride

Activity of NaCl	Molality of NaCl	Activity * Coefficient
0.001	0.00104	.966
0.003	0.00318	.945
0.009	0.00991	.909
0.027	0.03120	.863
0.081	0.10200	.796
0.243	0.33200	.723

* Temperature of 25°C.

Table VI

Data for the Preparation of the Standard Solutions of Barium Chloride

Activity of $BaCl_2$	Molality of $BaCl_2$	Activity * Coefficient
0.001	0.00114	.880
0.003	0.00364	.825
0.009	0.01270	.710
0.027	0.04140	.652
0.081	0.15700	.517
0.243	0.56100	.433

* Temperature of 25°C.

Table VII

Data for the Preparation of the Standard Solutions of Calcium Chloride

Activity of $CaCl_2$	Molality of $CaCl_2$	Activity * Coefficient
0.001	0.00112	.890
0.003	0.00362	.828
0.009	0.01220	.737
0.027	0.04220	.639
0.081	0.15000	.539
0.243	0.51000	.476

* Temperature of 25°C.

Table VIII

Data for the Preparation of the Standard Solutions of Cupric Chloride

Activity of $CuCl_2$	Molality of $CuCl_2$	Activity * Coefficient
0.001	0.00112	.890
0.003	0.00363	.827
0.009	0.01230	.732
0.027	0.04210	.641
0.081	0.14900	.543
0.243	0.52500	.463

* Temperature of 25°C.

Table IX

Data for the Preparation of the Standard Solutions of Ferrous Chloride

Activity of $FeCl_2$	Molality of $FeCl_2$	Activity * Coefficient
0.001	0.00112	.890
0.003	0.00357	.840
0.009	0.01180	.760
0.027	0.03960	.681
0.081	0.13600	.595
0.243	0.43700	.556

* Temperature of 25°C.

Table X

Data for the Preparation of the Standard Solutions of Magnesium Chloride

Activity of $MgCl_2$	Molality of $MgCl_2$	Activity * Coefficient
0.001	0.00106	.944
0.003	0.00330	.908
0.009	0.00115	.782
0.027	0.03980	.678
0.081	0.14900	.544
0.243	0.45900	.529

* Temperature of 25°C.

Table XI

Data for the Preparation of the Standard Solutions of Zinc Chloride

Activity of $ZnCl_2$	Molality of $ZnCl_2$	Activity * Coefficient
0.001	0.00114	.880
0.003	0.00367	.817
0.009	0.01290	.698
0.027	0.04350	.621
0.081	0.15500	.523
0.243	0.55300	.440

* Temperature of 25°C.

Specific Proceedures and Experimental Results

The experimental results of this investigation are concerned with the concentration potentials developed by Amberplex C-1 used as the membrane in a concentration cell. Ammonium chloride, lithium chloride, potassium chloride, sodium chloride, barium chloride, cupric chloride, ferrous chloride, magnesium chloride, and zinc chloride were the salts concerned in determining these potentials. These salts were used in solution alone and in the presence of a protein, gelatin, and in the presence of gelatin plus glucose.

Explanation of Tables. Table XII represents the concentration potentials which were obtained using Amberplex C-1 membranes which were previously soaked in the designated cation chloride. These cation membranes were used with like salt solutions as concentration cells over an activity range of .001 to .243. The various activity ratios in each case were three to one, having been calculated by means of data previously presented in Tables II through XI. The potentials obtained for each individual membrane have been listed under the heading "Potential for Membrane Number." Each number in its electrolyte group represents an individual cation membrane. This number refers to the same cation membrane in all tables of the same electrolyte throughout this investigation. Thus, any values for A_{K^+} recorded for C-1-K membrane 3 refers to membrane number 3 saturated with potassium chloride as used with potassium chloride solutions in Tables I, XII, XIII, XIV, and XV.

The heading "Theoretical Potential", refers to the maximum potential which could occur, provided the theoretical Nernst equation was obeyed. That is, it represents the maximum voltage obtainable for that concentration cell provided the membrane acted as an ideal membrane.

Table XIII records the data obtained using the same Amberplex C-1 membranes previously characterized in Table I and used in the potential measurements recorded in Table XII. In this series however, the activity of the electrolyte of the inner portion of the cell was held constant at 0.001 while the activities in the outer portion of the cell were varied. As before the theoretical potential is the maximum obtainable in each case as calculated by means of the Nernst equation. In the column entitled "average" is listed the average of the four potential readings of that particular cell, using the four membranes whose numbers are listed in the table. These average values are used in plotting the corresponding curves in Figures 2 through 11. The theoretical curve, is of course, plotted from the theoretical values of the potential for the activities present in each case.

Table XIV records the data obtained using the same Amberplex C-1 membranes previously characterized in Table I and used in potential measurements recorded in Tables XII and XIII. In this series the activity of the electrolyte of the inner portion of the

Table XII

Potentials Obtained for Amberplex C-1 Membranes

Activities Internal External	Potential in Millivolts for Membrane Number				Theoretical
$a_{NH_4^+}$	1	6	7	10	
0.001 - 0.003	28.6	28.0	28.0	28.5	28.2
0.009 - 0.003	29.1	28.6	28.0	27.9	28.2
0.009 - 0.027	27.9	28.2	27.8	28.1	28.2
0.081 - 0.027	27.6	28.1	26.0	28.3	28.2
0.081 - 0.243	25.1	28.1	27.5	27.5	28.2
a_{K^+}	1	4	5	10	
0.001 - 0.003	28.2	28.4	30.0	29.0	28.2
0.009 - 0.003	28.6	28.0	26.0	30.3	28.2
0.009 - 0.027	28.0	29.4	24.0	26.6	28.2
0.081 - 0.027	27.1	28.7	23.4	26.1	28.2
0.081 - 0.243	25.5	27.1	26.9	25.3	28.2
a_{Na^+}	2	3	5	8	
0.001 - 0.003	27.4	28.2	28.3	28.1	28.2
0.009 - 0.003	28.5	27.3	28.7	26.4	28.2
0.009 - 0.027	28.0	26.0	27.1	29.4	28.2
0.081 - 0.027	27.1	26.4	27.3	28.7	28.2
0.081 - 0.243	25.5	26.9	26.6	29.1	28.2
a_{Li^+}	2	3	6	8	
0.001 - 0.003	28.1	28.4	29.7	28.6	28.2
0.009 - 0.003	28.2	28.6	26.3	28.7	28.2
0.009 - 0.027	28.0	28.2	25.2	26.9	28.2
0.081 - 0.027	27.6	28.0	26.3	25.2	28.2
0.081 - 0.243	28.0	27.1	20.0	21.4	28.2
$a_{Ba^{++}}$	1	5	8	10	
0.001 - 0.003	14.7	13.5	13.2	13.5	14.1
0.009 - 0.003	14.0	12.7	13.5	14.5	14.1
0.009 - 0.027	14.0	12.4	13.0	13.1	14.1
0.081 - 0.027	13.0	12.0	13.4	13.0	14.1
0.081 - 0.243	12.2	12.5	12.3	12.7	14.1

Table XII Continued

Potentials Obtained for Amberplex C-1 Membranes

Activities Internal External	Potential in Millivolts for Membrane Number				Theoretical
$a_{Ca^{++}}$	1	5	6	10	
0.001 - 0.003	14.5	14.6	14.3	14.0	14.1
0.009 - 0.003	15.1	13.5	14.0	14.1	14.1
0.009 - 0.027	12.0	12.4	14.2	12.0	14.1
0.081 - 0.027	11.4	13.1	11.3	11.9	14.1
0.081 - 0.243	6.4	9.2	10.0	10.5	14.1
$a_{Mg^{++}}$	2	3	4	6	
0.001 - 0.003	14.7	14.0	13.2	14.8	14.1
0.009 - 0.003	13.3	12.6	13.9	13.7	14.1
0.009 - 0.027	14.1	12.0	12.3	13.9	14.1
0.081 - 0.027	12.6	12.0	13.2	12.8	14.1
0.081 - 0.243	10.3	11.4	12.3	10.8	14.1
$a_{Fe^{++}}$	1	3	5	9	
0.001 - 0.003	14.5	14.4	13.2	13.3	14.1
0.009 - 0.003	14.3	14.5	13.9	13.2	14.1
0.009 - 0.027	13.4	14.1	12.6	12.8	14.1
0.081 - 0.027	12.4	12.2	11.1	12.8	14.1
0.081 - 0.243	12.6	11.7	10.6	10.1	14.1
$a_{Cu^{++}}$	1	3	4	9	
0.001 - 0.003	14.2	14.1	14.6	14.3	14.1
0.009 - 0.003	13.9	12.2	13.8	12.8	14.1
0.009 - 0.027	13.5	9.2	12.6	13.2	14.1
0.081 - 0.027	12.4	12.3	12.6	11.2	14.1
0.081 - 0.243	11.8	7.1	9.5	10.0	14.1
$a_{Zn^{++}}$	1	6	8	10	
0.001 - 0.003	14.3	14.2	15.0	14.2	14.1
0.009 - 0.003	13.6	14.2	13.4	14.0	14.1
0.009 - 0.027	13.3	13.7	12.5	13.4	14.1
0.081 - 0.027	13.5	13.5	13.7	14.0	14.1
0.081 - 0.243	10.1	12.1	13.6	12.5	14.1

cell was held constant at 0.001 while the electrolyte activities in the outer portion of the cell were varied. However, one per cent purified gelatin was added to the external portion of the cell. These data make it possible to determine the effect a protein of this concentration has on the individual ion activities in the range investigated. The average values are graphically represented in curves in Figures 2 through 11.

Table XV records the data obtained using the same Amberplex C-1 membranes previously characterized in Table I and used in potential measurements recorded in Tables XII, XIII, and XIV. In this series the activity of the electrolyte of the inner portion of the cell was held constant at 0.001 while the electrolyte activities in the outer portion of the cell were varied. However, twenty-two per cent purified gelatin and one-tenth per cent U.S.P. glucose were added to the external portion of the cell. These data make it possible to determine the effect of a protein and glucose of these concentrations on the individual ion activities in the range investigated. This range of protein and glucose was chosen because it roughly represents the protein and sugar present in an animal body fluid, in this case, human blood. The average values are graphically represented in curves in Figures 2 through 11.

Tables XVI through XXV represent the activity and relative activities of the solutions. The measured activities of the pure solutions have been compared with the theoretical activities to obtain a relative activity. In the case of the gelatin solutions the

Table XIII

Potentials Obtained from Concentration Cells Using Amberplex C-1 Membranes

Activities Internal External	Potential in Millivolts for Membrane Number				Average	Theoretical
$a_{NH_4^+}$	1	6	7	10		
0.001 - 0.003	28.6	28.0	28.0	28.5	28.3	28.2
0.001 - 0.009	51.8	51.4	56.4	57.9	55.0	56.4
0.001 - 0.027	80.9	81.5	81.7	83.6	81.9	84.6
0.001 - 0.081	110.2	110.4	108.2	109.5	109.5	112.8
0.001 - 0.243	129.0	136.1	130.4	131.2	131.2	141.0
a_{K^+}	1	4	5	10		
0.001 - 0.003	28.2	28.4	28.0	29.0	28.5	28.2
0.001 - 0.009	54.2	54.0	57.1	56.7	55.5	56.4
0.001 - 0.027	84.1	86.4	84.2	82.7	84.4	84.6
0.001 - 0.081	108.0	103.4	109.7	111.8	108.3	112.8
0.001 - 0.243	129.9	133.8	125.9	117.8	126.8	141.0
a_{Na^+}	2	3	5	8		
0.001 - 0.003	27.4	28.3	28.3	28.1	28.0	28.2
0.001 - 0.009	55.0	59.3	49.2	56.7	55.0	56.4
0.001 - 0.027	88.1	83.6	86.4	79.3	84.4	84.6
0.001 - 0.081	114.4	116.4	106.0	101.4	109.6	112.8
0.001 - 0.243	110.9	143.0	108.6	114.6	125.5	141.0
a_{Li^+}	2	3	6	8		
0.001 - 0.003	28.1	28.4	29.7	28.6	28.2	28.2
0.001 - 0.009	55.7	54.5	49.7	59.6	55.0	56.4
0.001 - 0.027	86.8	79.4	82.8	89.8	84.7	84.6
0.001 - 0.081	102.1	103.6	109.7	109.7	106.3	112.8
0.001 - 0.243	115.9	128.7	117.9	117.5	120.0	141.0
$a_{Ba^{++}}$	1	5	8	10		
0.001 - 0.003	14.7	13.5	13.2	13.5	13.7	14.1
0.001 - 0.009	26.8	26.6	28.2	29.7	27.8	28.2
0.001 - 0.027	48.3	37.4	36.3	38.4	40.1	42.3
0.001 - 0.081	51.8	57.8	51.9	59.4	55.2	56.4
0.001 - 0.243	65.2	51.8	63.6	63.6	61.1	70.5

Table XIII Continued

Potentials Obtained from Concentration Cells Using
Amberplex C-1 Membranes

Activities Internal External	Potential in Millivolts for Membrane Number				Average	Theoretical
$a_{Ca^{++}}$	1	5	6	10		
0.001 - 0.003	14.5	14.6	14.3	14.0	14.4	14.1
0.001 - 0.009	26.3	29.3	28.6	24.9	27.3	28.2
0.001 - 0.027	39.2	44.3	39.7	36.8	40.0	42.3
0.001 - 0.081	51.3	51.0	50.1	58.6	52.8	56.4
0.001 - 0.243	68.2	65.2	56.6	56.8	61.8	70.5
$a_{Mg^{++}}$	2	3	4	6		
0.001 - 0.003	14.7	14.0	13.2	14.2	14.0	14.1
0.001 - 0.009	28.5	27.2	28.4	30.7	28.7	28.2
0.001 - 0.027	35.2	39.3	37.2	36.3	37.0	42.3
0.001 - 0.081	54.4	44.3	50.0	49.3	49.0	56.4
0.001 - 0.243	67.4	50.8	55.3	52.1	56.4	70.5
$a_{Fe^{++}}$	1	3	5	9		
0.001 - 0.003	14.5	14.8	13.2	13.3	14.0	14.1
0.001 - 0.009	27.1	27.4	29.0	28.2	27.9	28.2
0.001 - 0.027	42.2	43.6	41.5	40.7	42.0	42.3
0.001 - 0.081	54.8	52.7	56.9	50.7	53.8	56.4
0.001 - 0.243	62.8	66.3	59.7	58.5	61.8	70.5
$a_{Cu^{++}}$	1	3	4	9		
0.001 - 0.003	14.2	14.1	14.6	14.3	14.3	14.1
0.001 - 0.009	29.0	28.6	26.9	28.0	28.1	28.2
0.001 - 0.027	45.7	38.3	38.1	42.3	41.1	42.3
0.001 - 0.081	51.3	60.8	54.4	46.4	53.2	54.4
0.001 - 0.243	70.7	60.6	58.8	56.8	61.7	70.5
$a_{Zn^{++}}$	1	6	8	10		
0.001 - 0.003	14.3	14.2	15.0	14.2	14.4	14.1
0.001 - 0.009	30.7	25.5	26.9	29.1	28.1	28.2
0.001 - 0.027	37.4	47.3	39.5	33.7	39.5	42.3
0.001 - 0.081	59.8	42.1	43.6	59.7	51.3	54.4
0.001 - 0.243	60.7	51.1	61.9	59.7	58.4	70.5

Table XIV

Potentials Obtained from Concentration Cells Using Amberplex C-1 Membranes in the Presence of 1 Per Cent Gelatin

Activities Internal External	Potential in Millivolts for Membrane Number				Average	Theoretical
$a_{NH_4^+}$	1	6	7	10		
0.001 - 0.003	28.4	28.0	27.9	28.3	28.2	28.2
0.001 - 0.009	51.7	52.6	56.9	56.7	53.2	56.4
0.001 - 0.027	80.5	81.3	81.5	83.3	81.6	84.6
0.001 - 0.081	109.5	109.0	106.5	107.0	108.0	112.8
0.001 - 0.243	125.8	125.7	121.4	123.2	124.0	141.0
a_{K^+}	1	4	5	10		
0.001 - 0.003	28.0	28.1	28.0	29.5	28.4	28.2
0.001 - 0.009	52.7	53.6	56.9	55.7	54.0	56.4
0.001 - 0.027	84.0	85.9	83.7	82.0	83.9	84.6
0.001 - 0.081	107.1	102.9	109.0	110.9	107.5	112.8
0.001 - 0.243	120.1	120.6	113.4	116.0	117.4	141.0
a_{Na^+}	2	3	5	8		
0.001 - 0.003	26.9	28.4	29.2	28.0	28.1	28.2
0.001 - 0.009	54.1	54.1	51.6	56.0	54.0	56.4
0.001 - 0.027	86.3	78.8	81.9	88.6	83.9	84.6
0.001 - 0.081	106.3	105.3	111.6	110.7	108.5	112.8
0.001 - 0.243	117.7	121.8	114.6	116.7	118.2	141.0
a_{Li^+}	2	3	6	8		
0.001 - 0.003	27.9	27.4	28.1	28.0	27.9	28.2
0.001 - 0.009	54.2	58.6	49.9	56.1	54.7	56.4
0.001 - 0.027	87.5	83.1	85.3	78.4	83.6	84.6
0.001 - 0.081	112.5	114.8	105.0	101.3	108.4	112.8
0.001 - 0.243	100.2	126.9	119.5	114.9	115.1	141.0
$a_{Ba^{++}}$	1	5	8	10		
0.001 - 0.003	14.6	13.1	13.7	13.0	13.8	14.1
0.001 - 0.009	25.4	26.7	27.4	28.0	26.9	28.2
0.001 - 0.027	47.8	36.5	36.7	36.1	39.3	42.3
0.001 - 0.081	50.8	55.6	50.4	56.5	53.3	56.4
0.001 - 0.243	63.1	50.3	60.0	59.6	58.3	70.5

Table XIV Continued

Potentials Obtained from Concentration Cells Using Amberplex C-1 Membranes in the Presence of 1 Per Cent Gelatin

Activities Internal External	Potential in Millivolts for Membrane Number				Average	Theoretical
$a_{Ca^{++}}$	1	5	6	10		
0.001 - 0.003	14.3	14.2	14.8	13.3	14.2	14.1
0.001 - 0.009	25.6	27.2	27.6	24.9	26.5	28.2
0.001 - 0.027	37.9	40.3	41.0	37.2	39.1	42.3
0.001 - 0.081	50.7	48.2	47.6	50.9	49.4	56.4
0.001 - 0.243	64.4	60.8	54.5	52.3	58.0	70.5
$a_{Mg^{++}}$	2	3	4	6		
0.001 - 0.003	12.2	14.8	12.9	14.1	13.5	14.1
0.001 - 0.009	26.1	27.8	26.4	30.2	27.6	28.2
0.001 - 0.027	30.3	39.7	38.0	32.0	56.0	42.3
0.001 - 0.081	40.2	40.2	35.3	39.4	38.8	56.4
0.001 - 0.243	46.0	45.8	40.8	39.4	43.0	70.5
$a_{Fe^{++}}$	1	3	5	9		
0.001 - 0.003	14.3	14.7	13.3	13.7	14.0	14.1
0.001 - 0.009	27.6	27.6	28.5	27.9	27.9	28.2
0.001 - 0.027	39.3	39.6	39.5	37.0	38.9	42.3
0.001 - 0.081	45.8	45.4	48.0	43.4	45.7	56.4
0.001 - 0.243	55.7	57.0	55.5	50.1	54.6	70.5
$a_{Cu^{++}}$	1	3	4	9		
0.001 - 0.003	14.0	13.8	14.1	13.9	14.0	14.1
0.001 - 0.009	28.6	28.9	27.7	28.0	28.3	28.2
0.001 - 0.027	45.2	38.2	37.7	41.9	40.8	42.3
0.001 - 0.081	50.3	58.2	53.5	44.8	51.7	54.4
0.001 - 0.243	65.7	55.9	55.7	52.7	57.5	70.5
$a_{Zn^{++}}$	1	6	8	10		
0.001 - 0.003	13.8	13.4	13.1	13.1	13.4	14.1
0.001 - 0.009	25.6	27.4	27.1	24.9	26.5	28.2
0.001 - 0.027	35.7	42.8	39.3	38.3	39.0	42.3
0.001 - 0.081	50.6	40.3	40.0	49.4	45.1	54.4
0.001 - 0.243	56.1	48.3	43.7	51.5	49.9	70.5

