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ION EXCHANGE MEMBRANES

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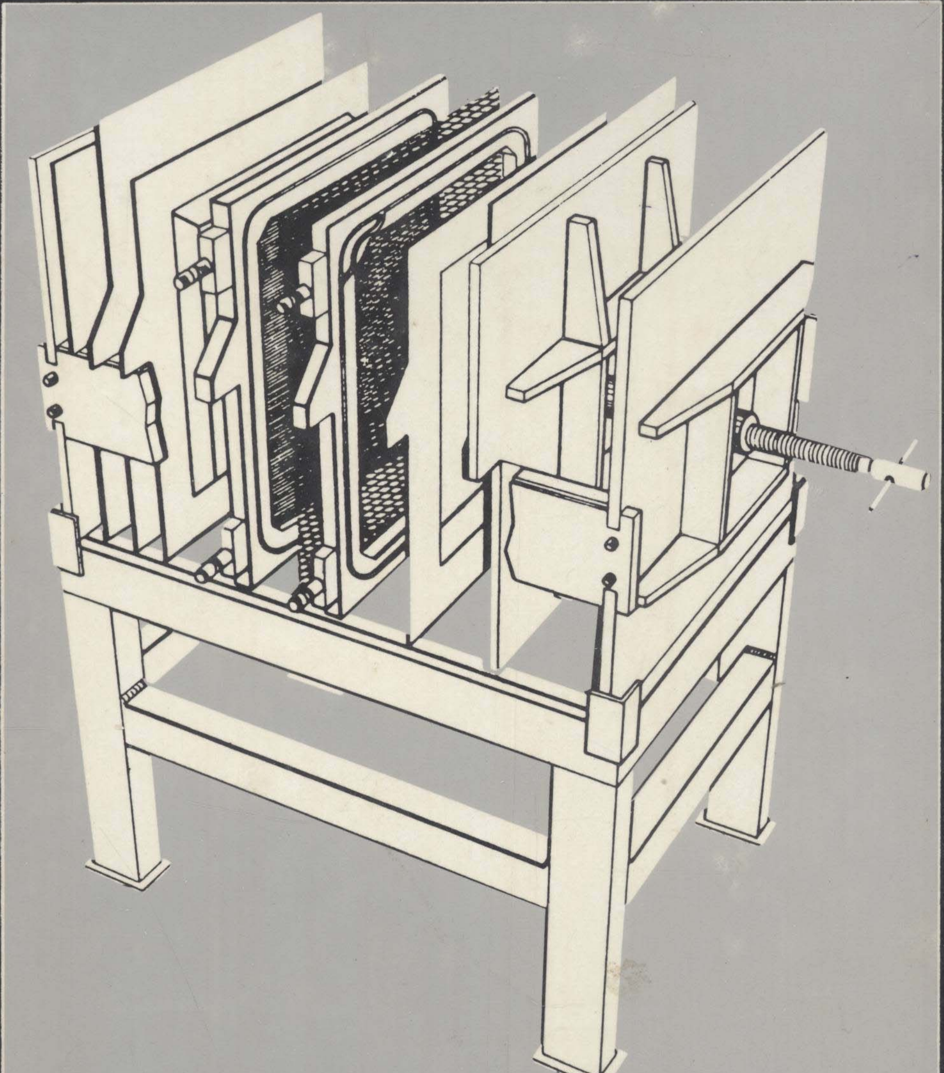

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Published for the
SOCIETY OF CHEMICAL INDUSTRY, London

by ELLIS HORWOOD LIMITED
Publishers · Chichester

First published in 1983 by

ELLIS HORWOOD LIMITED
Market Cross House, Cooper Street, Chichester, West Sussex, PO19 1EB, England

The publisher's colophon is reproduced from James Gillison's drawing of the ancient Market Cross, Chichester.

Distributors:

Australia, New Zealand, South-east Asia:
Jacaranda-Wiley Ltd., Jacaranda Press,
JOHN WILEY & SONS INC.,
G.P.O. Box 859, Brisbane, Queensland 40001, Australia

Canada:
JOHN WILEY & SONS CANADA LIMITED
22 Worcester Road, Rexdale, Ontario, Canada.

Europe, Africa:
JOHN WILEY & SONS LIMITED
Baffins Lane, Chichester, West Sussex, England.

North and South America and the rest of the world:
Halsted Press: a division of
JOHN WILEY & SONS
605 Third Avenue, New York, N.Y. 10016, U.S.A.

