pH Changes at Anion Selective Membranes under Realistic Flow Conditions

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ABSTRACT

The flow conditions and solution concentrations used in the investigation were similar to those present in practical electrodialysis cells. The concentration of hydroxyl ions which appeared on the receiving side of the polarizing anion selective membrane was measured as a function of current density. The important finding was the large effect traces of dissolved organic matter in the feed water had on the onset and concentration of alkali produced in the receiving stream. For unpoisoned membranes an i_o/c value of 4000 amp cm equiv^{-1} was obtained. This is an order of magnitude greater than reported in previous studies.

Multicompartment electrodialysis depends on the principle that the transference number of the counterion in an ion-selective membrane is greater than the transference number of the same ion in the surrounding solution (1). Thus for the layer of solution adjacent to the membrane on the donating side (2) there is for each ion an inequality in electrical migration and counterions are removed through the membrane at a greater rate than they are replaced from the bulk solution. Continuity of counterion migration is maintained by convective and diffusive transport from the bulk solution. As the membrane surface is approached the contribution due to convective transport decreases.

It is customary to simplify the real situation (3, 4) by postulating a layer of thickness δ (cm) adjacent to the membrane in which convective transport normal to the membrane is zero. By assuming a smooth flat membrane surface and a homogeneous current distribution it is then possible to describe the steady state for a single electrolyte by the following equation.

$$\frac{i(\bar{t}-t)}{\mathbf{F}} = \frac{D(c-c')}{\delta} \qquad [1]$$

where i is the current density (amp cm^{-2}), $\bar{t}$ and t are the counterion transference numbers in the membrane and solution, respectively, $\mathbf{F}$ is the faraday, D the diffusion coefficient of the electrolyte in the external solution (cm^2 sec^{-1}), and c and c' are the concentrations of electrolyte in solution in the bulk and at the membrane interface, respectively, (g equiv cm^{-3}). c' is less than c. (The situation on the receiving side is described by transposing c and c', and c' is greater than c).

The maximum inequality in electrical migration that can be balanced by diffusive transport is obtained when the solution concentration at the membrane interface is zero ($c' = 0$). From Eq. [1] the critical current density i_c at this condition is

$$i_c = \frac{DC\mathbf{F}}{(\bar{t}-t)\delta} \qquad [2]$$

At current densities higher than i_c additional current carriers are necessary. These are hydroxyl ions through anion-selective membranes and hydrogen ions through cation-selective membranes (5, 6). While this appears true for anion-selective membranes (7, 8) the amount of hydrogen ion transport through cation-selective membranes above the critical current density is much less than expected, and additional transport mechanisms have had to be invoked (7-11). This behavior with cation-selective membranes is not fully understood, but need not concern us further as the situation at the anion-selective membrane has proved to be of much greater importance in practical electrodialysis. A refinement is that the transport of hydroxyl ions through anion-selective membranes should commence not when the conditions are such that the interfacial concentration has fallen to zero but at a current density slightly lower than the critical value of Eq. [2] when the interfacial concentration is sufficiently small for the natural hydroxyl ion concentration of the donating solution to be competitive as an alternative migratory species (5, 6, 12).

In the vicinity of and above the critical current density the effects described give rise in practical electrodialysis units to (*i*) increased ohmic resistance due to layers of reduced concentration on the donating sides of membranes, (*ii*) increased counter concentration potentials across the membranes, (*iii*) reduced coulombic separation efficiencies, and (*iv*) transport of hydroxyl ions through the anion-selective membranes to make the receiving stream alkaline (12). Of these effects (*iv*) has the most serious repercussions (12, 13) as it results in the precipitation of hydroxides and carbonates of the alkaline earth metals which are present in most natural waters.

It is mandatory that electrodialysis units be operated below the critical current density. This is an important limitation since economically, current densities higher than the accepted critical values are desirable (13-16). Although suitable programming of electrodialysis operation (17) can reduce the economic effect of this limitation, the onset of hydroxyl ion transport through anion-selective membranes at the critical current density is probably the most serious restriction to electrodialysis at the present time (18).