Table XV

Potentials Obtained from Concentration Cells Using Amberplex C-1 Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Activities Internal External	Potential in Millivolts for Membrane Number				Average	Theoretical
$a_{NH_4^+}$	1	6	7	10		
0.001 - 0.003	25.8	25.7	25.4	24.2	25.3	28.2
0.001 - 0.009	43.9	44.0	49.3	50.9	47.0	56.4
0.001 - 0.027	75.7	75.8	74.0	77.3	75.7	84.6
0.001 - 0.081	100.6	100.9	97.1	98.7	99.2	112.8
0.001 - 0.243	116.1	115.3	110.4	114.7	114.1	141.0
a_{K^+}	1	4	5	10		
0.001 - 0.003	25.8	24.8	25.6	25.1	25.3	28.2
0.001 - 0.009	50.0	49.2	50.6	51.0	50.2	56.4
0.001 - 0.027	79.8	78.4	78.1	76.1	78.1	84.6
0.001 - 0.081	102.1	99.9	103.7	103.8	102.4	112.8
0.001 - 0.243	114.3	117.3	120.6	109.3	115.4	141.0
a_{Na^+}	2	3	5	8		
0.001 - 0.003	22.3	21.3	20.6	21.7	21.5	28.2
0.001 - 0.009	49.6	50.7	45.8	50.1	49.1	56.4
0.001 - 0.027	75.7	72.9	73.7	79.0	75.3	84.6
0.001 - 0.081	91.4	89.4	94.1	96.4	92.8	112.8
0.001 - 0.243	99.9	96.3	99.3	98.6	98.5	141.0
a_{Li^+}	2	3	6	8		
0.001 - 0.003	25.8	24.5	24.7	25.7	25.2	28.2
0.001 - 0.009	50.5	51.4	46.8	50.3	49.8	56.4
0.001 - 0.027	80.2	79.5	79.0	70.9	77.4	84.6
0.001 - 0.081	101.9	100.9	92.5	90.7	96.5	112.8
0.001 - 0.243	98.0	114.5	91.1	99.6	100.8	141.0
$a_{Ba^{++}}$	1	5	8	10		
0.001 - 0.003	13.3	13.3	13.5	12.1	13.1	14.1
0.001 - 0.009	24.5	24.3	24.7	25.0	24.6	28.2
0.001 - 0.027	46.8	35.6	33.9	34.7	37.8	42.3
0.001 - 0.081	47.5	50.5	46.7	51.5	49.1	56.4
0.001 - 0.243	60.9	47.2	47.8	55.7	52.9	70.5

Table XV Continued

Potentials Obtained from Concentration Cells Using Amberplex C-1 Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Activities Internal External	Potential in Millivolts for Membrane Number				Average	Theoretical
$a_{Ca^{++}}$	1	5	6	10		
0.001 - 0.003	14.1	14.0	14.0	13.1	13.8	14.1
0.001 - 0.009	25.2	27.3	27.3	25.0	26.2	28.2
0.001 - 0.027	35.1	40.0	34.1	34.1	35.8	42.3
0.001 - 0.081	47.1	44.6	43.6	46.2	45.4	56.4
0.001 - 0.243	59.9	55.2	46.3	47.6	50.3	70.5
$a_{Mg^{++}}$	2	3	4	6		
0.001 - 0.003	11.3	10.1	11.8	10.2	10.9	14.1
0.001 - 0.009	24.2	24.6	23.9	24.2	24.2	28.2
0.001 - 0.027	30.6	32.5	29.7	29.8	30.7	42.3
0.001 - 0.081	30.6	25.6	29.9	30.8	29.2	56.4
0.001 - 0.243	32.6	35.4	24.3	37.4	34.9	70.5
$a_{Fe^{++}}$	1	3	5	9		
0.001 - 0.003	10.0	11.1	9.5	11.1	10.4	14.1
0.001 - 0.009	24.5	23.7	25.9	23.3	24.4	28.2
0.001 - 0.027	30.2	30.5	30.9	33.6	31.3	42.3
0.001 - 0.081	34.8	35.3	35.7	34.7	35.1	56.4
0.001 - 0.243	35.7	35.6	35.6	35.1	35.5	70.5
$a_{Cu^{++}}$	1	3	4	9		
0.001 - 0.003	13.7	13.6	13.6	13.5	13.6	14.1
0.001 - 0.009	27.4	27.8	27.7	27.0	27.5	28.2
0.001 - 0.027	41.0	34.9	34.7	37.4	37.0	42.3
0.001 - 0.081	44.7	50.8	48.9	40.6	46.3	54.4
0.001 - 0.243	54.4	51.0	48.6	44.8	49.7	70.5
$a_{Zn^{++}}$	1	6	8	10		
0.001 - 0.003	10.6	11.6	11.1	10.7	11.0	14.1
0.001 - 0.009	20.6	18.5	20.7	19.2	19.8	28.2
0.001 - 0.027	29.8	27.7	30.1	29.7	29.3	42.3
0.001 - 0.081	31.4	35.3	31.8	32.8	32.8	54.4
0.001 - 0.243	35.5	37.9	39.4	36.6	37.4	70.5

measured activities have been compared to the measured activities of the pure solutions assuming them to be the maximum for that series of membranes. This makes it possible to compare the average performance of a series of membranes for a given electrolyte.

The Reliability of the Measurements

In pure solutions the inherent error resulting from unavoidable variation of solution composition is estimated to be of the order of ± 0.10 millivolt. Asymmetry potential, while practically eliminated is believed to have a maximum of ± 0.20 millivolt. The reproducibility of the individual measurements is ± 0.20 millivolt. Therefore, the pure solution measurements may be in error ± 0.50 millivolt. In solutions to which contaminants were added the error might be appreciably greater due to unexpected effects. The variation in most cases is believed to be much less than the maximum error.

V. SIGNIFICANCE OF EXPERIMENTAL RESULTS

Figures 2 through 11 represent graphically the values recorded in Tables XII through XV. Each electrolyte will be considered and discussed.

Figure 2 and Table XVI represent the results obtained with ammonium chloride as the electrolyte. They indicate that the potential of the pure solution approaches the theoretical maximum only in the most dilute solution. One per cent gelatin has little effect on the activity of the ammonium ion in concentrations of less than one-tenth molal. The high concentration of gelatin and glucose lowers the activity of the ammonium ion progressively as the ion concentration increases. The closest approach to the theoretical activity appears in the case of the most dilute solution.

Figure 3 and Table XVII represent the results obtained with potassium chloride as the electrolyte. These data indicate the pure solution approaches the theoretical potentials and activities in the case of the three more dilute solutions. One per cent gelatin has little or no effect on potassium ion activity except in the most concentrated solutions.

High concentrations of gelatin plus glucose adversely affect the potassium ion activity at all concentrations but has more effect at higher concentrations.

Figure 4 and Table XVIII show that the theoretical potential is approached with the C-1-Na membranes at external cell activities

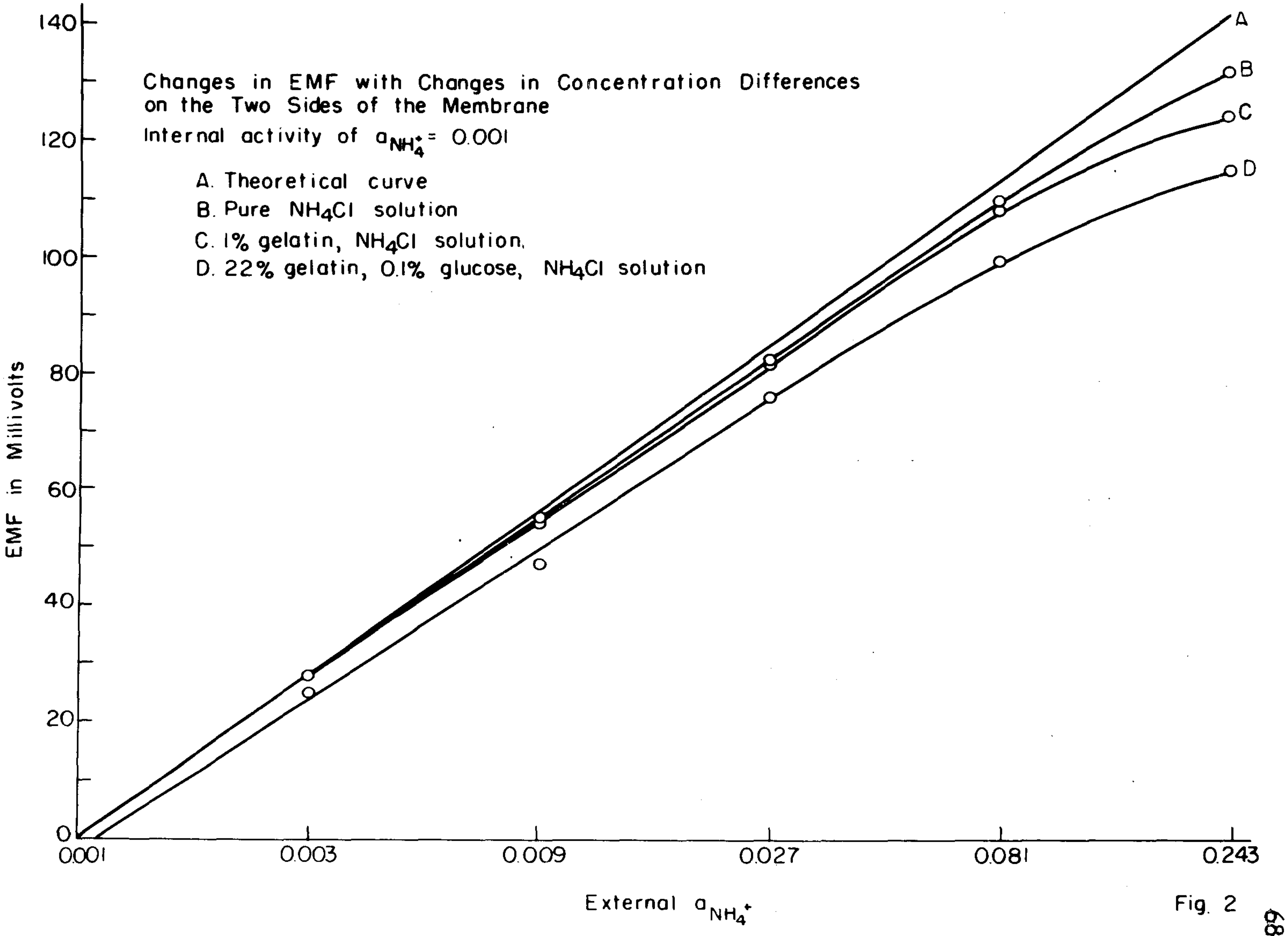

Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane
Internal activity of $a_{NH_4^+}$ = 0.001
A. Theoretical curve
B. Pure NH_4Cl solution
C. 1% gelatin, NH_4Cl solution.
D. 22% gelatin, 0.1% glucose, NH_4Cl solution
EMF in Millivolts
0
20
40
60
80
100
120
140
0.001
0.003
0.009
0.027
0.081
0.243
External $a_{NH_4^+}$
A
B
C
D

Fig. 2

Table XVI

A

Determination of Ammonium-Ion Activities in Concentration Cells Using Amberplex C-1-NH_4 Membranes

Calculated Activities of Electrolyte $a_{NH_4^+}$ Internal External	Measured Activity of External Half of Cell	Relative Ammonium-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00301	1.00
0.001 - 0.009	0.00852	0.95
0.001 - 0.027	0.0243	0.90
0.001 - 0.081	0.0713	0.88
0.001 - 0.243	0.166	0.68

B

Determination of Ammonium-Ion Activities in Concentration Cells Using Amberplex C-1-NH_4 Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte $a_{NH_4^+}$ Internal External	Measured Activity of External Half of Cell	Relative Sodium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00300	1.00
0.001 - 0.009	0.00820	0.96
0.001 - 0.027	0.0240	0.99
0.001 - 0.081	0.0072	0.94
0.001 - 0.243	0.125	0.75

C

Determination of Ammonium-Ion Activities in Concentration Cells Using Amberplex C-1-NH_4 Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Calculated Activities of Electrolyte $a_{NH_4^+}$ Internal External	Measured Activity of External Half of Cell	Relative Sodium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00268	0.89
0.001 - 0.009	0.00624	0.73
0.001 - 0.027	0.0191	0.79
0.001 - 0.081	0.0477	0.67
0.001 - 0.243	0.0853	0.51

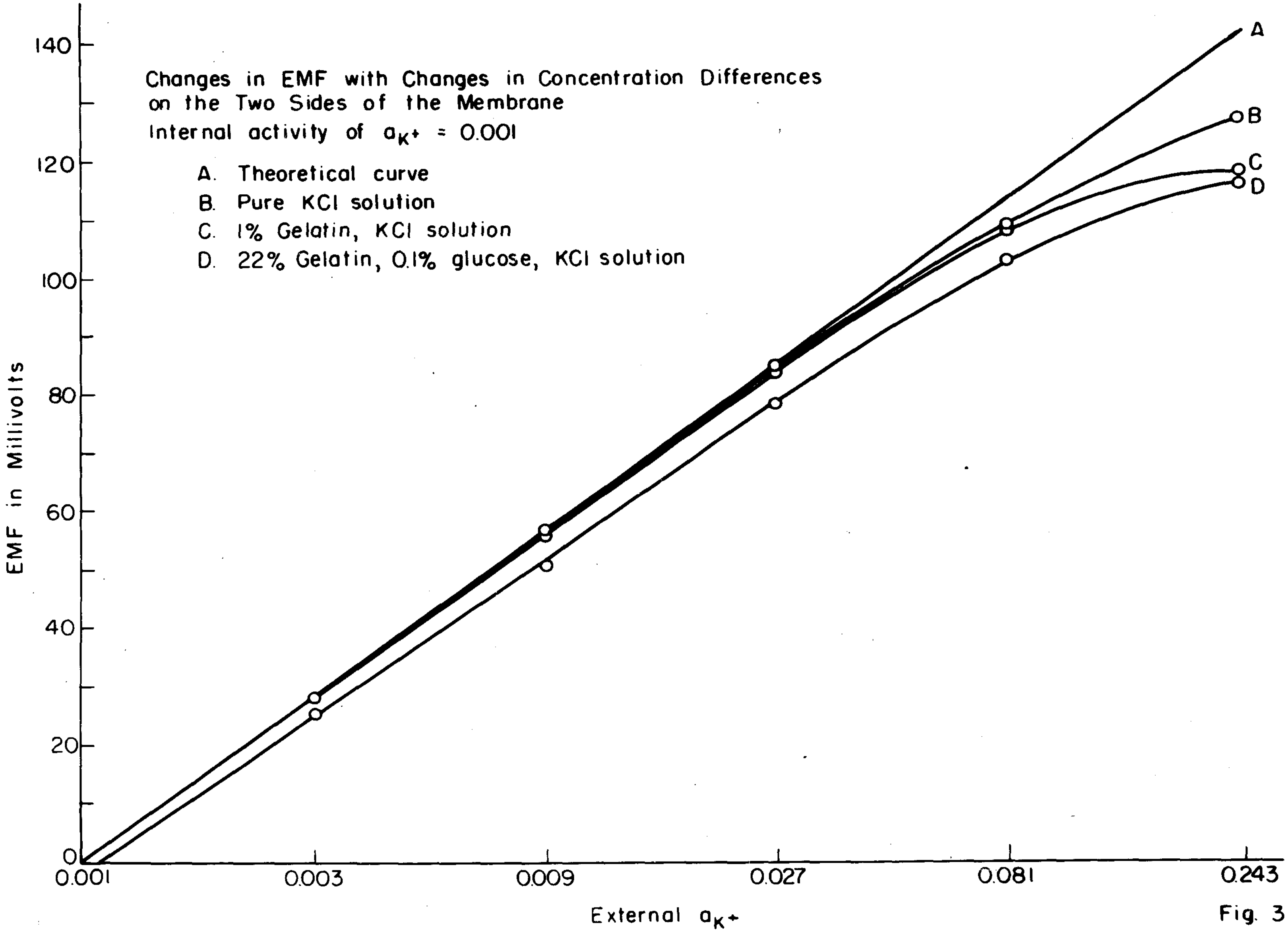

Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane
Internal activity of a_{K^+} = 0.001
A. Theoretical curve
B. Pure KCl solution
C. 1% Gelatin, KCl solution
D. 22% Gelatin, 0.1% glucose, KCl solution
A
B
C
D
EMF in Millivolts
140
120
100
80
60
40
20
0
0.001
0.003
0.009
0.027
0.081
0.243
External a_{K^+}

Fig. 3

Table XVII

A

Determination of Potassium-Ion Activities in Concentration Cells Using Amberplex C-1-K Membranes

Calculated Activities of Electrolyte a_{K^+} Internal External	Measured Activity of External Half of Cell	Relative Potassium-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00304	1.01
0.001 - 0.009	0.00869	0.97
0.001 - 0.027	0.0268	0.99
0.001 - 0.081	0.0680	0.84
0.001 - 0.243	0.140	0.58

B

Determination of Potassium-Ion Activities in Concentration Cells Using Amberplex C-1-K Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte a_{K^+} Internal External	Measured Activity of External Half of Cell	Relative Potassium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00302	0.99
0.001 - 0.009	0.00859	0.99
0.001 - 0.027	0.0263	1.00
0.001 - 0.081	0.0659	0.97
0.001 - 0.243	0.0969	0.69

C

Determination of Potassium-Ion Activities in Concentration Cells Using Amberplex C-1-K Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Calculated Activities of Electrolyte a_{K^+} Internal External	Measured Activity of External Half of Cell	Relative Potassium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00268	0.88
0.001 - 0.009	0.00707	0.81
0.001 - 0.027	0.0210	0.78
0.001 - 0.081	0.0540	0.79
0.001 - 0.243	0.0897	0.64

of 0.003 and 0.027. The external cell activity of 0.009 shows an average deviation of 5 per cent from theoretical while the two more concentrated solutions show deviations of 12 and 46 per cent from theoretical. One per cent gelatin appears to have no effect on the activity of the most dilute solution but has a progressively detrimental effect as the concentration increases. Twenty-two per cent gelatin and 0.1 per cent glucose appears to reduce the activity of the sodium ion greatly even at low concentrations and becomes progressively more detrimental as the concentration increases.

Figure 5 and Table XIX represent the results obtained using C-1-Li membranes. Theoretical potentials are reached at external cell activities of 0.003 and 0.027. The external cell activity of 0.009 shows an average deviation of 5 per cent from theoretical. External cell activities of 0.081 and 0.243 show average deviations of 22 and 66 per cent respectively. One per cent gelatin appears to have practically no effect on the activity of the lithium ion except in the most concentrated solution. The more concentrated solution of gelatin glucose is detrimental to the activity of the lithium ion at all concentrations, especially the higher ones.