British Library Cataloguing in Publication Data
Flett,D.S.
Ion Exchange Membranes
1. Chemical Engineering 2. Membrane (Technology)
3. Separation (Technology)
I. Flett, D.S.
660.2'842 TP156.S45

Library of Congress Card No. 83-4343

ISBN 0-85312-640-2 (Ellis Horwood Ltd)
ISBN 0-470-27452-2 (Halsted Press)

Organising Committee: Dr D. S. Flett (Chairman), Mr J. Melling (Secretary)
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Printed in Great Britain by Unwins of Woking

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Foreword

Dr D. S. Flett, Warren Spring Laboratory, Stevenage, Herts UK
Chairman, Organising Committee

The use of ion exchange membranes in the process industries has increased significantly in recent years and a continuation of this trend is anticipated. Particularly, the adoption of ion exchange membrane technology in chloralkali production is proving a considerable growth area. These developments in the chloralkali industry are being actively assessed in relation to electrodialysis and membrane cell processes in a wide range of industries including applications in hydrometallurgy and the chemical industry at large. The development of liquid membranes has recently received considerable attention although so far no commercial applications have taken place. Membranes have been developed for use in high temperature fused salt systems being considered for automotive battery applications and the like, while other membrane advances relate to the development of sensors which can have uses in on-line analysis for process control.

The Organising Committee have endeavoured to bring together in this Symposium a wide variety of papers on as many aspects of ion exchange membrane science, technology and application as possible. It is hoped that the Symposium will promote critical examination of the current ion exchange membrane scene and stimulate consideration of the research and development necessary to achieve further successful applications of this advancing technology.

I am very grateful for all the help afforded me by my Organising Committee Members and the Staff of the Society of Chemical Industry without which this Symposium would not have been possible.

PART 1 PLENARY LECTURE

CHAPTER 1

Trends in Ion-Exchange Membrane Science and Technology

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INTRODUCTION

Ion-exchange membranes became available commercially a little over thirty years ago. These early membranes were sulphonated and aminated derivatives of, usually, phenol-formaldehyde polycondensates. Chemically they were already familiar as particulate synthetic ion exchangers introduced before World War II. The basic chemistry of their preparation has been described many times and is well summarized by Helfferich [1]. In order to produce these materials in the form of coherent sheets it was found necessary to modify the recipes in order to provide a more highly water-swollen material with a lower exchange capacity than was desirable in particulate ion-exchange resins. If this were not done the membranes were too brittle to handle because the osmotic pressure of the counterions was sufficient to break down the phenol-formaldehyde molecular network. Even with this modification these early membranes were very fragile. Frequently they were reinforced by polymerizing the resin around a woven mesh of glass or nylon fibres and they were very thick (1 - 2 mm) by modern standards. It was extremely difficult to clamp them between cell flanges to provide a leak tight joint without rupture.

Although such membranes were obviously unsatisfactory for the development of technological membrane processes, they possessed features that enabled them to play an important role in the development of membrane science. As a result the trends in membrane science and technology diverged for a considerable period. More recent developments on both sides are bringing about a reconvergence which promises a bright future for the wider application of ion-exchange membranes to meeting the

the separation requirements of chemical industry.

THE PHYSICAL CHEMISTRY OF MEMBRANE TRANSPORT

The solution - diffusion model of transport across polymeric membranes was well established by the time ion-exchange membranes became available [2]. According to this theory transport through a membrane separating two reservoirs was a relatively slow process controlled by the rates of the molecular Brownian motion in the membrane itself. It was postulated that existence of the non-equilibrium transport processes did not disturb the maintenance of a thermodynamic equilibrium distribution of the transported substance between the membrane material and the ambient gas or liquid phases at the membrane surfaces or, in the case of a composite membrane made up of layers in series, at the interfaces between those layers. Thus the concentrations in the membrane at its surfaces could be uniquely related to the concentrations or partial pressures in the external phases, assumed to be homogeneous and well-stirred, by experimentally determinable partition or solubility coefficients s [3].

The membrane itself is thought of as a homogeneous, thermodynamically stable molecular solution of the permeant in the polymer. During transport there is a concentration gradient of the permeant regarded as solute in the polymer regarded as solvent. Diffusion takes place down this concentration gradient as a result of the random molecular heat motion of the permeant molecules and segments of polymer chains. This diffusion is described by Fick's law in terms of a diffusion coefficient D, which may be concentration dependent.

In the simplest cases s and D are constants at constant temperature and the permeation flux density J between reservoirs of a single permeant at concentrations c_1 and c_2 is given by

$$J = -Ds(c_2 - c_1)/l = -P(c_2 - c_1)/l \qquad (1)$$

where l is the membrane thickness and the permeability coefficient P is the product of s and D.