All the effects (*i*)-(*iv*) above have been used to study polarization phenomena. Cooke (7, 8) and Cooke and van der Walt (19) have demonstrated the advantages of the concentration potential method whereby actual interfacial concentrations are deduced. The method is most useful at current densities less than the critical value. Unfortunately the theoretical basis is less convincing in the vicinity of the critical current density when the potential due to different interfacial electrolyte concentrations may be complicated by pH values which also differ on the two sides of the membrane. Voltage-current or voltage-time plots to indicate an increased ohmic resistance and an in-

Key words: Anion-selective membranes, concentration polarization, desalination, electrodialysis, limiting current density, multicompartment cells, organic poisoning.

creased counter concentration potential under critical conditions (9, 20-24) have the merit of simplicity. A small yet damaging transport of hydroxyl ions at current densities less than the main critical value could, however, be undetected by the voltage method. Cooke and van der Walt have mentioned this possibility (19), and in practical units such conditions could also arise from nonuniform flow distribution, inhomogeneous membranes (25), and nonuniform current distribution. Cooke (26) has improved the sensitivity of the method, without entirely removing the objections, by the use of overpotential which is obtained by subtracting an extrapolated estimate of the voltage of a hypothetical unpolarized condition from the voltage of the real polarized condition. The expected decrease in coulombic efficiency has been observed above the critical current density (5, 6, 27, 28) but is not sufficiently sensitive to be useful. The measurement of *p*H changes, (5, 6, 11, 21) particularly of alkalinity on the receiving side of the membrane utilizes the most serious effect of polarization and is, therefore, the most direct method. Cooke has criticized the *p*H method (7), but his arguments apply only to cation-selective membranes with their low hydrogen ion transport above the critical current density. The measurement of alkalinity on the receiving side of the membrane has been preferred in this work.

While systems stirred mechanically (11, 19) and by natural convection (5, 7, 8, 11, 21, 23, 26) have provided valuable insight into the polarization phenomena, the uncertainties in extrapolating to practical systems are too great for these results to be of real value to the designer. Flowing systems must be used (6, 9, 19, 20, 22, 24, 28) under hydrodynamic conditions which approximate as closely as possible to those present in practical units (24). Data from flowing systems of small exposed membrane area, *e.g.*, 0.64 cm^2 (19), where the entry and exit conditions to the compartment may have a disproportionate influence on the hydrodynamic conditions within the compartment, must be regarded with caution. Block (25) has demonstrated the heterogeneity of many commercial membranes, and Solt (29) and Cooke (26) have reported particular examples. It is, therefore, important that the scale of scrutiny should be appropriate. From the design viewpoint this is a further argument against the use of very small areas of membrane. For flowing systems it is also desirable to provide information on flow distribution so that one can ascertain that the noted effects are not seriously complicated by stagnant regions within the compartment. The value of F-diagrams (30, 31) in this respect does not appear to have been appreciated.

The present work formed part of a design study, and everything possible was done to ensure that conditions were similar to those that would be present in the actual stack. Compartment dimensions, compartment filling, linear flow rate, and exit and entry arrangements were identical. It was not practical in the laboratory to carry out very prolonged runs, and we compromised by following the *p*H of the receiving solution for 3 hr. Our important findings are consequent on the continuation of runs for this period. No information is given on the duration of runs in previous studies (6, 19, 20, 22, 24). Theoretically (Eq. [2]) and experimentally (11, 17) the critical current density is directly related to the donating-side concentration. Thus the polarization limitation is first apparent at the most dilute donating concentration in the unit, *i.e.*, the effluent concentration of the dialysate stream. This study was therefore carried out with a donating concentration equivalent to the planned concentration of the dialysate effluent.

Experimental

The membrane and flow arrangement is shown in Fig. 1. The anion-selective membrane whose polarization was under examination was at position 3. The

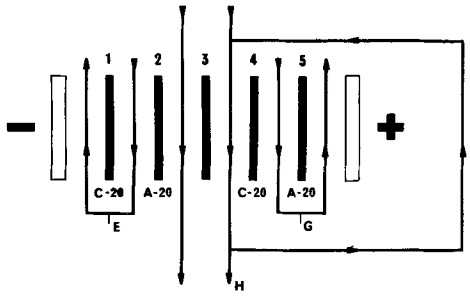

Fig. 1. Membrane and flow arrangement

donating and receiving solutions for this membrane flowed through compartments 2-3 and 3-4, respectively.

Membranes.—Two membranes were used in position 3, Permaplex A-20 (The Permutit Company Ltd.) and T.N.O. C-60 (Nederlandse Centrale Organisatie voor toegepast—Natuurwetenschappelijk Onderzoek). Permaplex A-20 and C-20 membranes were used in positions 1, 2, 4, and 5.

Permaplex A-20 is of the heterogeneous type and consists of a finely divided conventional anion exchange resin imbedded in an inert polyethylene binder with an inert reinforcing fabric of fine open mesh pressed against each face (32). The basic membrane has been described (5), and the influence of the reinforcing fabric is similar to that already noted for the cation-selective type (33).