Figure 6 and Table XX represent the data obtained with membranes C-1-Ba. The potentials approach the theoretical only at activities of 0.003 and 0.009 in the pure solutions and 0.003 in the presence of gelatin. The response becomes progressively worse with increase in concentration. Twenty-two per cent gelatin and 0.1 per cent glucose presents a curve and relative activity that is close to

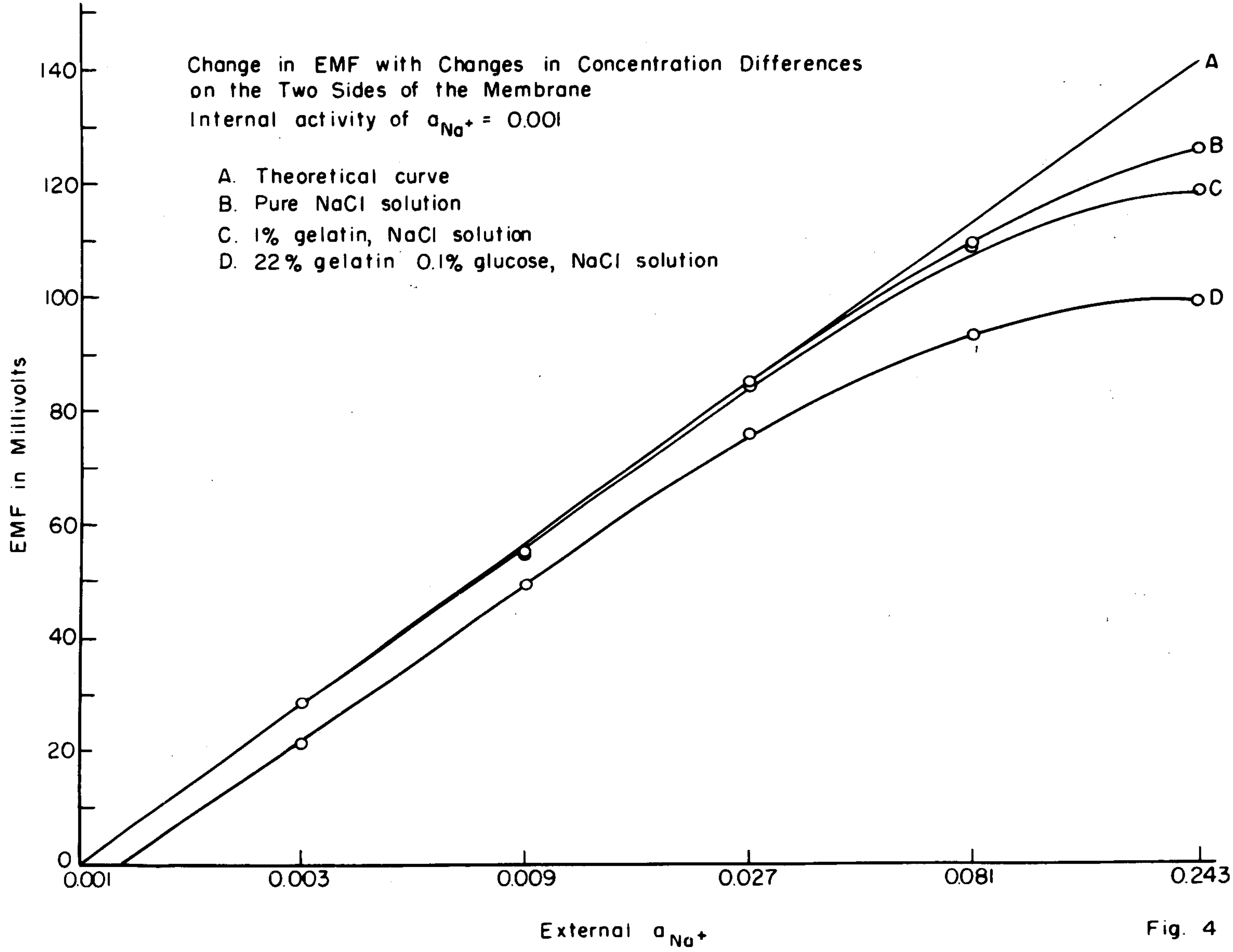

Change in EMF with Changes in Concentration Differences on the Two Sides of the Membrane
Internal activity of a_{Na^+} = 0.001
A. Theoretical curve
B. Pure NaCl solution
C. 1% gelatin, NaCl solution
D. 22% gelatin 0.1% glucose, NaCl solution
A
B
C
D
EMF in Millivolts
140
120
100
80
60
40
20
0
0.001
0.003
0.009
0.027
0.081
0.243
External a_{Na^+}

Fig. 4

Table XVIII

A

Determination of Sodium-Ion Activities in Concentration Cells Using Amberplex C-1-Na Membranes

Calculated Activities of Electrolyte a_{Na^+} Internal External	Measured Activity of External Half of Cell	Relative Sodium-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00298	0.99
0.001 - 0.009	0.00853	0.95
0.001 - 0.027	0.0268	0.99
0.001 - 0.081	0.0715	0.88
0.001 - 0.243	0.033	0.54

B

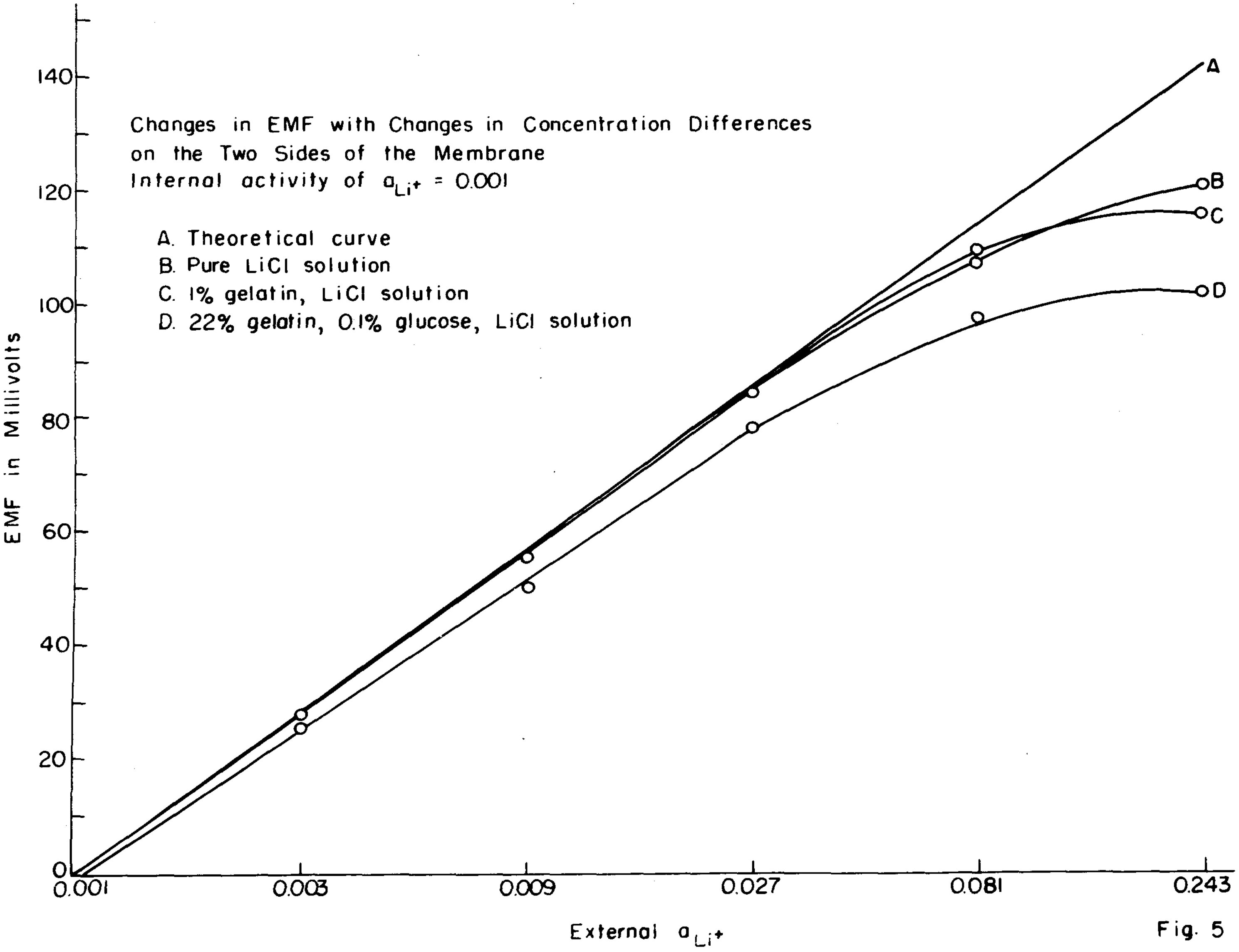
Determination of Sodium-Ion Activities in Concentration Cells Using Amberplex C-1-Na Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte a_{Na^+} Internal External	Measured Activity of External Half of Cell	Relative Sodium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00299	1.00
0.001 - 0.009	0.00820	0.96
0.001 - 0.027	0.0263	0.98
0.001 - 0.081	0.0685	0.96
0.001 - 0.243	0.100	0.75

C

Determination of Sodium-Ion Activities in Concentration Cells Using Amberplex C-1-Na Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Calculated Activities of Electrolyte a_{Na^+} Internal External	Measured Activity of External Half of Cell	Relative Sodium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00231	0.78
0.001 - 0.009	0.00677	0.79
0.001 - 0.027	0.0188	0.70
0.001 - 0.081	0.0464	0.65
0.001 - 0.243	0.0372	0.28


Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane

Internal activity of $a_{Li^+} = 0.001$

A. Theoretical curve
B. Pure LiCl solution
C. 1% gelatin, LiCl solution
D. 22% gelatin, 0.1% glucose, LiCl solution

Fig. 5

Table XIX

A

Determination of Lithium-Ion Activities in Concentration Cells Using Amberplex C-1-Li Membranes

Calculated Activities of Electrolyte a_{Li^+} Internal External	Measured Activity of External Half of Cell	Relative Lithium-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00300	1.00
0.001 - 0.009	0.00852	0.95
0.001 - 0.027	0.0271	1.00
0.001 - 0.081	0.0629	0.78
0.001 - 0.243	0.107	0.44

B

Determination of Lithium-Ion Activities in Concentration Cells Using Amberplex C-1-Li Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte a_{Li^+} Internal External	Measured Activity of External Half of Cell	Relative Lithium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00297	0.99
0.001 - 0.009	0.00842	0.99
0.001 - 0.027	0.0260	0.96
0.001 - 0.081	0.0683	1.08
0.001 - 0.243	0.0886	0.83

C

Determination of Lithium-Ion Activities in Concentration Cells Using Amberplex C-1-Li Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

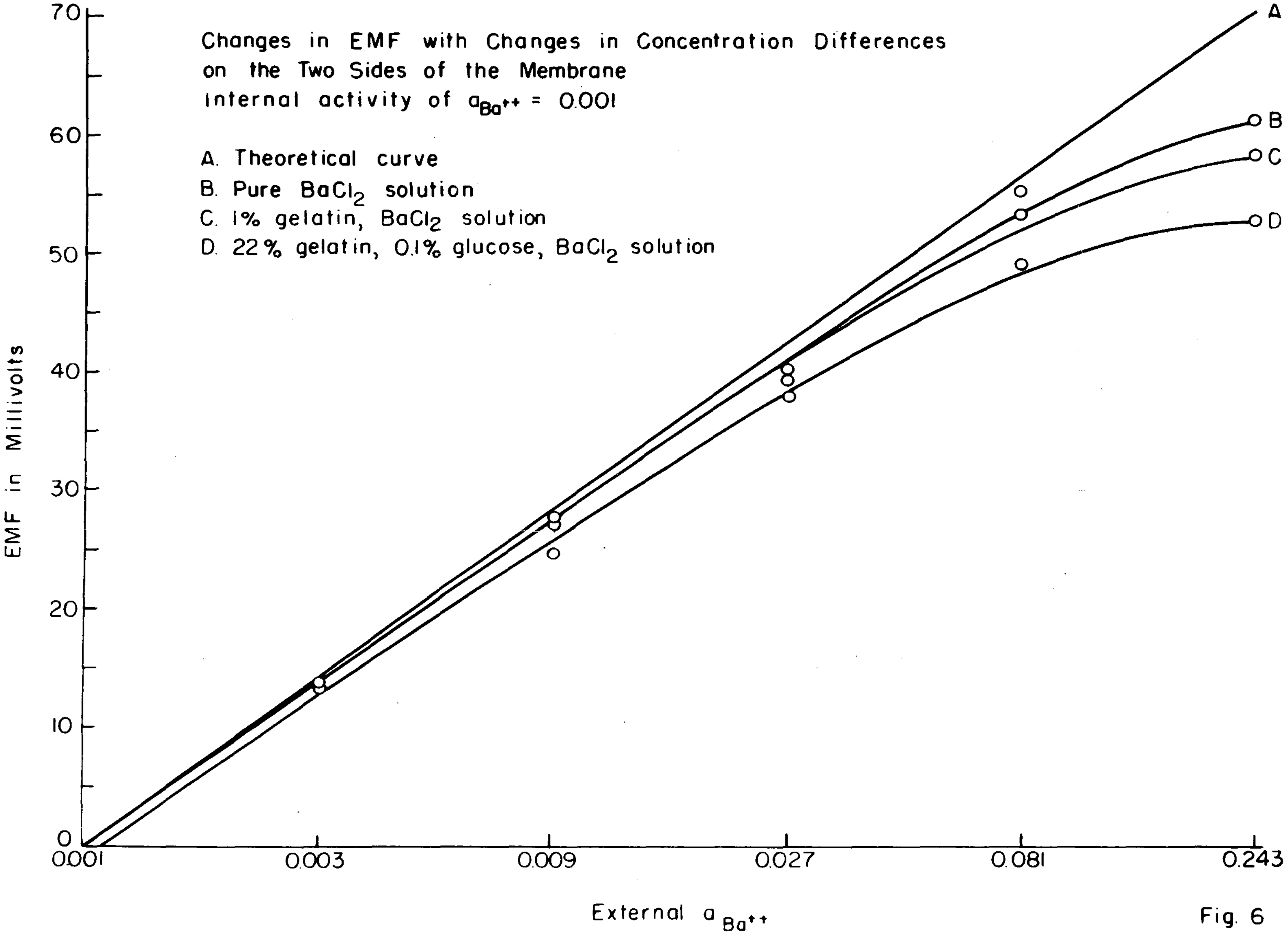
Calculated Activities of Electrolyte a_{Li^+} Internal External	Measured Activity of External Half of Cell	Relative Lithium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00267	0.89
0.001 - 0.009	0.00696	0.82
0.001 - 0.027	0.0204	0.75
0.001 - 0.081	0.0429	0.68
0.001 - 0.243	0.0508	0.47

that of the pure solution at an activity of 0.003. The remainder of the potentials deviate progressively as the concentration increases.

Figure 7 and Table XXI show that the average potential obtained with calcium chloride and the C-1-Ca membranes is slightly above the theoretical at an activity of 0.003. This is true in both the pure solution and the solution containing 1 per cent gelatin. At this concentration the potential also approaches theoretical in the presence of twenty-two per cent gelatin and 0.1 per cent glucose. All the rest of the average deviate progressively as the concentrations increase. The pure solution deviating less than the 1 per cent gelatine and twenty-two per cent gelatin, 0.1 per cent glucose solution and the 1 per cent gelatin deviating less than the twenty-two per cent gelatin, 0.1 per cent glucose solutions.

Figure 8 and Table XXII represents the data obtained with C-1-Mg membranes in the presence of magnesium chloride. As with other electrolytes the theoretical potential is approached at activities of 0.003 and 0.009. With all other concentrations in both pure solutions and in the presence of the higher protein content the average results deviate widely but regularly from the expected.

Figure 9 and Table XXIII. The response of the C-1-Fe membranes in the presence of ferrous chloride is very good at the lower concentrations in both the pure solution and in the presence of 1.0 per cent gelatin. The results in the presence of 1.0 per cent



Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane

Internal activity of $a_{Ba^{++}}$ = 0.001

Fig. 6

Table XX

A

Determination of Barium-Ion Activities in Concentration Cells Using Amberplex C-1-Ba Membranes

Calculated Activities of Electrolyte $a_{Ba^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Barium-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00291	0.97
0.001 - 0.009	0.00876	0.97
0.001 - 0.027	0.0229	0.85
0.001 - 0.081	0.0743	0.92
0.001 - 0.243	0.118	0.49

B

Determination of Barium-Ion Activities in Concentration Cells Using Amberplex C-1-Ba Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte $a_{Ba^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Barium-Ion Activity: Measured/ Meas. from Pure Solution
0.001 - 0.003	0.00294	1.03
0.001 - 0.009	0.00816	.93
0.001 - 0.027	0.0215	.94
0.001 - 0.081	0.0644	.86
0.001 - 0.243	0.0947	.80

C

Determination of Barium-Ion Activities in Concentration Cells Using Amberplex C-1-Ba Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Calculated Activities of Electrolyte $a_{Ba^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Barium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00275	0.95
0.001 - 0.009	0.00682	0.78
0.001 - 0.027	0.0191	0.83
0.001 - 0.081	0.0462	0.62
0.001 - 0.243	0.0621	0.53

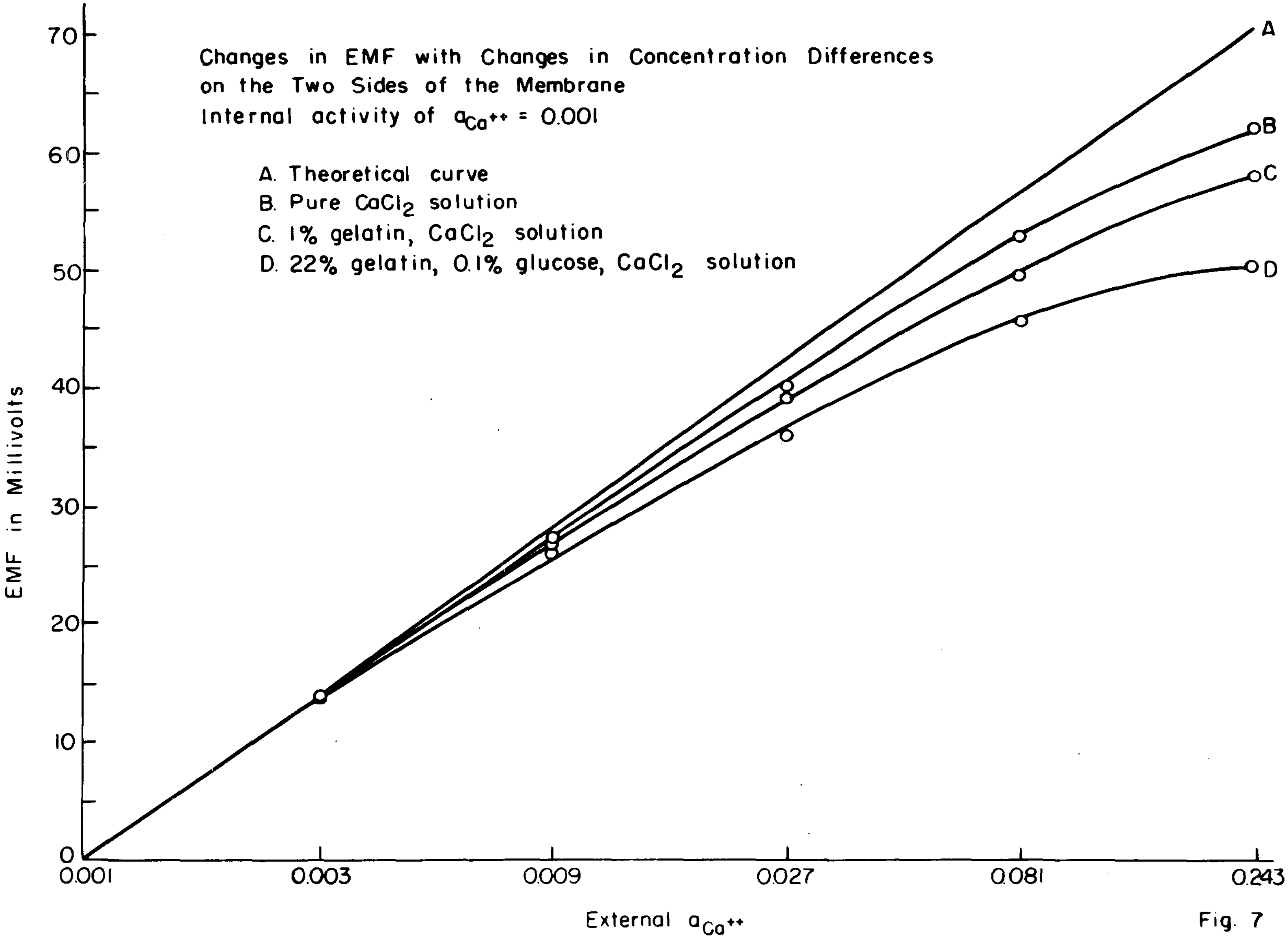

Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane
Internal activity of $a_{Ca^{++}}$ = 0.001
A. Theoretical curve
B. Pure $CaCl_2$ solution
C. 1% gelatin, $CaCl_2$ solution
D. 22% gelatin, 0.1% glucose, $CaCl_2$ solution
A
B
C
D
EMF in Millivolts
0
10
20
30
40
50
60
70
0.001
0.003
0.009
0.027
0.081
0.243
External $a_{Ca^{++}}$

Fig. 7

Table XXI

A

Determination of Calcium-Ion Activities in Concentration Cells Using Amberplex C-1-Ca Membranes

Calculated Activities of Electrolyte $a_{Ca^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Calcium-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00308	1.03
0.001 - 0.009	0.00842	0.94
0.001 - 0.027	0.0227	0.84
0.001 - 0.081	0.0616	0.76
0.001 - 0.243	0.124	0.51

B

Determination of Calcium-Ion Activities in Concentration Cells Using Amberplex C-1-Ca Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte $a_{Ca^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Calcium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00303	0.98
0.001 - 0.009	0.00791	0.94
0.001 - 0.027	0.0212	0.93
0.001 - 0.081	0.0472	0.77
0.001 - 0.243	0.0954	0.77

C

Determination of Calcium-Ion Activities in Concentration Cells Using Amberplex C-1-Ca Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