The solution - diffusion model was found to fit the transport of simple gases in polymeric membranes very well and even to be applicable as a technique for studying the molecular dynamics of polymers [4]. Quantitative departures from eqn. (1), observed with organic vapours as permeants, were explained through thermodynamic non-ideality i.e. concentration dependence of s and the influence of the permeant molecules on the dynamics of the polymer segmental motions i.e. concentration dependence of D. In extreme cases, slow dimensional changes of the polymer delayed the setting up of the boundary equilibria and the steady state concentration profile during transport leading to anomalous behaviour.

The success of the solution - diffusion model in describing the transport of non-ionic substances through uncharged membranes made it a natural starting point for a theory of transport in ion-exchange membranes. Seen in retrospect, it is rather surprising that no one was apparently worried by the fact that the solution - diffusion model had been developed and tested for single permeants transported in pure, usually soft, polymers. No systematic studies had been made using plasticized or highly swollen polymers. Indeed this remains true today except for two special areas: reverse osmosis separations using aqueous solutions and facilitated transport processes employing carriers supported in swollen polymers.

In fact a theory of electro-chemical membrane phenomena had been developed by biologists and refined by chemists before ion-exchange membranes, as we know them, were available. This theory, known usually as the Teorell-Meyer and Sievers fixed-charge theory [5-10], was devoted to the interpretation of potentials and conductances of biological and synthetic membranes with low fixed charge densities and low permeabilities. It followed the lines of the solution - diffusion model but replaced Henry's law by the Donnan distribution to describe the interfacial ionic equilibria and Fick's law by the Nernst-Planck equation to describe ion transport in the membrane.

The Teorell-Meyer and Sievers theory permitted the correlation of a number of measurable properties of systems in which ions permeated selectively through membranes, but searching quantitative tests became possible only when the new high-flux ion-exchange membranes were introduced.

EQUILIBRIUM BETWEEN MEMBRANES AND ELECTROLYTES

The equilibrium distribution of ions between membrane and solution phases has to be written in terms of activities a_i rather than concentrations because interionic attractions cause major departures from ideality [11]. Thus for the co-ions, subscript n, one has

$$\bar{a}_n = a_n \exp - (\Delta\mu^o_n + z_n F \psi_D)/RT \qquad (2)$$

where $\bar{a}_n$ is the activity in the membrane and a_n that in solution of the co-ions valency (with charge sign) z_n. ψ_D is the Donnan potential $(\bar{\psi} - \psi)$ and $\Delta\mu^o_n$ the difference between the standard chemical potentials in the membrane and solution.

Instead of trying to estimate the free energy of transfer $\Delta\mu^o_n$, standard states were defined to make this quantity zero and the consequences transferred into the activity coefficient $\bar{\gamma}_n$. This device works reasonably conveniently in highly swollen membranes but would be misleading if applied to some less swollen modern membranes.

In particular it should be noted that the Donnan distribution eqn. (2) depends on there being single valued potentials ψ and $\bar{\psi}$ characteristic of the solution and the membrane. In fact the widely accepted Debye-Hückel treatment of aqueous electrolyte solutions is founded on the principle that the potential varies from point to point, on the molecular scale, in response to the locations of nearby ions. Nevertheless the rapid Brownian motion in a solution ensures that the spatial average potential at any instant is equal to the time average potential at every point and ψ can be assigned a unique value.

In the membrane a different situation exists. The polymeric material and the imbibed water have very different dielectric constants. The electric field around an ion is not therefore spherically symmetrical. This is especially true for the fixed ions which are directly bonded to the matrix. Furthermore the diffusional Brownian motions of the matrix segments are comparatively sluggish and restricted in range. Thus the potential is not the same at all points even on a time average basis where the time scale is dictated by the motions of the free ions i.e. counterions and co-ions. The membrane does not behave as if it can, even at equilibrium with a solution, be characterized by a single average internal potential $\bar{\psi}$.

In order to keep the osmotic swelling pressure at levels bearable by the network bonds the fixed charges have to be relatively widely spaced along the polymer chains and the random nature of the polymerization reactions results in the steric arrangements of fixed charges and crosslinks being somewhat irregular. Thus the electric potential in any membrane has a pattern of spatial variation characteristic of the membrane structure.