The homogeneous membrane T.N.O. (34, 35) A-60 is based on a polyethylene film in which styrene and a few per cent of divinyl benzene have been polymerized. Quarternary ammonium groups are introduced on the aromatic nuclei by established procedures. In regard to the homogeneity, the comments of Block (25) and Cooke (26) are noteworthy.

Cell design.—Each compartment was bounded by two membranes (or a membrane and an electrode) and a Klingerit gasket 0.127 cm thick. The plan of the gasket for compartment 2-3 is shown in Fig. 2. The central square area is 27 x 27 cm. Rectangular holes A registered with similar holes in other components of the stack to form the supply conduits to the compartment. Similarly holes B formed part of the withdrawal conduits.

Flow between conduits and the compartment was via inserts C (36). The inserts were 0.127 cm thick, to correspond with gasket thickness, and were made from rigid epoxy resin. A series of small circular tunnels, 0.051 cm diameter, on the thickness center-line and spaced with centers 0.127 cm apart formed the connecting passages. Experience has shown that these inserts prevent intercompartmental solution leakage which is a serious problem in other stack designs (37).

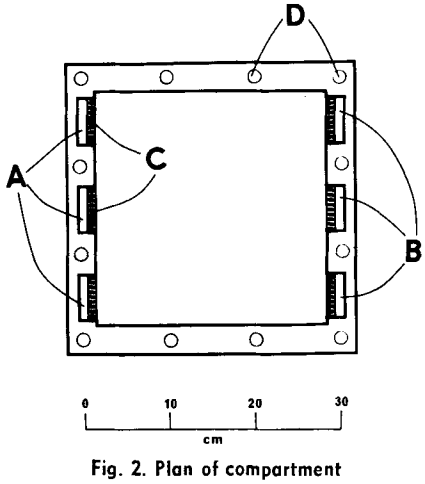

Fig. 2. Plan of compartment

The solution thus entered substantially all along one edge of the compartment and left by exits substantially all along the opposite edge (38). Such an arrangement encouraged uniform liquid distribution. Good distribution was further aided by a close fitting filling of a corrugated perforated sheet of polyvinyl chloride (39, 40) which was orientated so that flow resistance was greater in the forward than in the sideways direction (40), *i.e.*, with the corrugations normal to the direction of flow. This orientation promotes turbulent flow (24), thus reducing δ and increasing the critical current density (Eq. [2]). The polyvinyl chloride sheet was 0.025 cm thick and perforated with holes of diameter 0.23 cm to give an open area of 44.5%. The amplitude and wave length of the corrugations was 0.064 cm and 0.43 cm, respectively. A slightly higher pressure was maintained in the compartments on either side of compartment 2-3 so that the membranes conformed to the corrugated filling thereby ensuring a uniform 0.127 cm thickness throughout compartment 2-3.

The gasket for compartment 3-4 was similar except that solution now flowed between the other two edges, *i.e.*, at 90° to the flow in compartment 2-3. The filling was also turned through 90° to maintain the corrugations normal to the direction of flow. The remaining compartments were similar. Each end assembly consisted of an impregnated carbon electrode in a rigid polyvinyl chloride mounting, and a steel backing plate. The whole was held together by suitably insulated nuts and 1.27 cm diameter threaded rods, which passed through holes D.

To establish hydrodynamic suitability of the compartment design, additional experiments were made to obtain an F-diagram (30) and a log (pressure loss)-log (flow rate) plot (24).

Operating conditions.—The feed to compartment 2-3 was 0.01N NaCl. This compartment was bounded by two anion-selective membranes to avoid bulk concentration changes which complicate the interpretation of polarization data (6). The feed to compartments 1-2, 3-4, and 4-5 was 0.2*N* NaCl.

The flow rate in compartment 2-3 was 1500 cm^3 min^{-1} (7.3 cm sec^{-1}). The flow rate in compartment 3-4 was 1000 cm^3 min^{-1} and the feed-and-bleed rate 100 cm^3 min^{-1}.

The transport of hydroxyl ions to compartment 3-4 was measured by monitoring *p*H at position H. The *p*H was also monitored at positions E and G to ensure that the effects noted at H were not complicated by the *p*H changes which occurred in the electrode compartments. A series of current densities was used and at each the run duration was 3 hr. In this time 270 liters of solution passed through compartment 2-3. Unless stated otherwise hydroxyl ion transference numbers were calculated from measurements made at the finish of the 3-hr runs.

Room temperature was used for all runs. There are claims that critical current density is not very dependent on temperature (11, 41).