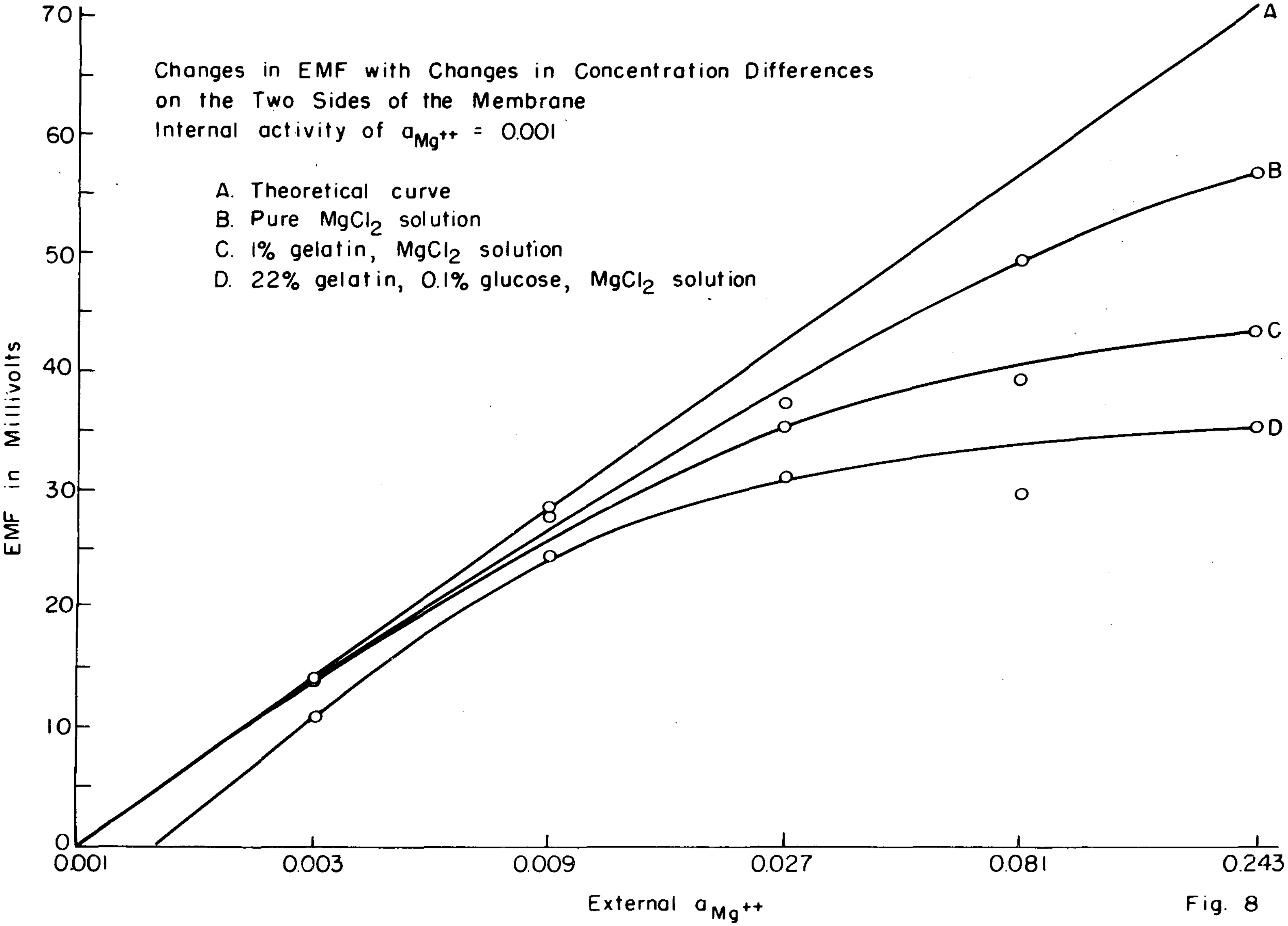
Calculated Activities of Electrolyte $a_{Ca^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Calcium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00294	0.95
0.001 - 0.009	0.00773	0.92
0.001 - 0.027	0.0164	0.72
0.001 - 0.081	0.0346	0.56
0.001 - 0.243	0.0507	0.31

gelatin are somewhat erratic at higher concentrations. The potentials obtained in the presence of twenty-two per cent gelatin and 0.1 per cent glucose deviate greatly from the expected.

Zinc chloride solutions separated by C-1-Zn membranes gave potentials and ion activities approaching theory only at activities of 0.003 and 0.009 in pure solutions. These data are represented in Figure 10 and Table XXIV. With all other concentrations in both pure solutions and in the presence of the protein the average results deviate widely but regularly from the expected.

Figure 11 and Table XXV represent the data obtained with C-1-Cu membranes in the presence of cupric chloride. In the presence of pure solutions and one per cent gelatin the theoretical is approached or obtained at activities of 0.003 and 0.009. The results progressively deviate as the concentration increases. In the presence of twenty-two per cent gelatin and 0.1 per cent glucose the results approach the theoretical at these two activities also with a greater deviation at higher activities.

Comparison of the measured potentials show that the EMF of electrolytic concentration cells with a given permselective membrane approaches theoretical values more closely in dilute solutions than in more concentrated ones. Concentrations higher than 0.1 molal show increasingly wide deviations. This bears out the theoretical explanation presented in the "Literature Review", that the ideal membrane can act as such only so long as the ion population is low. As the ion population increases, charge effects act upon the



Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane

Internal activity of $a_{Mg^{++}} = 0.001$

Fig. 8

Table XXII

A

Determination of Magnesium-Ion Activities in Concentration Cells Using Amberplex C-1-Mg Membranes

Calculated Activities of Electrolyte $a_{Mg^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Magnesium-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00298	0.99
0.001 - 0.009	0.00939	1.04
0.001 - 0.027	0.0180	0.68
0.001 - 0.081	0.0458	0.57
0.001 - 0.243	0.0816	0.34

B

Determination of Magnesium-Ion Activities in Concentration Cells Using Amberplex C-1-Mg Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte $a_{Mg^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Magnesium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00287	0.96
0.001 - 0.009	0.00862	0.92
0.001 - 0.027	0.0154	0.86
0.001 - 0.081	0.0207	0.45
0.001 - 0.243	0.0287	0.35

C

Determination of Magnesium-Ion Activities in Concentration Cells Using Amberplex C-1-Mg Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Calculated Activities of Electrolyte $a_{Mg^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Magnesium-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00234	0.82
0.001 - 0.009	0.00661	0.70
0.001 - 0.027	0.0110	0.61
0.001 - 0.081	0.00977	0.21
0.001 - 0.243	0.0152	0.19

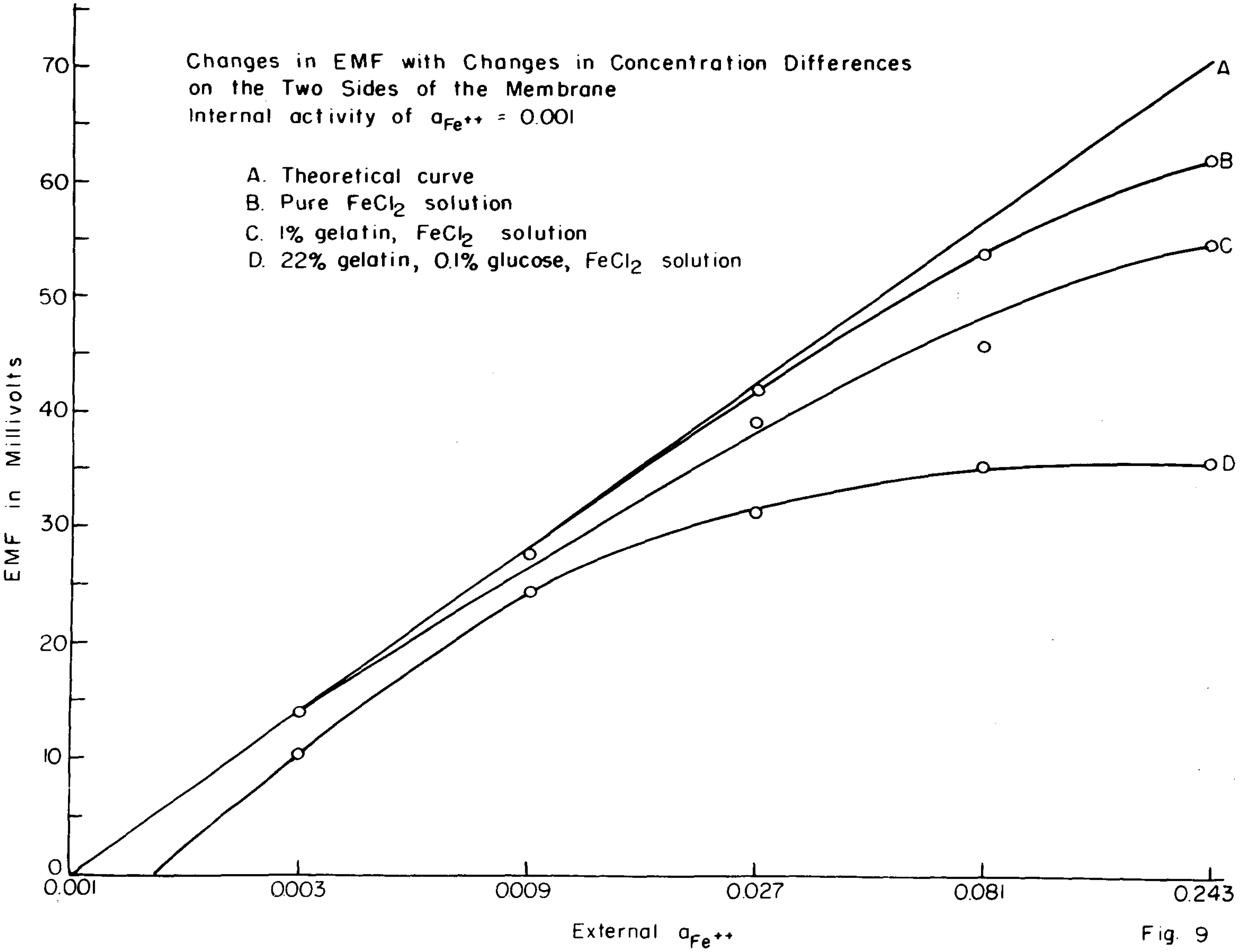

Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane
Internal activity of $a_{Fe^{++}}$ = 0.001
A. Theoretical curve
B. Pure $FeCl_2$ solution
C. 1% gelatin, $FeCl_2$ solution
D. 22% gelatin, 0.1% glucose, $FeCl_2$ solution
A
B
C
D
EMF in Millivolts
70
60
50
40
30
20
10
0
0.001
0.003
0.009
0.027
0.081
0.243
External $a_{Fe^{++}}$

Fig. 9

Table XXIII

A
Determination of Ferrous-Ion Activities in Concentration Cells Using Amberplex C-1-Fe Membranes

Calculated Activities of Electrolyte $a_{Fe^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Ferrous-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00298	0.99
0.001 - 0.009	0.00882	0.98
0.001 - 0.027	0.0265	0.98
0.001 - 0.081	0.0666	0.82
0.001 - 0.243	0.124	0.51

B
Determination of Ferrous-Ion Activities in Concentration Cells Using Amberplex C-1-Fe Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte $a_{Fe^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Ferrous-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00298	1.00
0.001 - 0.009	0.00883	1.00
0.001 - 0.027	0.0208	0.78
0.001 - 0.081	0.0354	0.53
0.001 - 0.243	0.0709	0.57

C
Determination of Ferrous-Ion Activities in Concentration Cells Using Amberplex C-1-Fe Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Calculated Activities of Electrolyte $a_{Fe^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Ferrous-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00225	0.76
0.001 - 0.009	0.00672	0.76
0.001 - 0.027	0.0115	0.43
0.001 - 0.081	0.0155	0.23
0.001 - 0.243	0.0155	0.13

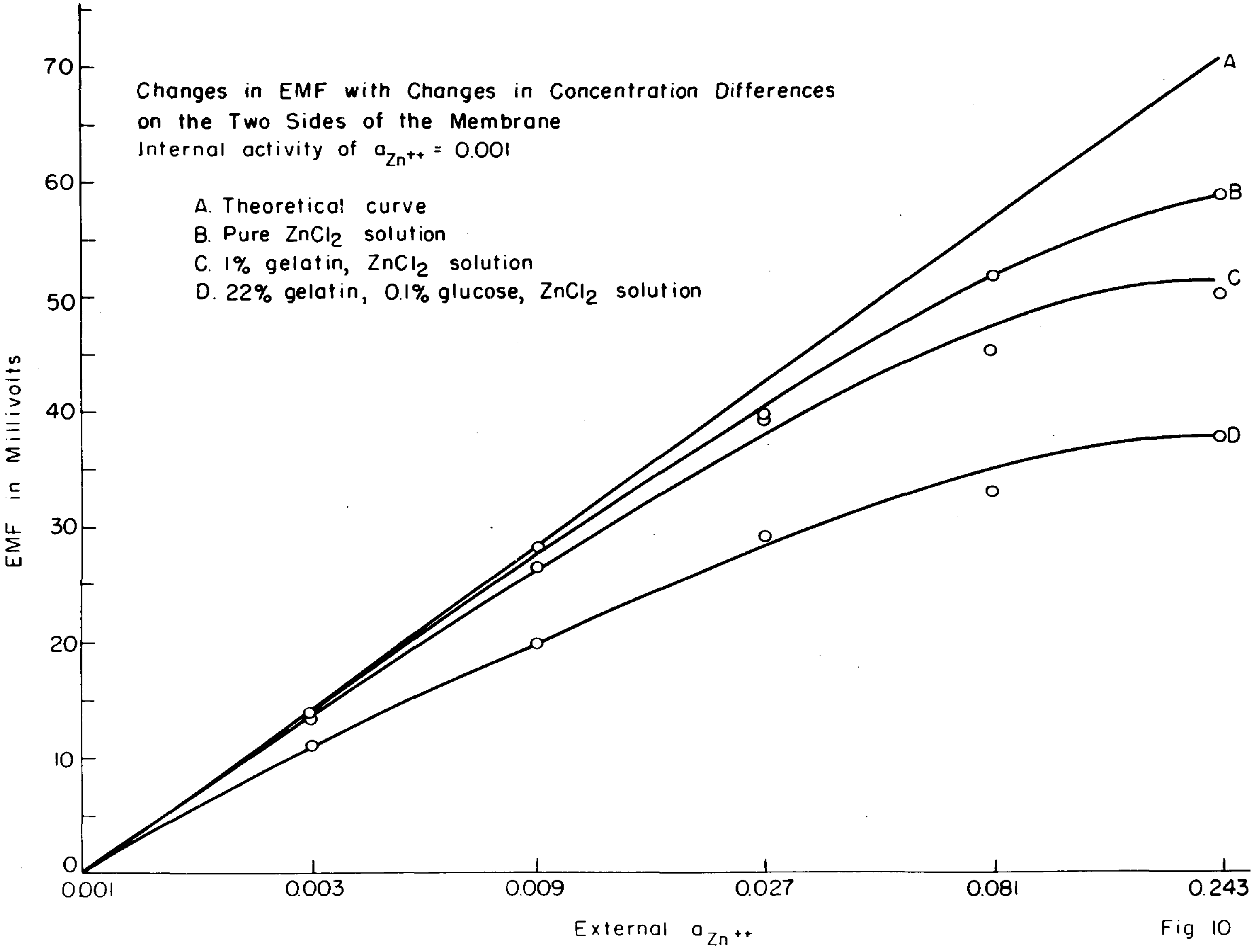

Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane
Internal activity of $a_{Zn^{++}}$ = 0.001
A. Theoretical curve
B. Pure $ZnCl_2$ solution
C. 1% gelatin, $ZnCl_2$ solution
D. 22% gelatin, 0.1% glucose, $ZnCl_2$ solution
A
B
C
D
EMF in Millivolts
70
60
50
40
30
20
10
0
0.001
0.003
0.009
0.027
0.081
0.243
External $a_{Zn^{++}}$

Fig 10

Table XXIV

A
Determination of Zinc-Ion Activities in Concentration Cells Using Amberplex C-1-Zn Membranes

Calculated Activities of Electrolyte $a_{Zn^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Zinc-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00308	1.03
0.001 - 0.009	0.00896	1.00
0.001 - 0.027	0.0218	0.81
0.001 - 0.081	0.0548	0.68
0.001 - 0.243	0.0954	0.39

B
Determination of Zinc-Ion Activities in Concentration Cells Using Amberplex C-1-Zn Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte $a_{Zn^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Zinc-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00285	0.93
0.001 - 0.009	0.00791	0.88
0.001 - 0.027	0.0210	0.96
0.001 - 0.081	0.0338	0.62
0.001 - 0.243	0.0491	0.51

C
Determination of Zinc-Ion Activities in Concentration Cells Using Amberplex C-1-Zn Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Calculated Activities of Electrolyte $a_{Zn^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Zinc-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00236	0.83
0.001 - 0.009	0.00469	0.52
0.001 - 0.027	0.00985	0.45
0.001 - 0.081	0.0129	0.23
0.001 - 0.243	0.0185	0.19

membrane, permitting anions as well as cations to penetrate, thus decreasing the specific influence of the membrane. Further increases in ion population thus give potentials which are farther and farther from theoretical.

At the lower activities one per cent gelatin apparently has a beneficial effect on the potential developed. This might be explained if it is assumed that the wider channels of the membrane are infiltrated by the gelatin, thus blocking them. This would, in effect give a more homogeneous membrane porosity, which in turn would be expected to produce potentials approaching theoretical values over a wider range of activities.

As the ionic concentration increases, one per cent gelatin appears to have an increasingly detrimental effect on the more highly hydrated ions than on ions carrying a smaller number of water molecules.

Twenty-two per cent gelatin and 0.1 per cent glucose has a very detrimental effect on the expected potential and thus on the relative cationic activities. This detrimental effect increases with the concentration of the ion concerned. Likewise, the larger solvated cations are more adversly affected than the smaller ones.

Since the larger solvated cations carry a larger hydration shell, i.e., carry more molecules of water, than the smaller solvated cations, a hydrophilic material such as gelatin would be expected to affect them more adversely than the less hydrated molecules.