By writing an equation analogous to (2) for the counterions, subscript g, eliminating ψ_D between these equations and setting $\Delta\mu^o$ at zero, one finds

$$\bar{m}^{\nu_n}(\bar{m} + \bar{M}/\nu_n\nu_g)^{\nu_g} = (m\,\gamma_\pm/\gamma_\pm)^{\nu} \qquad (3)$$

Here ν_n and ν_g are the numbers of co-ions and counterions per molecule of electrolyve, $(\nu = \nu_g + \nu_n)$, m and $\bar{m}$ are the molalities of the electrolyte, with $\bar{m}$ defined as $\bar{m}_n/\nu_n$, $\bar{M}$ is the molality of the fixed charges and $\gamma_\pm$ and $\bar{\gamma}_\pm$ are the mean activity coefficients in solution and membrane respectively.

Eqn. (3) can be tested by measuring m, $\bar{M}$ and $\bar{m}$ and using the data to calculate $\bar{\gamma}_\pm$. When this is done it is found that $\bar{\gamma}_\pm$ decreases from values comparable with $\gamma_\pm$ when $m > \bar{M}$ to very low values when $m \ll \bar{M}$ [12]. Since the ionic strength in the membrane remains almost constant for values of m much less than $\bar{M}$ one expects $\bar{\gamma}_\pm$ to remain almost constant for $m < \bar{M}$. Thus the real meaning of the experimental observations is that the uptake of co-ions, is much greater than the Donnan equation (3) would lead one to expect even after making allowance for the non-ideality of electrolytes. As a result the membrane selectivity in dilute solutions is less good than expected.

Three theories have been advanced to account for these observations. The polymer chains bearing the fixed charges have been regarded as bearing a smeared uniform charge density and all counterions situated within the regions close to the chains where $z_g e\phi/kT > 1$ (e is the protonic charge and ϕ the potential expressed relative to the mid-plane between two chains) may be regarded as bound to the chains [13]. This theory effectively claims that the effective value of $\bar{M}$ is lower than the value determined analytically. It accounts qualitatively but not quantitatively for the experimental results.

The distances apart of the fixed charges along the chains are comparable with the distances between chains in many membranes and the smeared charge model is not a good approximation. The statistical theory of flexible polyelectrolytes takes account of the discreteness of the fixed charges and when applied to a crosslinked network predicts a lowering of activity coefficient of the absorbed electrolyte [12]. Agreement with experiment is good for divalent counterions but for univalent counterions the polyelectrolyte effect is insufficient to account for the full effect observed.

These two approaches have now become somewhat overlooked as the result of a treatment introduced later [14] in which attention is focussed on structural irregularities in the polymer network arising during its manufacture. Thus the membrane is to be thought of as possessing not a single effective value of $\bar{M}$ but a distribution of values, weighted according to some function determined by the network structure. A precise theory of this approach has been developed and found to fit the experimental facts although the distribution function for $\bar{M}$ is, in effect, a fitting parameter. Expressed in a simplified form, the outcome of this approach is to replace eqn. (3) by

$$\bar{m}^{\nu_n}((\bar{m}+\bar{M})/\nu_n\nu_g)^{\nu_g} = (\alpha m)^{\beta\nu} \qquad (4)$$

On plotting the logarithm of the left side of eqn. (4) against log m a straight line should be obtained from which α and β can be determined [15]. This equation fits most published experimental data very well. $\alpha\,(=\gamma_{\pm}/\bar{\gamma}_{\pm})$ turns out to be close to unity and independent of *m*, as though counterion binding and polyelectrolyte effects were negligible. β is independent of the electrolyte type and is a characteristic of the non-uniformity of the network structure.

THE SWELLING OF ION-EXCHANGE MEMBRANES

When immersed in aqueous solutions ion-exchange membranes swell and imbibe water as well as ions. Without this water to dissociate the ions and plasticize the polymer the conductances of membranes in use today would be too low for practical exploitation.

Four factors can be distinguished as driving water into the membrane [11]. Polymers tend always to absorb solvents to increase their total configurational entropy. The extent to which water is absorbed is determined by the hydrophobic - hydrophilic balance of the polymeric material to which the fixed ions are attached. Usually the hydrophobic character predominates and the swelling would not be large but addition - polymer networks and polycondensates may differ considerably, the latter being more hydrophilic than the former. The fixed charges and counterions will readily bind water of hydration to extents which depend on the size, charge and polarizability of the ions concerned. There is no reason why the hydration tendencies of ions in a membrane should differ markedly from their behaviours in simple solutions. Once hydrated, the counterions and fixed charges become dissociated and the normally higher molality in the membrane than in the surrounding solution creates an osmotic pressure driving more water into the membrane. Fourthly the dissociation of the counterions from the fixed charges exposes them to electrostatic repulsions along the chains which, just as with polyelectrolytes, extends them and expands the network still further.