Power supply was single phase, 50 cycles sec^{-1} with full wave rectification unless otherwise noted.

Some experiments were also carried out in a smaller cell (exposed area 10 x 10 cm). General design principles, gasket thickness, and linear flow rates were identical with those used in the larger cell. There was no significant difference between the results obtained with the two cells.

Concentration of organic matter.—During the program it became necessary to assess the amount of organic matter in the solutions fed to the electrodialysis cell. The standard procedure of measuring the oxygen absorbed by the solutions from acid permanganate under precisely specified conditions was adopted. We used 4 hr at 27°C (42) which is one of several conditions that are standard practice. The results depend on the oxidation conditions chosen and the various procedures are, therefore, not directly comparable. The concentration of organic matter is obtained in terms of oxygen absorbed (O.A.) from permanganate and is expressed throughout this work as ppm O.A. Unpublished work at the Permutit Laboratories has shown that an approximate weight concentration for the organic matter present in these studies may be calculated by mutliplying ppm O.A. by three.

The chemical method is time consuming, and it was frequently more convenient to use an optical method (43) in which the optical density of a solution is compared with that of triply distilled water at a wavelength of 3000Å. Silica cells 10 cm in length were necessary for the required sensitivity. For the organic matter present in these studies, optical absorbency is related to chemically determined concentrations by the following equation

$$\frac{30 \times \text{optical density}}{\text{optical path length (cm)}} = \text{ppm O.A.}$$

Results and Discussion

Hydrodynamic considerations.—Consider liquid A flowing through a vessel and suppose at some instant a property of the liquid, *e.g.*, color, concentration, etc., is changed so that from this instant a second liquid, B, enters the vessel. A plot from this instant of the fraction of the new liquid B in the effluent against the ratio, effluent volume/vessel volume, is an F-diagram (30). Holdback, which may be determined from the F-diagram, is the fraction of liquid A that is in the vessel after a volume of liquid B equal to the volume of the vessel has entered the vessel (30). If perfect piston flow exists in the vessel, holdback is zero. If flow is confined to a narrow channel with a large proportion of the liquid in the vessel stagnant, then holdback approaches unity. Holdback for our compartment design was 0.05. With Newtonian fluids perfect piston flow is not possible due to the viscous drag of the walls of the vessel and in our case also of the compartment filling. A value of 0.05 for the holdback indicates very good flow distribution and a close approach to perfect piston flow.

The change in the log (pressure loss) *vs.* log (flow rate) plot from unit slope to a higher value occurred at a linear flow rate of 2.2 cm sec^{-1}. (Linear flow rates are not corrected for compartment filling.) This is in general agreement with Wilson's reported slope change at 4.4 cm sec^{-1} with a similar filling and identical filling orientation (24). His compartment was thinner so the higher figure is to be expected. In compartment 3-4 the flow rate was 7.3 cm sec^{-1}, which is above the point of slope change, and we conclude that the flow in our work was of turbulent type. Seko (44) has deduced from the value of the slope that flow is of turbulent type in Asahi's design of compartment in the same region of linear flow rates. [Although Seko (44) cites 1.51 for the slope, the plot given has a value of only 1.26.]

Polarization experiments.—Permaplex A-20 was studied first. Initial results were puzzling in that the amount of alkali found in the receiving stream under apparently identical conditions was quite irreproducible. Further, although a steady state should be attained fairly quickly the *p*H of the receiving stream in polarizing runs, *i.e.*, those in which there was hydroxyl ion transference, drifted upward and had not reached a steady value after 3 hr or even, when runs were extended, after 6 hr.

Our first constructive results were obtained from a cyclic series of runs in which current density was increased and then decreased in successive steps. Hydroxyl ion transport, shown in Fig. 3, exhibited hysteresis. The hydroxyl ion transference number when current density was decreasing was much higher than had previously been obtained when current density was increased.

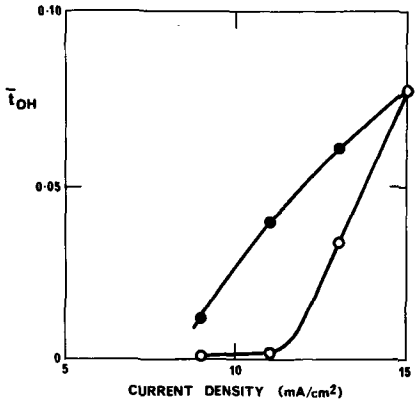

Fig. 3. Hydroxyl ion transference number *vs.* current density, Permaplex A-20. ○ after increase in current density, ● after decrease in current density.