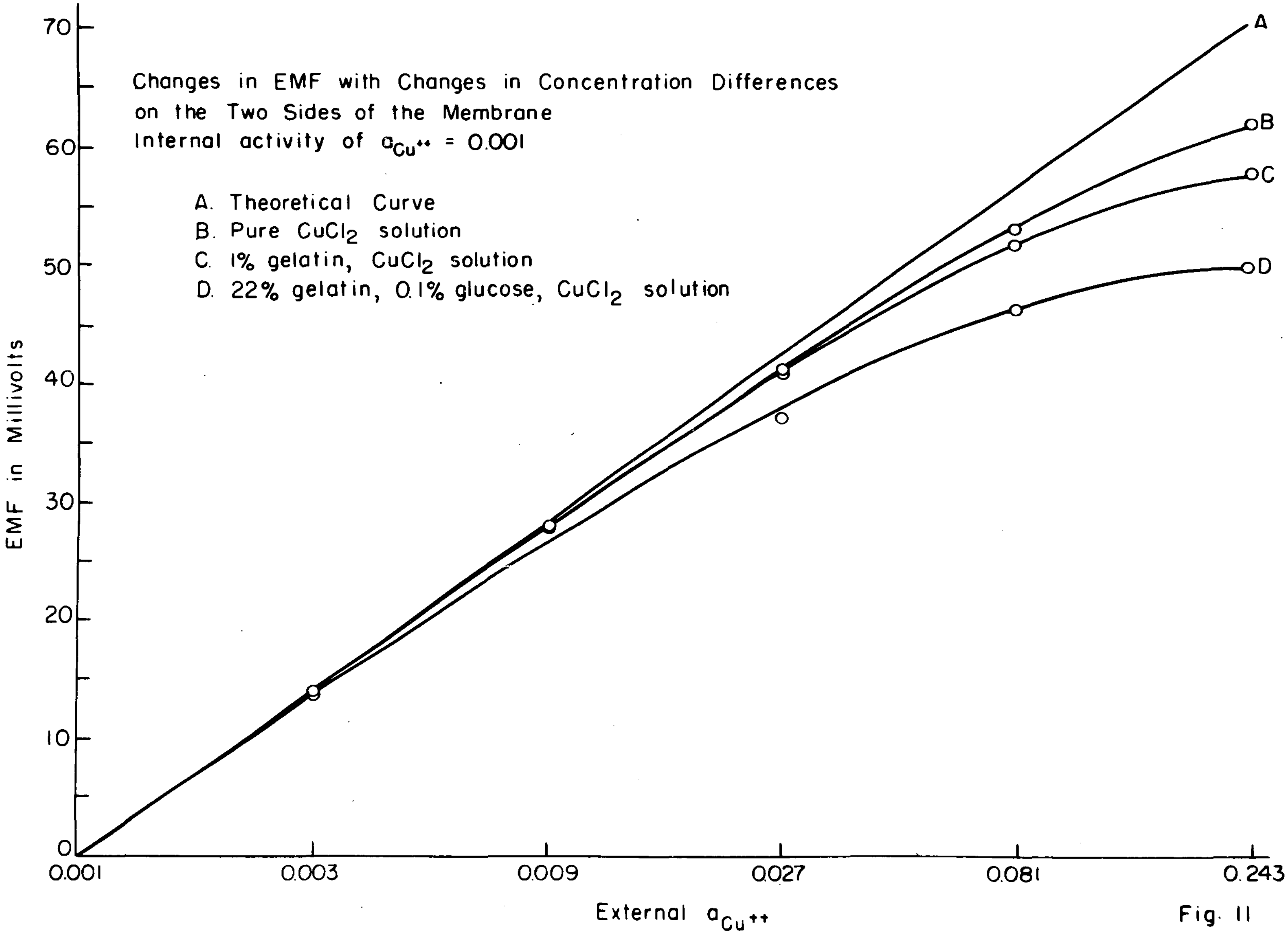

Changes in EMF with Changes in Concentration Differences
on the Two Sides of the Membrane
Internal activity of $a_{Cu^{++}}$ = 0.001
A. Theoretical Curve
B. Pure $CuCl_2$ solution
C. 1% gelatin, $CuCl_2$ solution
D. 22% gelatin, 0.1% glucose, $CuCl_2$ solution
A
B
C
D
EMF in Millivolts
0
10
20
30
40
50
60
70
0.001
0.003
0.009
0.027
0.081
0.243
External $a_{Cu^{++}}$

Fig. 11

Table XXV

A

Determination of Cupric-Ion Activities in Concentration Cells Using Amberplex C-L-Cu Membranes

Calculated Activities of Electrolyte $a_{Cu^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Cupric-Ion Activity: Measured/ Calculated Activity
0.001 - 0.003	0.00305	1.02
0.001 - 0.009	0.00896	1.00
0.001 - 0.027	0.0247	0.91
0.001 - 0.081	0.0636	0.79
0.001 - 0.243	0.124	0.51

B

Determination of Cupric-Ion Activities in Concentration Cells Using Amberplex C-1-Cu Membranes in the Presence of 1 Per Cent Gelatin

Calculated Activities of Electrolyte $a_{Cu^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Cupric-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00298	1.00
0.001 - 0.009	0.00911	1.02
0.001 - 0.027	0.0242	0.98
0.001 - 0.081	0.566	0.89
0.001 - 0.243	0.0889	0.72

C

Determination of Cupric-Ion Activities in Concentration Cells Using Amberplex C-1-Cu Membranes in the Presence of 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Calculated Activities of Electrolyte $a_{Cu^{++}}$ Internal External	Measured Activity of External Half of Cell	Relative Cupric-Ion Activity: Measured/ Measured from Pure Solution
0.001 - 0.003	0.00289	0.95
0.001 - 0.009	0.00855	0.95
0.001 - 0.027	0.0180	0.73
0.001 - 0.081	0.0371	0.58
0.001 - 0.243	0.0484	0.39

The following treatment of the data will tend to bear out the influence of ion size on actual response of the membrane.

Figures 12 through 17 compare the average values obtained using different electrolytes under like experimental conditions. These curves have been presented separately in an earlier section.

It has previously been stated that ion size had a direct bearing on maximum potential obtainable with a small pore membrane. It was pointed out that highly hydrated cations, would, because of their larger size, move across a membrane with greater difficulty than less highly hydrated ions. The potentials obtained with the smaller hydrated cations would therefore tend to approach the theoretical value more closely than the larger cations under like experimental conditions.

Hartley and Raikes (105) gave radii values of solvated ions in water. These values, given in Table XXVI are used in the following comparisons.

Table XXVI

Radii of Solvated Ions

NH_4^+	1.18	Cu^{++}	3.05
K^+	1.22	Ca^{++}	3.05
Na^+	1.79	Fe^{++}	3.36
Li^+	2.30	Zn^{++}	3.36
Ba^{++}	2.83	Mg^{++}	3.44

Figure 12 shows that in pure salt solutions the smaller monovalent cations give average potential values which are closer to

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(105) Hartley, H. and Raikes, H. R., Transactions of the Faraday Society 23, 394-96 (1927)

theoretical than do the larger cations. In the case of divalent cations this comparison is not as clear cut. The cations of barium, copper, calcium, and iron give average potentials over the activity range which are very similar. Zinc and magnesium give values which are very similar. Zinc and magnesium, which are the largest hydrated ions give average potentials which that are less than the other four.

Figure 14 indicates that monovalent ions in the presence of one per cent gelatin again follow the size rule but not as definitely. Solvated divalent cations, Figure 15, fall into direct order. The average potentials obtained are closer to theoretical in the case of the smaller ions. The largest cations giving the greatest deviation.

Figure 16 represents the potentials observed for solvated monovalent cations in the presence of twenty-two per cent gelatin and 0.1 per cent glucose. These data show that the two smaller ions gave average potentials closer to theoretical than did the two larger ions, however the smallest ion did not have the closest approach to theoretical. Likewise the largest ion did not have the greatest deviation from theoretical. Figure 17, which represents the solvated divalent ions under the same experimental conditions falls into two distinct groups. The three smaller ions gave potentials which were closer to the theoretical values than did the three larger ions. Thus, one may conclude that solvated ion size has a very definite effect on the potential obtained with a given membrane.

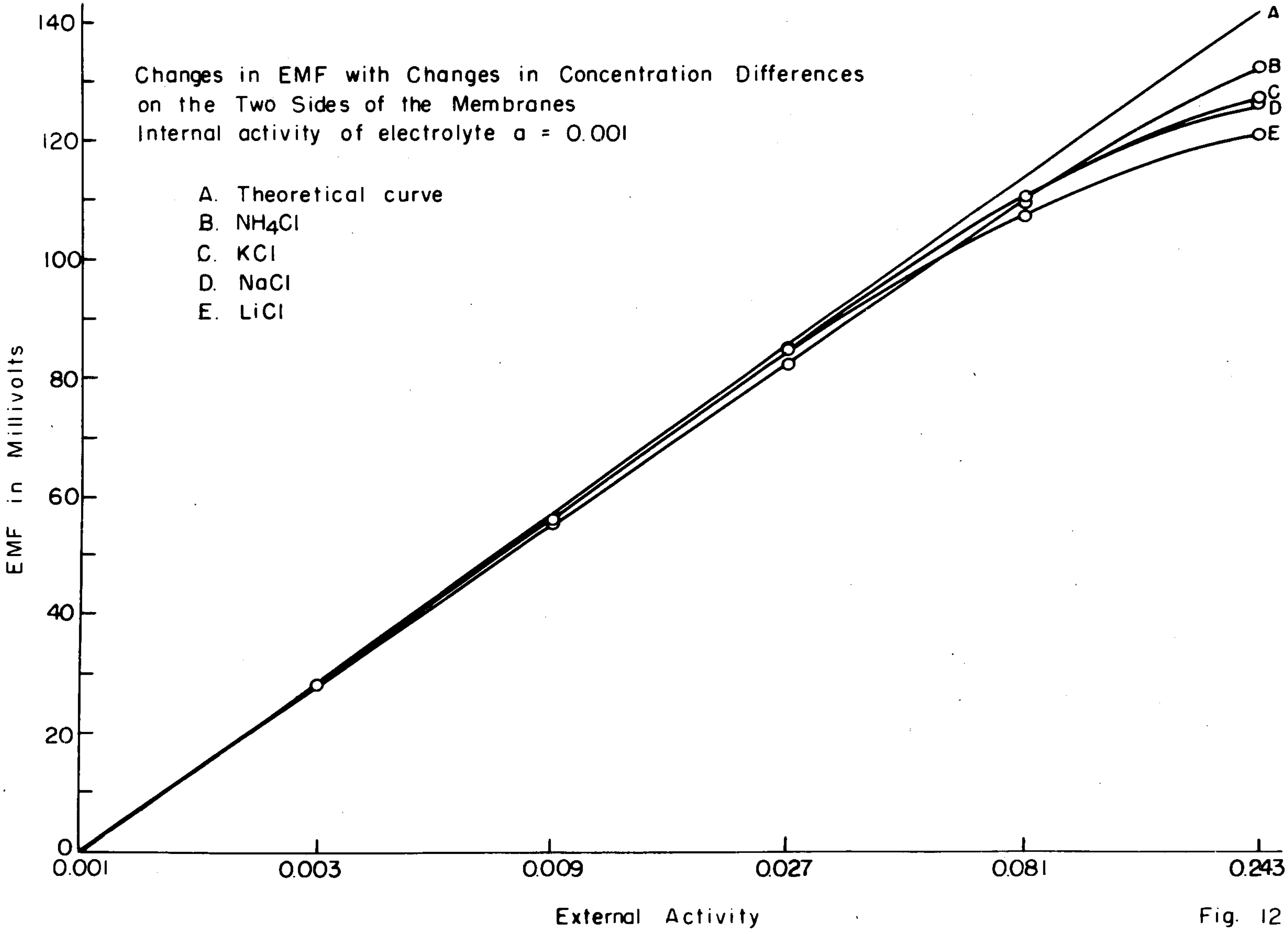

Changes in EMF with Changes in Concentration Differences
on the Two Sides of the Membranes
Internal activity of electrolyte a = 0.001
A. Theoretical curve
B. NH_4Cl
C. KCl
D. NaCl
E. LiCl
EMF in Millivolts
0
20
40
60
80
100
120
140
External Activity
0.001
0.003
0.009
0.027
0.081
0.243
A
B
C
D
E

Fig. 12

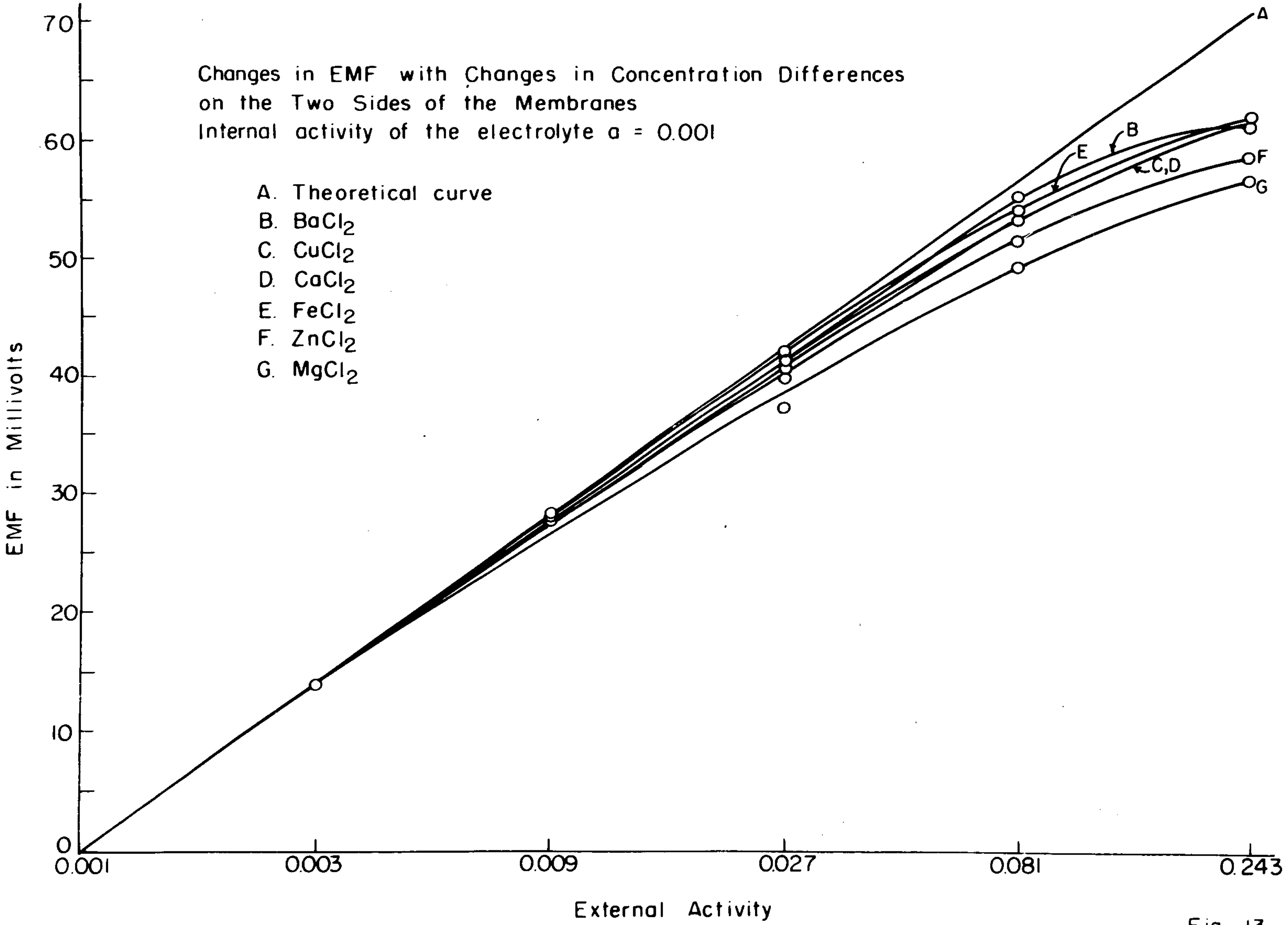

Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membranes
Internal activity of the electrolyte a = 0.001
A. Theoretical curve
B. $BaCl_2$
C. $CuCl_2$
D. $CaCl_2$
E. $FeCl_2$
F. $ZnCl_2$
G. $MgCl_2$
A
B
E
C,D
F
G
EMF in Millivolts
0
10
20
30
40
50
60
70
0.001
0.003
0.009
0.027
0.081
0.243
External Activity

Fig. 13

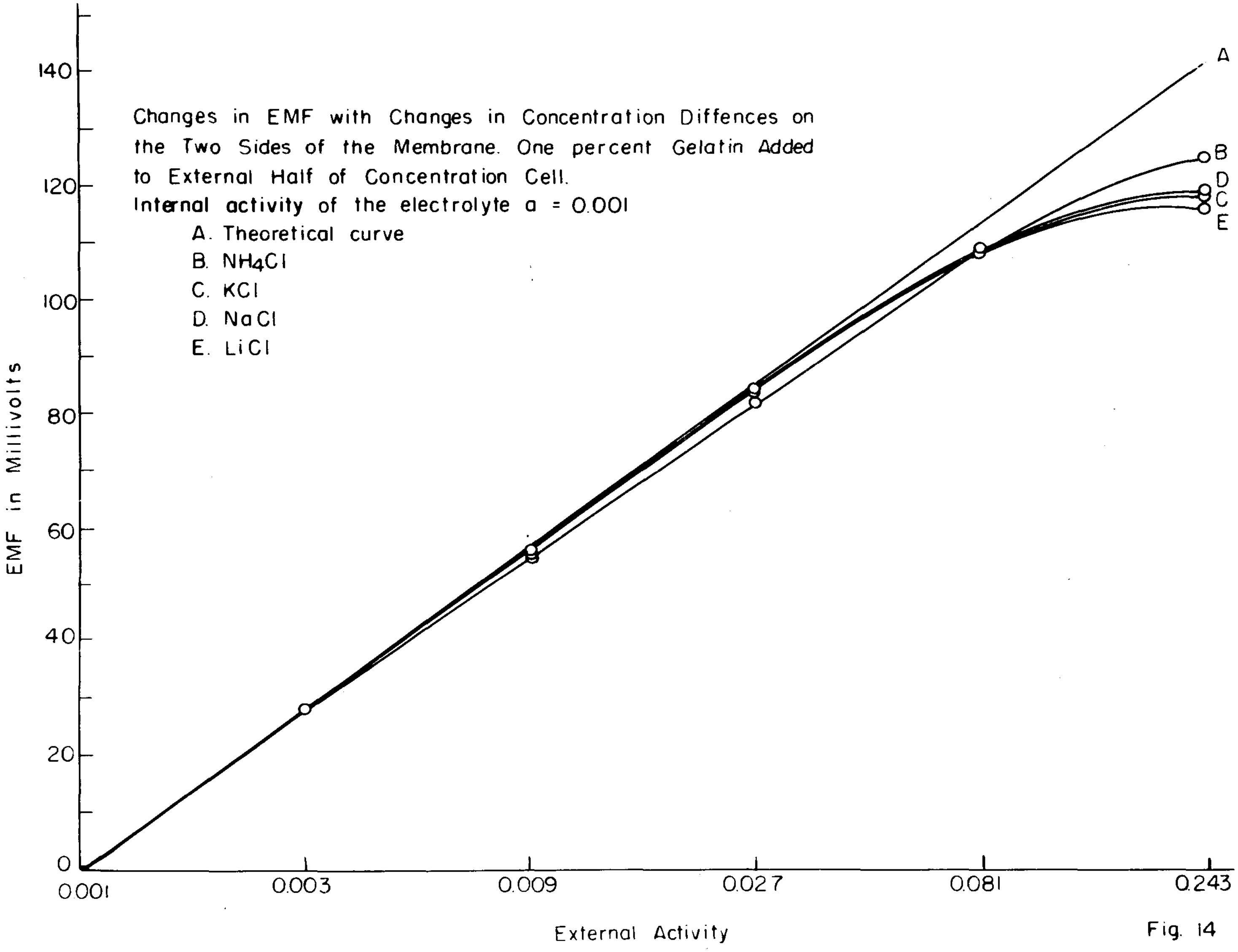

Changes in EMF with Changes in Concentration Diffences on the Two Sides of the Membrane. One percent Gelatin Added to External Half of Concentration Cell.
Internal activity of the electrolyte a = 0.001
A. Theoretical curve
B. NH_4Cl
C. KCl
D. NaCl
E. LiCl
EMF in Millivolts
0
20
40
60
80
100
120
140
External Activity
0.001
0.003
0.009
0.027
0.081
0.243
A
B
D
C
E

Fig. 14

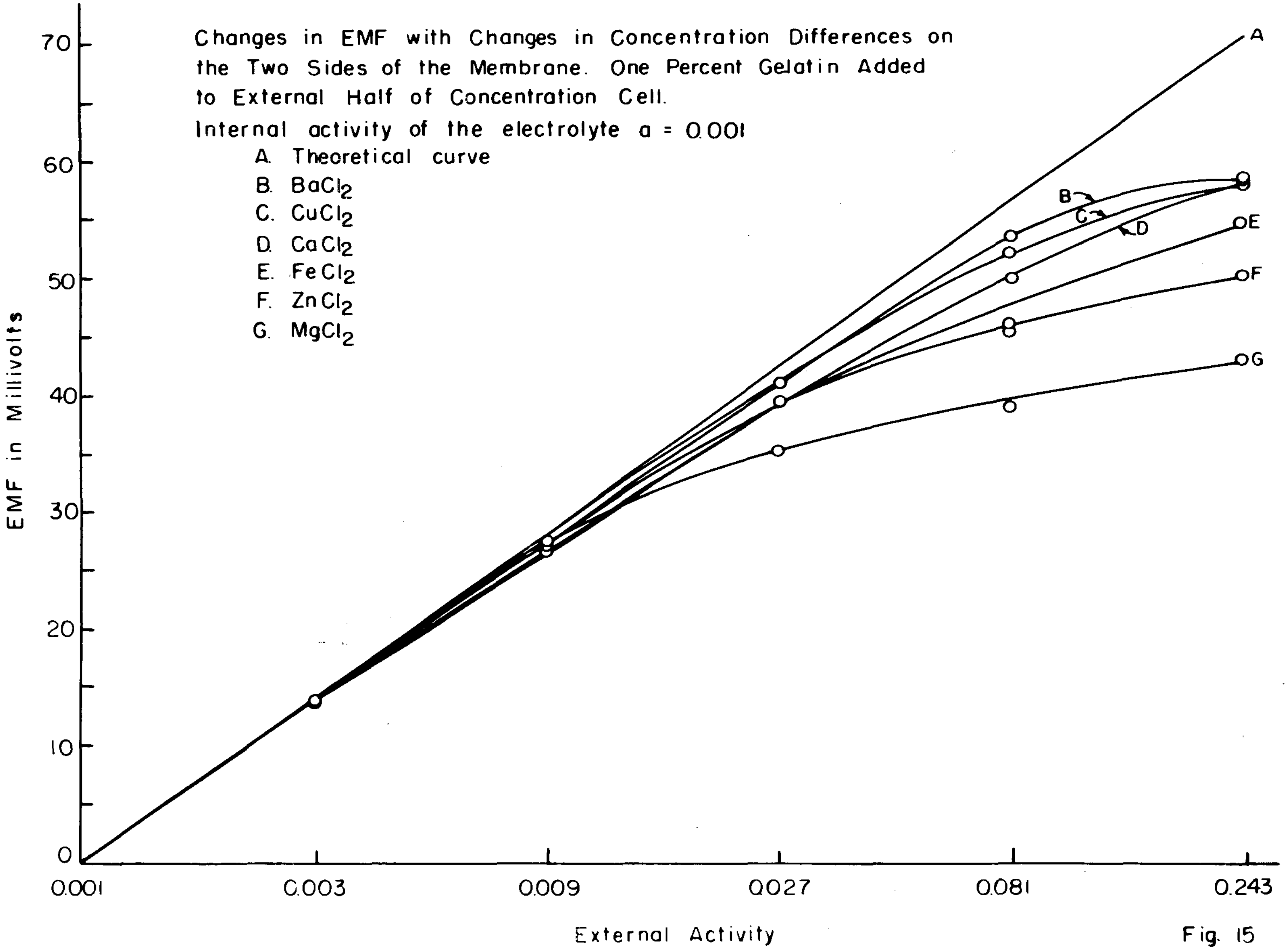

Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane. One Percent Gelatin Added to External Half of Concentration Cell.
Internal activity of the electrolyte a = 0.001
A. Theoretical curve
B. $BaCl_2$
C. $CuCl_2$
D. $CaCl_2$
E. $FeCl_2$
F. $ZnCl_2$
G. $MgCl_2$
EMF in Millivolts
0
10
20
30
40
50
60
70
0.001
0.003
0.009
0.027
0.081
0.243
External Activity
A
B
C
D
E
F
G