The extent of swelling is limited by the elastic tensions set up in the chain segments running between fixed points. In early membranes the fixed points were chemical crosslinks between the chains but other types of non-swelling inclusions exist in more modern membranes.

Particularly interesting is the way in which the extent of swelling varies with the concentration of the ambient solution. Transferring a membrane from pure water to a dilute solution results in a marked shrinkage, greater than can be accounted for by the change in osmotic pressure. It is probable that the introduction of even a small concentration of sorbed electrolyte decreases the repulsions between the fixed charges and permits the polymer chains to adopt a less extended conformation [12].

At concentrations from about 0.5 $\bar{M}$ to 1.5 $\bar{M}$ the swelling remains relatively constant. At higher concentrations the swelling becomes reduced as the osmotic pressure difference between external solution and membrane decreases [16].

When electrodialytic desalination was the principal process employing ion-exchange membranes the solutions were only rarely sufficiently concentrated to make the changes in swelling very important. Today there is a demand for processing at much higher concentrations and in the presence of a variety of counterions. Membrane volume changes are becoming more important and a new phase of work in this area is due.

IONIC MOBILITIES AND THE NERNST-PLANCK EQUATION

According to the Nernst-Planck equation the local flux density J_i of ions i in the membrane is given by

$$J_i = -D_i \bar{c}_i [\mathrm{d} \ln \bar{c}_i + (z_i F/RT)\, \mathrm{d}\psi]/\mathrm{d}x \tag{5}$$

where D_i is the diffusion coefficient of ions i in the membrane. Analogous equations can be written for counterions and co-ions and, knowing that their fluxes are related by the electric current density, the equations can be combined to eliminate $\mathrm{d}\psi$. The resulting equation has to be integrated across the membrane and to do this it is usual to assume the diffusion coefficients are constants and also that the total ionic charges just balance at each plane x i.e. local electrical neutrality prevails.

The latter assumption has recently been shown to be inaccurate because even at zero current the differing ionic mobilities give rise to a diffusion potential gradient. The existence of such a field can occur only if there is a finite charge density. It has been shown that in the case of the diffusion of a single electrolyte the solutions for the ionic concentrations and fluxes are scarcely affected when the Nernst-Planck and Poisson equations are combined without the assumption of local electroneutrality [17]. So far the cases of a mixture of counterions and non-zero electric currents have not been examined and some unexpected results may emerge.

The ionic diffusion coefficients have been studied experimentally in two ways [18]: by measuring the fluxes of radiotracer ions and by measuring ionic conductances u_i using the Nernst-Einstein equation

$$D_i = u_i RT \tag{6}$$

Many studies have been published in which tracers have been used to determine diffusion coefficients of co-ions and counterions in ion-exchange resins as well as membranes [11,19]. The findings in the case of the co-ions have not been easy to interpret. The measurements are difficult to make accurately and some workers have used steady and some transient state methods. These two methods would give different values of D_n if the membrane contained blind pores or regions which did not contribute to through-permeation pathways. A part of the difficulty in interpretation may arise therefore from experimental artefacts.

Trying to summarize a great deal of data in a few sentences risks being misleading. In some simple cases of relatively homogeneous membranes D_n appeared to vary relatively little with the concentration of the bathing solution and to decrease somewhat at high concentrations due to the osmotic shrinkage of the membrane. The ratio of D_n to the value D_n^o in free solution for various co-ions appeared to be almost constant. A reasonable interpretation of these findings is that the co-ions diffuse along tortuous aqueous pathways avoiding contact with the polymer chains by which they are repelled electrostatically. The activation energies for co-ion diffusion in the membrane were found to be close to the values in water and this supported the above explanation. In several cases it was found that [20]

$$D_n/D_n^o = [v_w/(2-v_w)]^2 \tag{7}$$

fitted the data well, where v_w is the volume fraction of water in the swollen membrane. This correction for tortuosity has been widely used since.

Unfortunately this simple picture breaks down in membranes which are not highly swollen ($v_w < 0.3$) and where the resin is inhomogeneous with respect to the fixed charge density $\bar{M}$. In such cases the co-ions may be forced into frictional as well as electrostatic interaction with the matrix and will not be uniformly distributed in the membrane. Then D_n may increase or decrease with increasing external concentration depending on whether the membrane can be better regarded as regions of high fixed charge density dispersed in a continuum of low fixed charge density or vice versa.

The diffusion coefficients of counterions obey a more consistent though not more easily explained pattern. In dilute solutions the diffusion coefficients are low and increase by a factor of two or more as concentration increases. They