Fig. 15

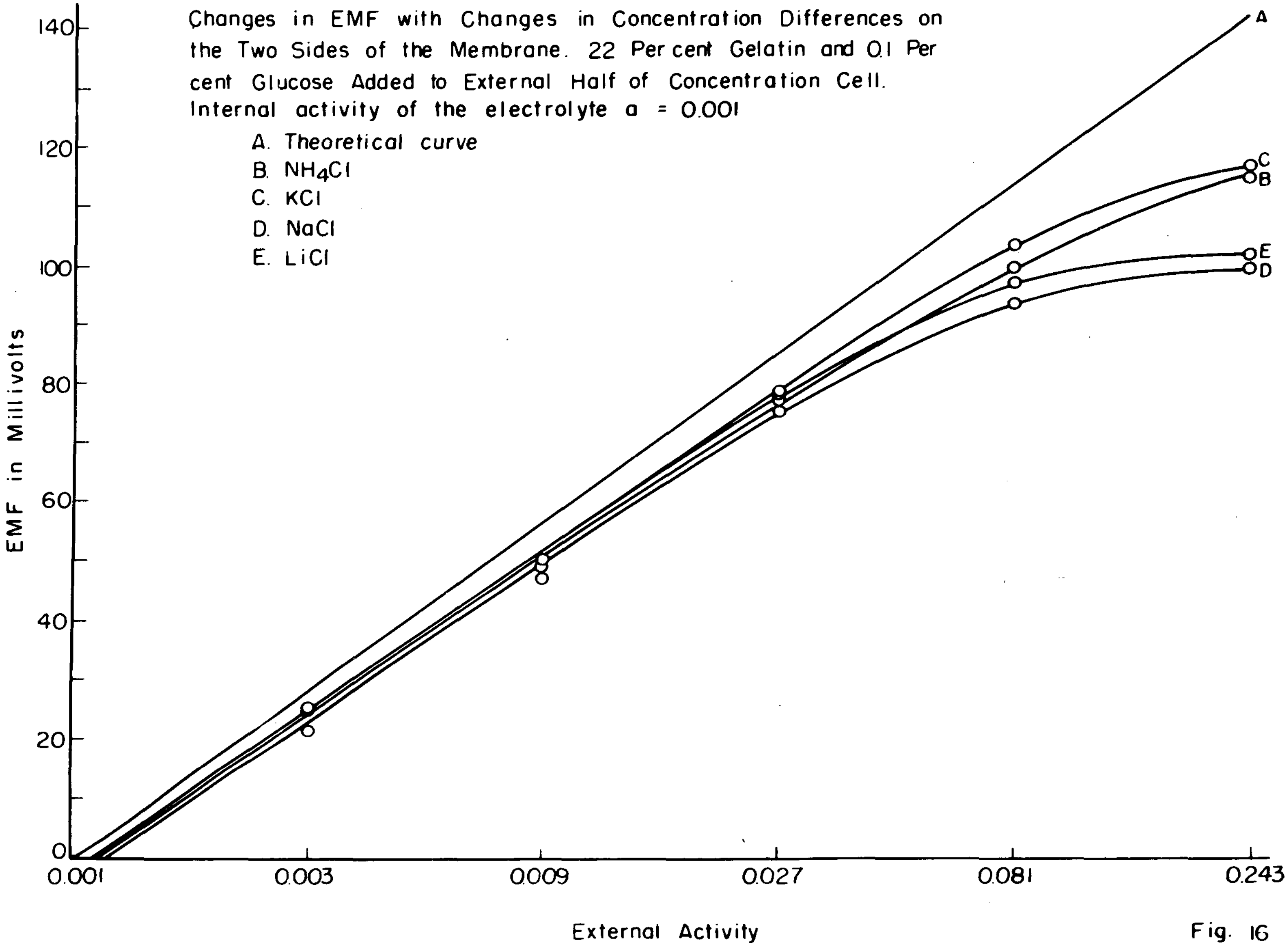
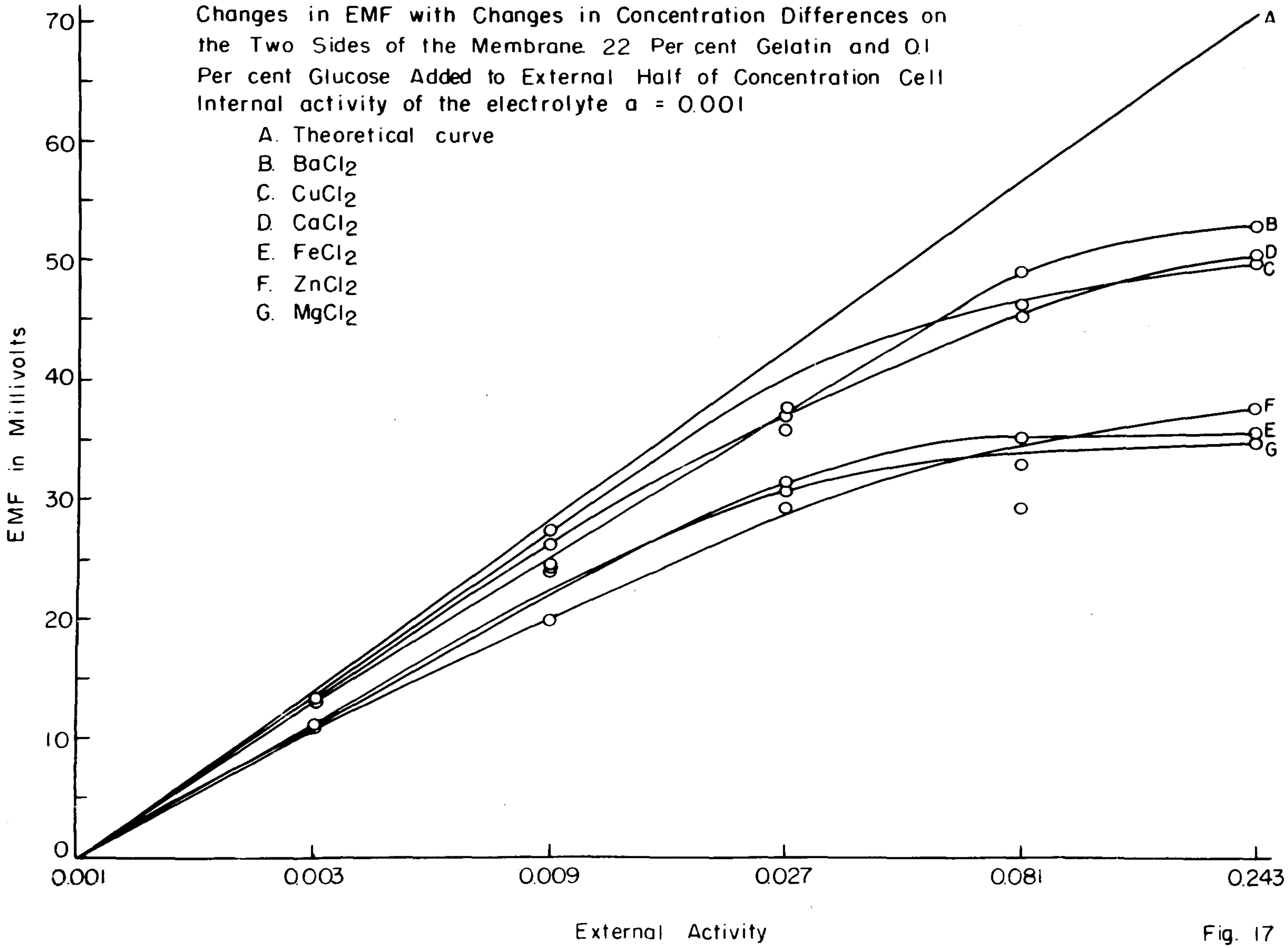

Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane. 22 Per cent Gelatin and 0.1 Per cent Glucose Added to External Half of Concentration Cell. Internal activity of the electrolyte a = 0.001

Fig. 16



Changes in EMF with Changes in Concentration Differences on the Two Sides of the Membrane 22 Per cent Gelatin and 0.1 Per cent Glucose Added to External Half of Concentration Cell Internal activity of the electrolyte a = 0.001

Fig. 17

Table XXVII

Average Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions

Activities Internal External	E(mv)	E_o(mv)	t_+ mobile ion	t_o mobile ion	p.x 100
NH_4^+					
0.001 - 0.003	28.3	28.2	1.00	0.491	100.0
0.001 - 0.009	55.0	56.4	0.998	0.491	97.6
0.001 - 0.027	81.9	84.6	0.984	0.491	96.9
0.001 - 0.081	109.5	112.8	0.985	0.491	97.1
0.001 - 0.243	131.2	141.0	0.965	0.491	93.1
Li^+					
0.001 - 0.003	28.2	28.2	1.00	0.333	100.0
0.001 - 0.009	55.0	56.4	0.988	0.330	98.2
0.001 - 0.027	84.7	84.6	1.00	0.327	100.0
0.001 - 0.081	106.3	112.8	0.971	0.320	95.7
0.001 - 0.243	120.0	141.0	0.926	0.300	89.4
K^+					
0.001 - 0.003	28.5	28.2	1.01	0.496	101.0
0.001 - 0.009	55.5	56.4	0.992	0.496	98.4
0.001 - 0.027	84.4	84.6	0.999	0.496	99.8
0.001 - 0.081	108.3	112.8	0.980	0.496	96.0
0.001 - 0.243	126.8	141.0	0.950	0.496	91.0
Na^+					
0.001 - 0.003	28.0	28.2	0.996	0.392	99.3
0.001 - 0.009	55.0	56.4	0.988	0.392	98.0
0.001 - 0.027	84.4	84.6	0.999	0.390	99.8
0.001 - 0.081	109.6	112.8	0.986	0.385	97.7
0.001 - 0.243	125.5	141.0	0.945	0.382	97.7
Ba^{++}					
0.001 - 0.003	13.7	14.1	0.989	0.443	98.0
0.001 - 0.009	27.8	28.2	0.993	0.440	98.8
0.001 - 0.027	40.1	42.3	0.974	0.437	95.4
0.001 - 0.081	55.2	56.4	0.989	0.429	98.1
0.001 - 0.243	61.1	70.5	0.933	0.414	88.6

Table XXVII Continued

Average Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions

Activities Internal External	E(mv)	E_o(mv)	t_+mobile ion	$t_o$mobile ion	p.x 100
Ca^{++}					
0.001 - 0.003	14.4	14.1	1.01	0.430	101.0
0.001 - 0.009	27.3	28.2	0.984	0.428	97.2
0.001 - 0.027	40.0	42.3	0.973	0.423	95.3
0.001 - 0.081	52.8	56.4	0.968	0.410	94.6
0.001 - 0.243	61.8	70.5	0.938	0.400	89.7
Cu^{++}					
0.001 - 0.003	14.3	14.1	1.01	0.416	101.0
0.001 - 0.009	28.1	28.2	0.998	0.406	99.7
0.001 - 0.027	41.1	42.3	0.986	0.355	97.8
0.001 - 0.081	53.2	56.4	0.972	0.302	96.0
0.001 - 0.243	61.7	70.5	0.938	0.284	91.3
Fe^{++}					
0.001 - 0.003	14.0	14.1	0.996	0.460	99.3
0.001 - 0.009	27.9	28.2	0.995	0.435	99.1
0.001 - 0.027	42.0	42.3	0.996	0.410	99.3
0.001 - 0.081	53.8	56.4	0.977	0.380	96.3
0.001 - 0.243	61.8	70.5	0.938	0.355	90.4
Mg^{++}					
0.001 - 0.003	14.0	14.1	0.996	0.400	99.3
0.001 - 0.009	28.7	28.2	1.01	0.394	101.0
0.001 - 0.027	37.0	42.3	0.937	0.390	89.7
0.001 - 0.081	49.0	56.4	0.934	0.385	89.3
0.001 - 0.243	56.4	70.5	0.900	0.381	83.8
Zn^{++}					
0.001 - 0.003	14.4	14.1	1.01	0.410	100.0
0.001 - 0.009	28.1	28.2	0.998	0.387	99.7
0.001 - 0.027	39.5	42.3	0.967	0.374	94.7
0.001 - 0.081	51.3	54.4	0.937	0.355	90.2
0.001 - 0.243	58.4	70.5	0.914	0.335	87.1

Table XXVIII

Average Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions External Half of Cell Also Contains 1 Per Cent Gelatin

Activities Internal	External	E(mv)	E_o(mv)	t_+ mobile ion	t_o mobile ion	p.x 100
NH_4^+						
0.001	- 0.003	28.2	28.2	1.00	0.491	100.0
0.001	- 0.009	54.0	56.4	0.979	0.491	95.9
0.001	- 0.027	81.6	84.6	0.982	0.491	96.5
0.001	- 0.081	108.0	112.8	0.979	0.491	95.9
0.001	- 0.243	124.0	141.0	0.940	0.491	88.2
Li^+						
0.001	- 0.003	27.9	28.2	0.995	0.333	99.3
0.001	- 0.009	54.7	56.4	0.985	0.330	97.8
0.001	- 0.027	83.6	84.6	0.994	0.327	99.1
0.001	- 0.081	108.4	112.8	0.980	0.320	97.1
0.001	- 0.243	115.1	141.0	0.908	0.300	86.9
K^+						
0.001	- 0.003	28.4	28.2	1.00	0.496	100.0
0.001	- 0.009	55.2	56.4	0.989	0.496	97.8
0.001	- 0.027	83.9	84.6	0.996	0.496	99.2
0.001	- 0.081	107.5	112.8	0.977	0.496	95.4
0.001	- 0.243	117.4	141.0	0.916	0.496	83.3
Na^+						
0.001	- 0.003	28.1	28.2	0.998	0.392	99.7
0.001	- 0.009	54.0	56.4	0.979	0.392	96.5
0.001	- 0.027	83.9	84.6	0.996	0.390	99.3
0.001	- 0.081	108.5	112.8	0.981	0.385	96.9
0.001	- 0.243	118.2	141.0	0.919	0.382	86.9
Ba^{++}						
0.001	- 0.003	13.8	14.1	0.989	0.443	98.0
0.001	- 0.009	26.9	28.2	0.977	0.440	95.9
0.001	- 0.027	39.3	42.3	0.965	0.437	93.8
0.001	- 0.081	53.3	56.4	0.973	0.429	95.3
0.001	- 0.243	58.3	70.5	0.913	0.414	85.2

Table XXVIII Continued

Average Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions External Half of Cell Also Contains 1 Per Cent Gelatin

Activities		E(mv)	E_o(mv)	t_+mobile ion	$t_o$mobile ion	p.x 100
Internal	External					
Ca^{++}						
0.001 -	0.003	14.2	14.1	1.00	0.430	100.0
0.001 -	0.009	26.5	28.2	0.970	0.428	94.8
0.001 -	0.027	39.1	42.3	0.962	0.423	93.4
0.001 -	0.081	49.4	56.4	0.938	0.410	89.5
0.001 -	0.243	58.0	70.5	0.911	0.400	85.2
Cu^{++}						
0.001 -	0.003	14.0	14.1	0.996	0.416	99.3
0.001 -	0.009	28.3	28.3	1.00	0.406	100.0
0.001 -	0.027	40.8	40.8	0.982	0.335	97.2
0.001 -	0.081	51.7	51.7	0.958	0.302	94.0
0.001 -	0.243	57.5	57.5	0.908	0.284	87.2
Fe^{++}						
0.001 -	0.003	14.0	14.1	0.996	0.460	99.3
0.001 -	0.009	27.9	28.2	0.995	0.435	99.1
0.001 -	0.027	38.9	42.3	0.960	0.410	93.2
0.001 -	0.081	45.7	56.4	0.905	0.380	84.7
0.001 -	0.243	54.6	70.5	0.887	0.355	82.5
Mg^{++}						
0.001 -	0.003	13.5	14.1	0.979	0.400	96.5
0.001 -	0.009	27.6	28.2	0.989	0.394	98.5
0.001 -	0.027	35.0	42.3	0.914	0.390	85.9
0.001 -	0.081	38.8	56.4	0.844	0.385	74.6
0.001 -	0.243	43.0	70.5	0.805	0.381	68.5
Zn^{++}						
0.001 -	0.003	13.4	14.1	0.975	0.410	95.8
0.001 -	0.009	26.5	28.2	0.970	0.387	95.1
0.001 -	0.027	39.0	42.3	0.961	0.374	93.8
0.001 -	0.081	45.1	54.4	0.882	0.355	81.7
0.001 -	0.243	49.9	70.5	0.854	0.335	78.0

Table XXIX

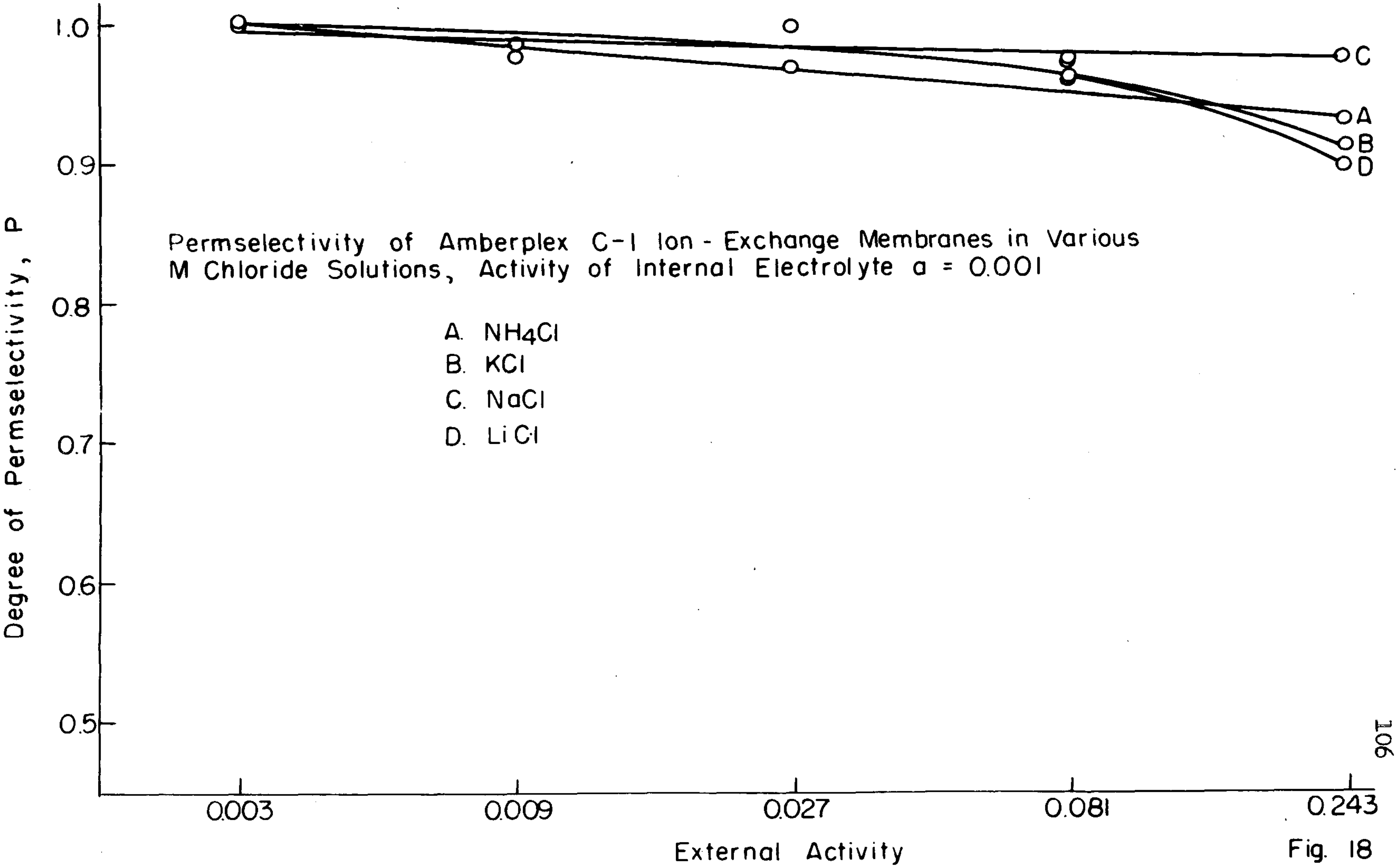
Average Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions External Half of Cell Also Contains 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Activities Internal External	E(mv)	E_0(mv)	t_+ mobile ion	t_0 mobile ion	p.x 100
NH_4^+					
0.001 - 0.003	25.3	28.2	0.949	0.491	90.0
0.001 - 0.009	47.0	56.4	0.917	0.491	83.7
0.001 - 0.027	75.7	84.6	0.947	0.491	89.8
0.001 - 0.081	99.2	112.8	0.940	0.491	88.2
0.001 - 0.243	114.1	141.0	0.905	0.491	81.3
Li^+					
0.001 - 0.003	25.2	28.2	0.947	0.333	92.1
0.001 - 0.009	49.8	56.4	0.941	0.330	91.2
0.001 - 0.027	77.4	84.6	0.957	0.327	93.6
0.001 - 0.081	96.5	112.8	0.928	0.320	89.4
0.001 - 0.243	100.8	141.0	0.857	0.300	79.6
K^+					
0.001 - 0.003	25.3	28.2	0.948	0.496	89.7
0.001 - 0.009	50.2	56.4	0.945	0.496	89.1
0.001 - 0.027	78.1	84.6	0.962	0.496	92.5
0.001 - 0.081	102.4	112.8	0.954	0.496	90.9
0.001 - 0.243	115.4	141.0	0.909	0.496	81.9
Na^+					
0.001 - 0.003	21.5	28.2	0.881	0.392	90.4
0.001 - 0.009	49.1	56.4	0.935	0.392	89.3
0.001 - 0.027	75.3	84.6	0.945	0.390	91.0
0.001 - 0.081	92.8	112.8	0.911	0.385	85.5
0.001 - 0.243	98.5	141.0	0.849	0.382	75.6
Ba^{++}					
0.001 - 0.003	13.1	14.1	0.965	0.443	93.7
0.001 - 0.009	24.6	28.2	0.936	0.440	88.6
0.001 - 0.027	37.8	42.3	0.947	0.437	90.5
0.001 - 0.081	49.1	56.4	0.935	0.429	88.6
0.001 - 0.243	52.9	70.5	0.875	0.414	78.6

Table XXIX Continued

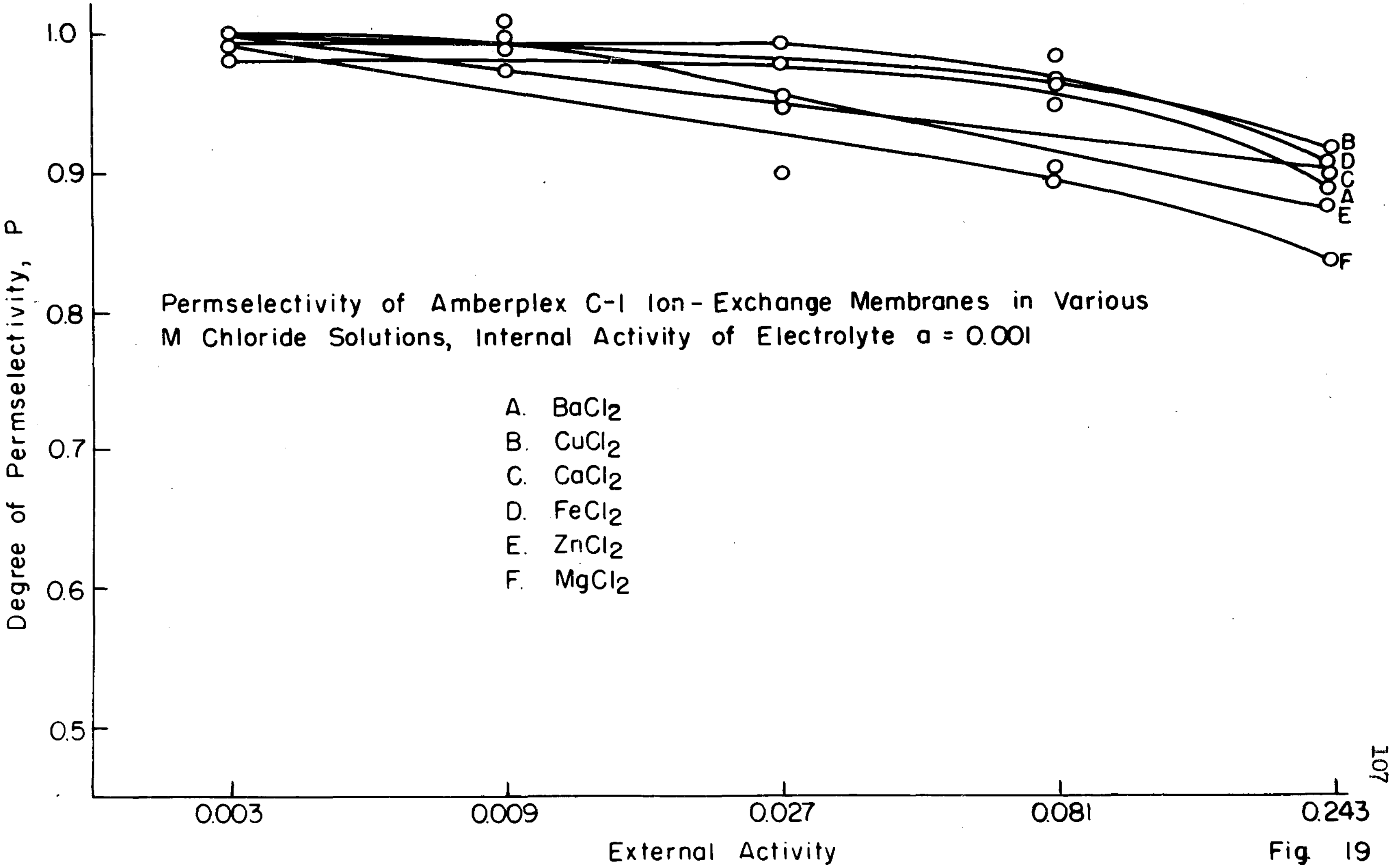
Average Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions External Half of Cell Also Contains 22 Per Cent Gelatin and 0.1 Per Cent Glucose

Activities Internal External	E(mv)	E_0(mv)	t_+mobile ion	$t_o$mobile ion	p.x 100
Ca^{++}					
0.001 - 0.003	13.8	14.1	0.989	0.430	98.1
0.001 - 0.009	26.2	28.2	0.965	0.428	93.9
0.001 - 0.027	35.8	42.3	0.923	0.423	86.7
0.001 - 0.081	45.4	56.4	0.902	0.410	83.4
0.001 - 0.243	50.3	70.5	0.857	0.400	76.2
Cu^{++}					
0.001 - 0.003	13.6	14.1	0.982	0.416	96.9
0.001 - 0.009	27.5	28.2	0.988	0.406	98.0
0.001 - 0.027	37.0	42.3	0.937	0.355	90.2
0.001 - 0.081	46.3	56.4	0.910	0.302	87.1
0.001 - 0.243	49.7	70.5	0.852	0.284	79.3
Fe^{++}					
0.001 - 0.003	10.4	14.1	0.869	0.460	75.7
0.001 - 0.009	24.4	28.2	0.933	0.435	88.1
0.001 - 0.027	31.3	42.3	0.882	0.410	80.0
0.001 - 0.081	35.1	56.4	0.811	0.380	69.5
0.001 - 0.243	35.5	70.5	0.752	0.355	61.6
Mg^{++}					
0.001 - 0.003	10.9	14.1	0.887	0.400	81.2
0.001 - 0.009	24.2	28.2	0.929	0.394	88.6
0.001 - 0.027	30.7	42.3	0.864	0.390	77.7
0.001 - 0.081	29.2	56.4	0.759	0.385	60.8
0.001 - 0.243	34.9	70.5	0.748	0.381	59.3
Zn^{++}					
0.001 - 0.003	11.0	14.1	0.890	0.410	81.4
0.001 - 0.009	19.8	28.2	0.851	0.387	75.7
0.001 - 0.027	29.3	42.3	0.846	0.374	75.4
0.001 - 0.081	32.8	54.4	0.773	0.355	64.8
0.001 - 0.243	37.4	70.5	0.765	0.335	64.7



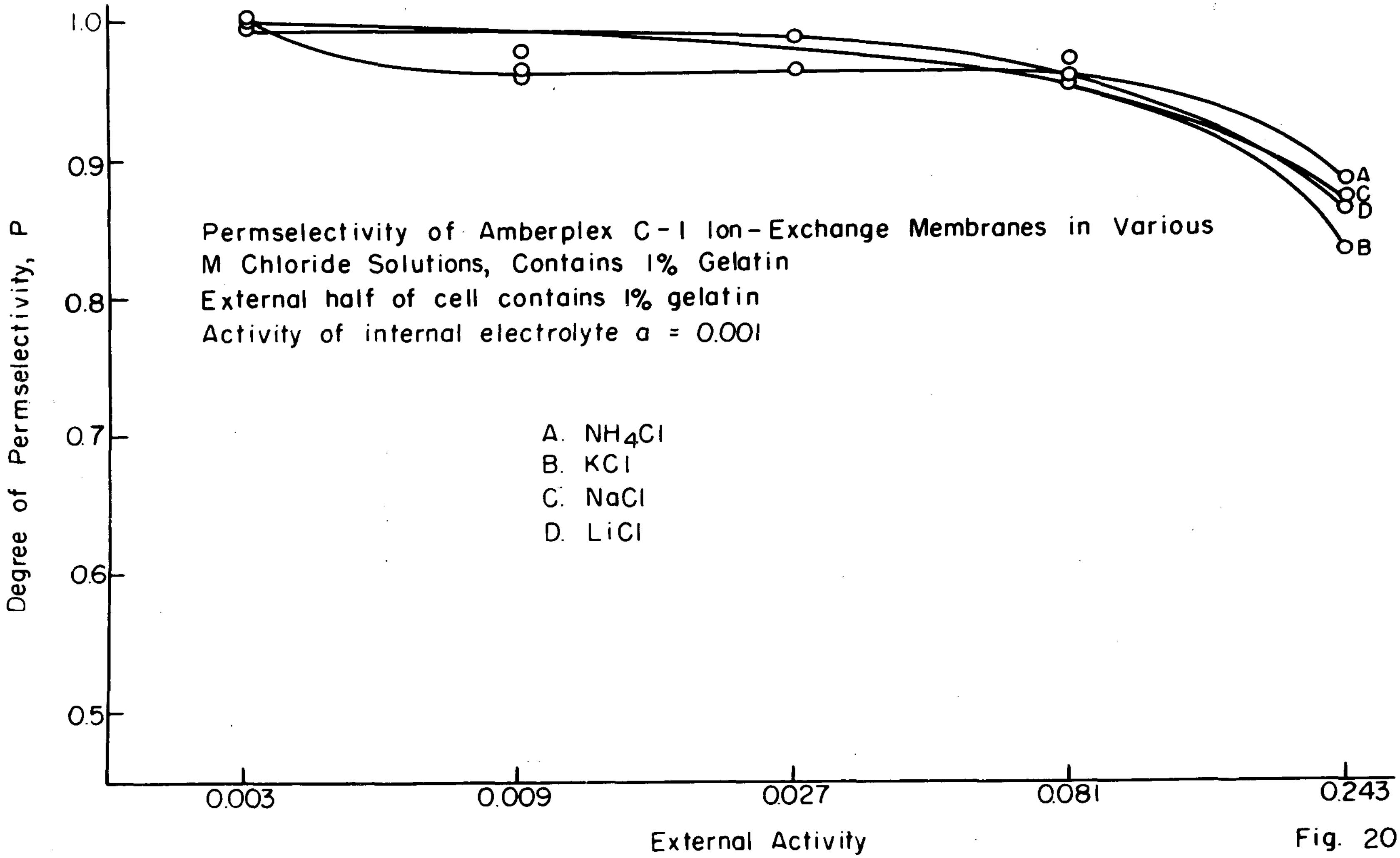
Permselectivity of Amberplex C-1 Ion - Exchange Membranes in Various M Chloride Solutions, Activity of Internal Electrolyte $a = 0.001$

Fig. 18



Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions, Internal Activity of Electrolyte a = 0.001

Fig. 19



Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions, Contains 1% Gelatin

External half of cell contains 1% gelatin

Activity of internal electrolyte a = 0.001

Fig. 20

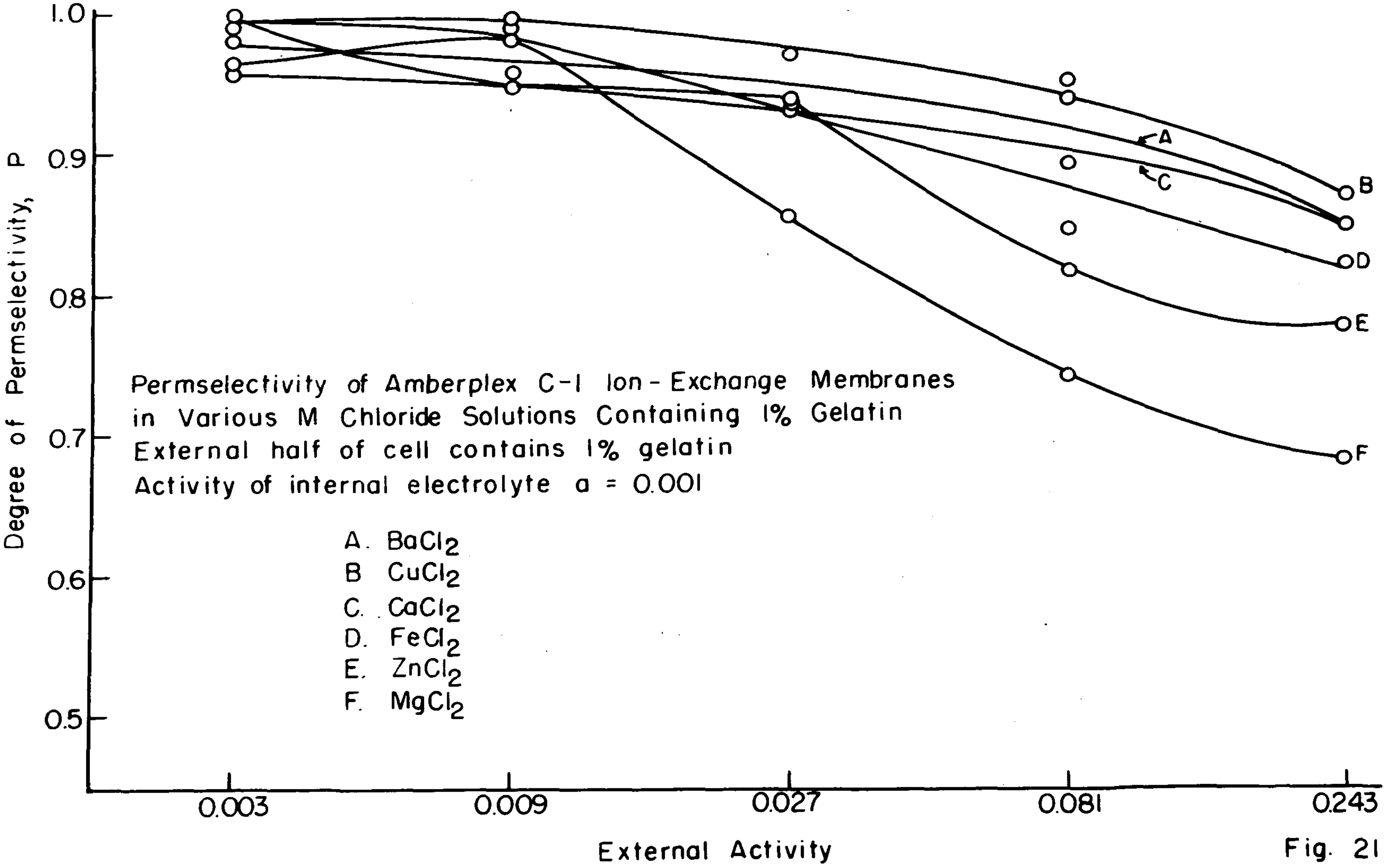
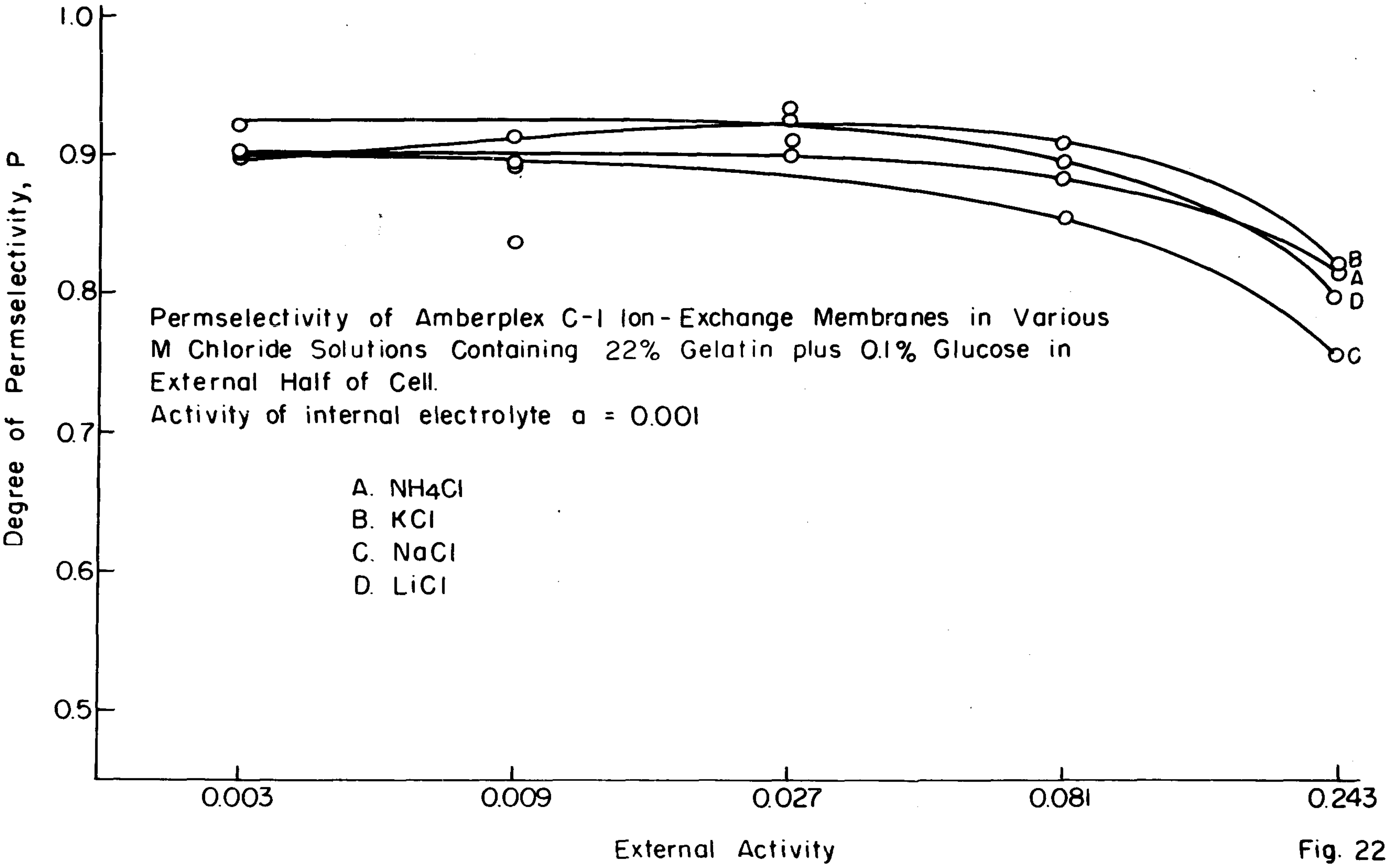

Permselectivity of Amberplex C-1 Ion-Exchange Membranes
in Various M Chloride Solutions Containing 1% Gelatin
External half of cell contains 1% gelatin
Activity of internal electrolyte a = 0.001
A. BaCl$_2$
B CuCl$_2$
C. CaCl$_2$
D. FeCl$_2$
E. ZnCl$_2$
F. MgCl$_2$
Degree of Permselectivity, P
1.0
0.9
0.8
0.7
0.6
0.5
External Activity
0.003
0.009
0.027
0.081
0.243
A
B
C
D
E
F

Fig. 21



Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions Containing 22% Gelatin plus 0.1% Glucose in External Half of Cell.
Activity of internal electrolyte a = 0.001

Fig. 22

Permselectivity of Amberplex C-1 Ion-Exchange Membranes in Various M Chloride Solutions Containing 22% Gelatin plus 1% Glucose in External Half of Cell. Activity of internal electrolyte a = 0.001.

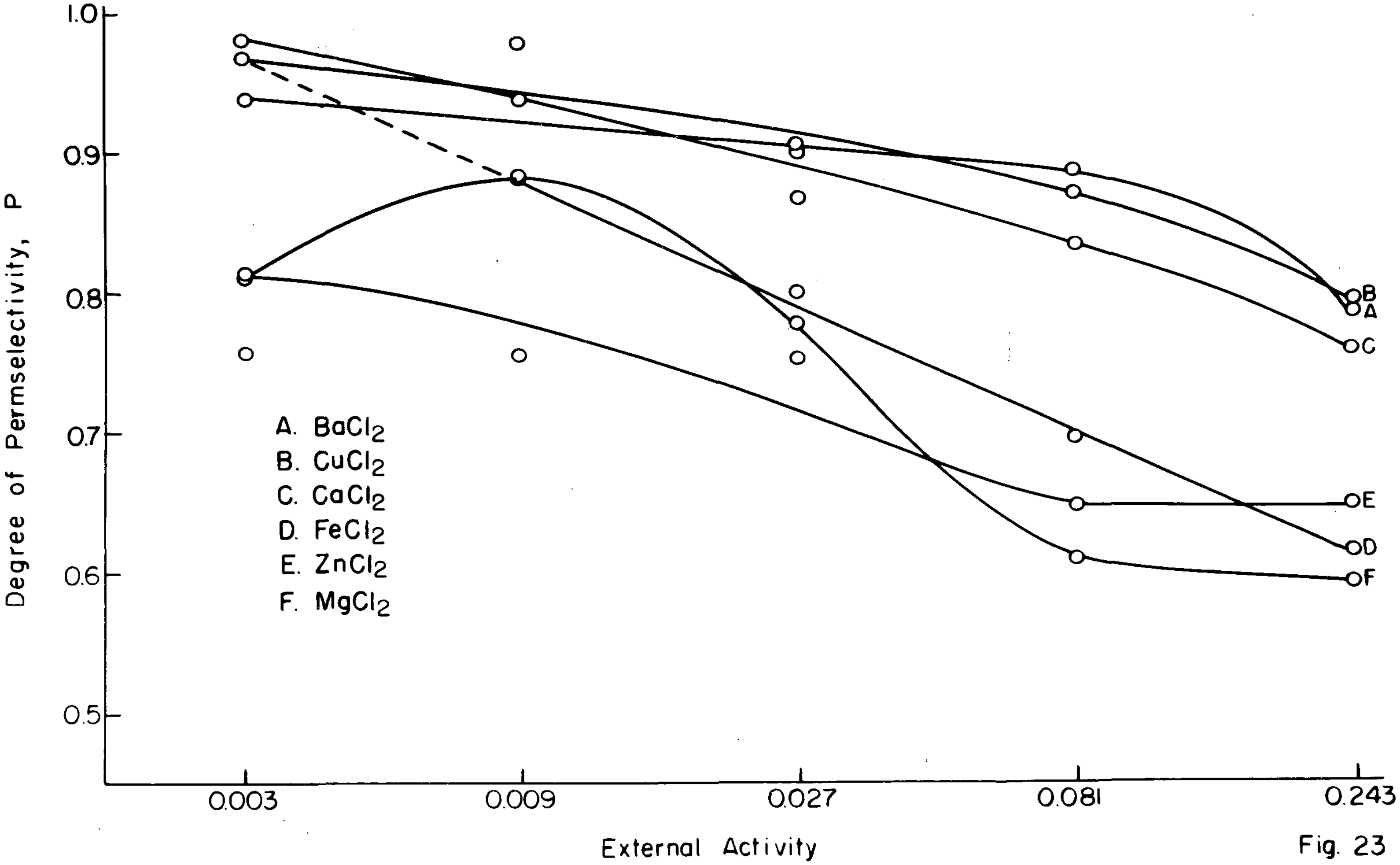


Fig. 23

By the use of equations 8 and 9, previously developed, the relative transference of the cation may be calculated and then using this transference value the permselectivity of the membrane may be calculated.

Table XXVII and Figures 18 and 19 represent the permselectivity of Amberplex C-1 membranes in various chloride salts. While the larger, more hydrated ions generally give the largest deviation from theoretical, lithium, which is the largest monovalent ion deviates the least.

Table XXVIII and Figures 20 and 21 represent the permselectivity of Amberplex C-1 membranes in various chloride salts with one per cent gelatin added to the external half of the cell. The membrane is less permselective at higher concentrations in the presence of one per cent gelatin but is little affected at the lower concentrations. The permselectivity of the membrane toward zinc and magnesium ions is greatly affected by one per cent gelatin. In general, the membrane is not as permselective in the case of large hydrated ions as it is in the case of smaller hydrated ions.

Table XXIX and Figures 22 and 23 represent the permselectivity of Amberplex C-1 membranes in various chloride salts with twenty-two per cent gelatin plus 0.1 per cent glucose added to the external half of the cell. The permselectivity of the membrane is adversely affected by gelatin of this concentration at all activity levels and very badly affected in the cases of iron, zinc, and magnesium. This is only a general correlation between hydrated ion size and permselectivity.

While the preceding data can be used to explain certain deviations, other factors, which it has not been possible to measure also play their part. Any membrane now available must be assumed to be a mosaic of wider and narrower channels. The potential developed under ideal conditions using a heteroporous membrane would give values only approaching theoretical. This is due to the fact that the larger channels, even under ideal conditions would be so large their electrical influence could not completely exclude anions.

A great number of membranes in the preliminary work had to be discarded because cracks developed in the membrane. These cracks were the result of swelling during soaking. It is only reasonable to assume that some of the membranes which were used in this investigation contained undetectable microscopic cracks which permitted excessive "leaks" and thus give erroneous potentials. Kressman (106) suggested that sintered glass be used as a supporting material for membranes. Bergin and Heyn (107) had a commercial company form the membranes directly in fritted glass discs which has been sealed into 10m.m. glass tubing. The mechanical strength of the resulting membrane was thus increased greatly. The results obtained with the glass supported membrane bear out the suspicion that low mechanical strength is very detrimental to this type of work.

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(106) Kressman, T. R. E., Nature, 165, 568 (1954)
(107) Bergin, M. J. and Heyn, Arno H. A., Journal of the American Chemical Society, 76, 4765-4769 (1954)

Since the cations are hydrated to a greater or lesser extent there will be a transfer of water across the membrane. Thus the potential of even a perfect membrane electrode will be different from that of an ideal membrane by an amount equal to the difference between the activities of water in the two solutions separated by the membrane. Other theoretical sources of error may be the osmotic flow of water across the membrane and the transference of water by electroosmosis. While these are admittedly insignificant and unimportant sources of error they point out one fact. Even with a mechanically perfect membrane electrode it is impossible to obtain the exact theoretical potential which would be achieved by an "ideal" membrane electrode. Perfect membrane action would only be achieved in the absence of any form of "leak" and thus in the passage of only the desired cation.

In an effort to reduce the difficulties which were believed to be caused by microscopic cracks a much smaller membrane was used. It was very difficult to obtain reliable reading with this membrane, probably because it was so difficult to saturate it after it had been sealed to the tube.

It was found that large areas of the membranes used could be covered with sealing compound without effecting the potential developed as long as a central uncontaminated area was left for the membrane surface to contact the solution. This extra cement did not appear either to help or harm the membrane response. The surface area exposed is apparently of little importance to the potential developed.

VI SUMMARY

The potential and permselectivity obtained with the various concentration cells using Amberplex C-1 membrane material approached theoretical values in most cases at electrolyte activities of 0.003 and 0.009. As the electrolyte activities were increased the potential deviated more and more from theoretical. This was most apparent in the cases of the divalent cations zinc and magnesium.

One per cent gelatin added to the outer concentration cell had little or no apparent detrimental effect at the lower electrolyte activities. In higher electrolytic concentrations gelatin apparently has a more detrimental effect on the activity of cations, especially the divalent cations iron, zinc and magnesium. One per cent added gelatin appears to give potentials more closely approaching theoretical values in the intermediate concentration range than pure solutions. This appears also as a greater permselectivity value for the membrane in that range.

Large concentrations of gelatin had a very detrimental effect on cation activity with almost every electrolyte at all concentrations. Again, this is especially true in the cases of the divalent ions iron, zinc, and magnesium.

An effort was made to account for the deviations from the theoretical potential apparently caused by gelatin. This was done assuming an x/m vs c curve can be used to explain the deviation from linearity. As all the salts produced similar curves only one is shown.

A representative family of curves may be seen in Figure 24. None of these curves have the linear form of Freundlich adsorption isotherms. Likewise, rough estimations show that gelatin is capable of adsorbing only 0.002 moles of cation per gram. If adsorption were held accountable for the potential deviations obtained, gelatin would be responsible for adsorbing 0.01 moles of cation per gram. At the lower salt concentrations, there appears to be no adsorption whatever. The protein has little or no effect on cation activity when the cation concentration is low. As the cation concentration is increased there appears to be a great decrease in activity due to the protein. Thus, it is apparent that adsorption of cations by gelatin is not solely responsible for the potential deviations.

In a solution of less than pH 7 the protein would assume a positive charge which is opposite to that of the membrane. Therefore, a Donnan potential would arise which would be in opposition to that of the membrane. However, the pH of the solution was near to the isoelectric point of the gelatin and thus the magnitude of the counter EMF would never be large enough to have an appreciable effect on the measured EMF.

The potentials of the concentration cells deviate so widely from theoretical when larger concentrations of cation are present with gelatin that it is logical to consider the membrane itself as the source of trouble. It was previously pointed out that the membrane is considered a mosaic of large and small pores.

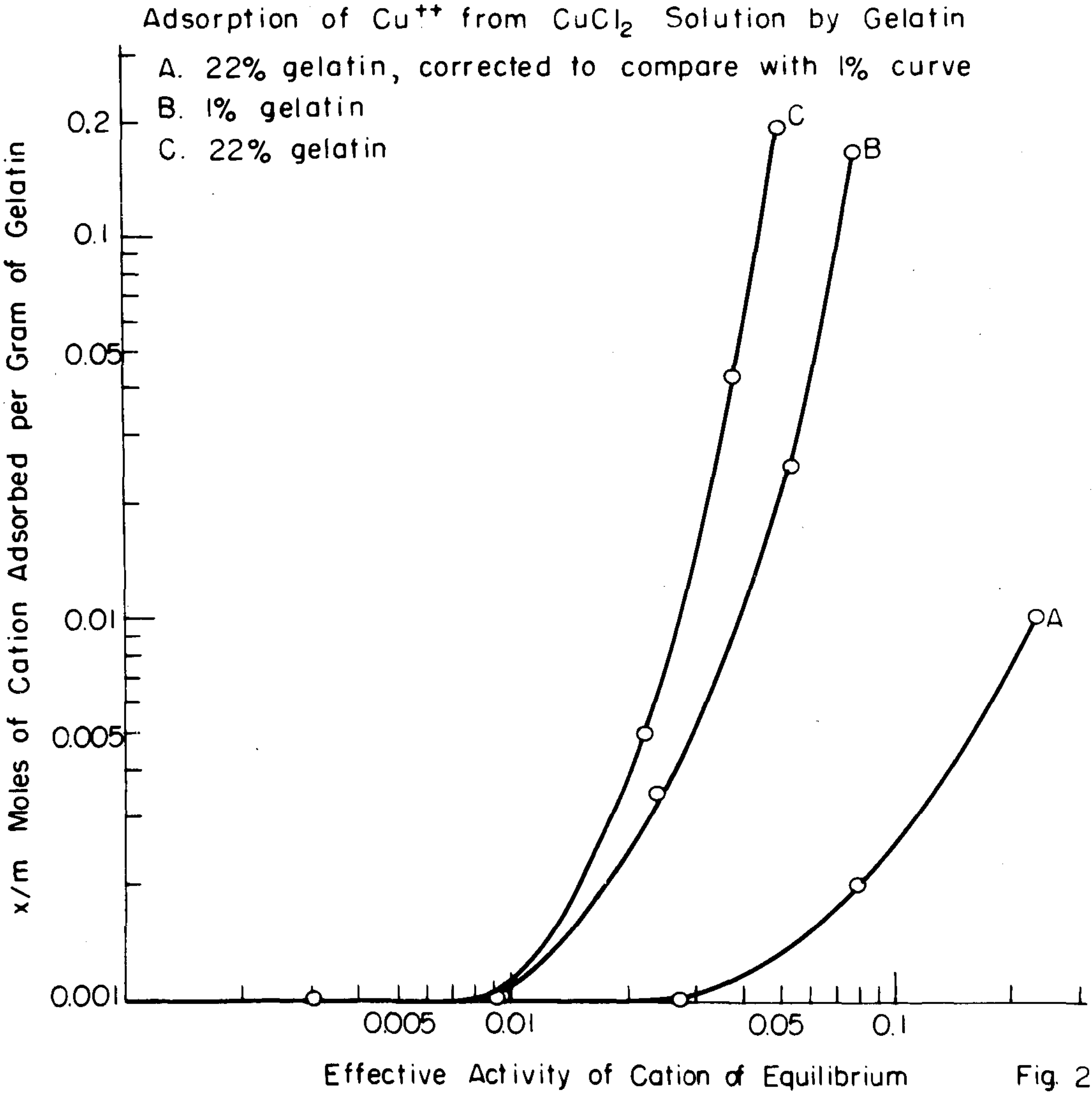
Adsorption of Cu^{++} from $CuCl_2$ Solution by Gelatin
A. 22% gelatin, corrected to compare with 1% curve
B. 1% gelatin
C. 22% gelatin
x/m Moles of Cation Adsorbed per Gram of Gelatin
0.2
0.1
0.05
0.01
0.005
0.001
0.005
0.01
0.05
0.1
C
B
A
Effective Activity of Cation of Equilibrium

Fig. 24

Gelatin is a large molecule which is easily adsorbed to many surfaces. Thus gelatin may form a monomoleuclar layer across the face of the membrane. In doing this many of the smaller pores would be plugged and thus become impermeable. While the larger pores would not be plugged their walls would be partially covered with gelatin.

Coulombic forces decrease inversely to the square of the distance. Thus, the large gelatin molecule by its blocking action has converted a membrane of high selectivity to a membrane of low selectivity. It was previously mentioned that weakly negative membranes of low capacity gave potentials which approached theoretical values at low ionic concentrations but gave wide deviations at higher concentrations. Therefore one would expect the same effect to take place in a partially blocked membrane. As the ionic atmosphere becomes more dense the membrane quickly becomes less permselective giving potentials which deviate greatly from theoretical.

The membranes are apparently more permselective to smaller hydrated ions than to the larger hydrated ions. This might be explained as follows: the coulombic forces decrease inversly to the square of the distance, therefore, one would expect an ion with a larger hydration shell to have a lower coulombic influence than one with a smaller hydration shell because its charge would be more shielded than the charge of the smaller ion. The permselectivity of a membrane is a function of the attraction of the fixed charges of the membrane and the fixed charges of the counter ion. If this attraction is great, i.e., if the opposite charges are unshielded, the membrane will have high selectivity. If the attraction is low, the membrane will have low selectivity. Thus, one would expect the ions with the smaller hydration shells to be attracted to the counter charged membrane more strongly than those with the larger hydration shells. Thus the membranes would be more permselective to smaller hydrated ions.

It is believed that a near mechanically perfect membrane may be constructed using fritted glass as a supporting medium in place of the plastic material now in use. Thus, the ion exchange resin could be formed directly within the net-work of the glass. This would give one control over such factors as the distance between supporting media particles, "holes" formed in the resin during polmerization and microscopic cracks produced by swelling during soaking. These factors are believed to be the main sources of error in the present work.

If membranes of adjusted porosity could be produced at will it may be possible in a dialysis apparatus to use them to separate monovalent cations from divalent cations by utilizing their difference in size.

VII CONCLUSIONS

The conclusions may be divided into two parts. 1. Those conclusions concerning the membrane material and its function as an electrode in the salts investigated. 2. The application and unique advantage of this type of cell in biochemical investigations.

Membranes from Amberplex C-1 more nearly approach the "ideal" permselective membrane than any other material. This is true as a group. Occasionally a rare almost perfect membrane will occur using most membrane materials but they are "accidental".

In addition to the lithium, sodium, potassium, ammonium and magnesium ions, it was found that Amberplex C-1 acts as a permselective membrane for the copper, zinc, barium, and ferrous ions and therefore when saturated with one of these ions can act as an electrode of that particular ion.

The principal difficulty in the use of this type of material as an electrode is the fragility of the membrane which is a function of the inactive supporting material. It is felt that this can be eliminated by forming the ion exchange resin in a fritted glass disk which has been previously sealed to a glass tube. This would probably eliminate the major potential deviations which are believed to be of mechanical origin, i.e., cracks etc.

The resulting electrode might then be reliably used as a tool in the determination of cation activities in pure solutions of one salt or in the determination of cation activity in a solution of mixed salts with a common cation. With previous calibration it could be used in dilute solutions to determine cation activity of a single salt in the presence of a protein or the cation activity of a common cation in the presence of a protein in a mixed salt solution.

In 1 per cent solution of gelatin containing known concentration of M Chloride, the activity of the M ions was found to be the same as in pure solutions except at the higher concentrations. This elucidates a problem which has been long in contention. There is apparently little cation interaction with the protein at lower cation concentrations. Adsorption of one per cent gelatin apparently modifies the membrane to such an extent that it is not permselective in a dense ionic atmosphere and therefore becomes less reliable as the ionic concentration increases.

Twenty-two per cent gelatin apparently modifies the membrane to such an extent that its permselectivity is relatively low and unreliable over the whole range of concentrations.

At salt concentrations of 0.1 molal or less and protein concentrations of 1.0% or less these experiments indicate that the method employed offers a relatively simple technique for measuring the actual concentrations of active ions present in solution. The determination of total concentration of a given ion has long been possible but the determination of the activity of the ion in solution has been extremely difficult.

This technique may also be used to determine the interaction of proteins with various ions. Thus, one may determine to what extent a given ion may interact with various ion sensitive proteins. This may be an especially valuable technique in the study of purified enzymes which are activated by cations as potassium, cobalt, calcium, or magnesium. Muscle proteins in the presence of the potassium ion may also be advantageously studied by this method.

AUTOBIOGRAPHY

I, Carl J. Ish, was born in Mansfield, Ohio, March 20, 1919. I received my secondary school education in the public schools of Mansfield, Ohio. My undergraduate schooling was obtained at Ashland College, Ashland, Ohio, from which I received the degree Bachelor of Arts in 1942.

I was employed as a Process Chemist by the United States Rubber Company until July 1943 at which time I accepted a position as a Senior Chemist with the Crown Central Petroleum Corporation, Houston, Texas.

In January 1946 I entered the Graduate School of The Ohio State University. During 1946 I was employed as an Assistant in the Department of Chemistry. In 1947, I received an appointment as an Ohio State University Research Foundation Fellow until I received the degree of Master of Science in 1948.

In 1948 I accepted a position with The Battelle Memorial Institute as a Principal Chemist. This position I have held while completing the requirements for the degree of Doctor of Philosophy in the Department of Agricultural Biochemistry.