These results might be explained by an accumulation of hydroxyl ions within the membrane. Thus during the run at 15 ma cm^{-2} hydroxyl ions accumulated, and the subsequent gradual release of these from the membrane when current density was decreased caused the hydroxyl ion transference number to be higher than the values obtained on the increasing part of the cycle. To check this suggestion the effect of prior conversion of the membrane to the hydroxyl form by immersion in alkali was investigated. Figure 4 shows that hydroxyl ions initially present were cleared from the membrane in 90 min at 4 ma cm^{-2} and in 60 min at 7 ma cm^{-2}. Thus at the higher current densities used in the cyclic series, 9-15 ma cm^{-2}, one would expect any hydroxyl ion content present at the start of a run to be cleared from the system after about 40 min. Certainly no effect on measurements taken after 3 hr would be expected. Further evidence against this suggestion was obtained by suddenly dropping the current density to 5 ma cm^2 during a run on the decreasing part of the cycle whereupon the hydroxyl ion transference number fell to zero.

For the work described so far demineralized water was used to prepare the sodium chloride solutions. The anion-exchange resin in the unit was weakly basic and of a type which removed very little of the organic matter in the supply water (Metropolitan Water Board, London). During the investigation the organic content of the M.W.B. supply water varied between 0.7 and 1.5 ppm O.A., and most of this passed into the electrodialysis cell. The affinity of the organic matter in supply waters for strongly basic anion-exchange resins and the accompanying fouling problems are well known (45, 46). The functional groups in Permaplex A-20 and in most anion-selective membranes are strongly basic. Accumulation of organic matter by the membrane would thus be expected and might result in a gradually increasing polarization tendency. Hysteresis could be explained in these terms.

For the next stage of the work the sodium chloride solutions were prepared with M.W.B. water that had been demineralized by mixed bed ion exchange with a strongly basic anion-exchange resin. The solutions were further treated by passage through trap columns (4 in. diameter x 18 in.) of De-Acidite FF (The Permutit Company Ltd.) in the chloride form immediately before entering the electrodialysis cell. By this means the organic matter in the solutions fed to the cell was reduced more than tenfold to 0.06 ppm O.A. With these conditions the upward drift of *p*H with time was rectified except in the sensitive region between *p*H 6 and 8 (Fig. 5). *p*H was constant for at least the final hour. Figure 6 shows that hysteresis had also disappeared. This demonstrates that our earlier difficulties were the result of organic matter in the influent solution accumulating on the anion-selective membrane. The only previous workers to report a reversibility or hysteresis examination are Cowan and Brown (20) and they noted irreversibility. Since they used a flowing system and treated municipal water to prepare their solutions it is possible that organic matter may have been the responsible factor in this case also.

Figure 6 clearly shows there is no sharp onset of hydroxyl ion transport with either of the membranes examined but a gradually accelerating increase in transference number. Similarly Cooke and van der Walt (19) found no sharp change in interfacial concentration at a particular current density in flowing systems although this was observed under naturally convective conditions (7, 8). The compartment filling presumably causes local variations in linear flow rate, film thickness δ and current density which could blur the effects of criticality. However Cooke and van der Walt (19) have indicated there was no sharp change in interfacial concentration even in the absence of compartment filling. Poor flow distribution on a macroscopic scale could account for the interfacial concentration results (19), but is unlikely in the present

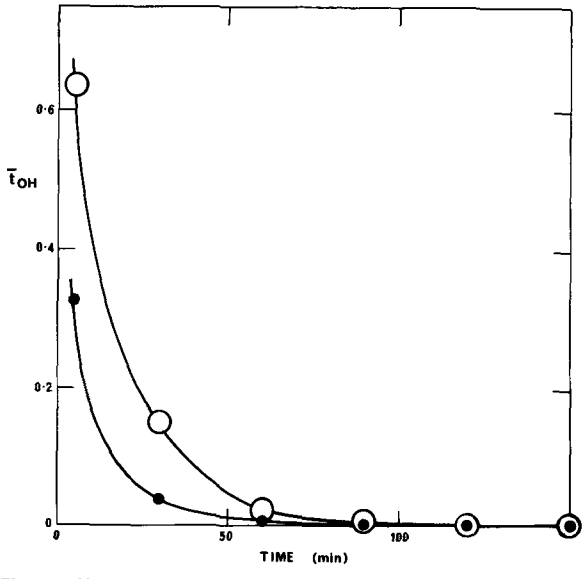

Fig. 4. Hydroxyl ion transference number *vs.* time, Permaplex A-20 initially in hydroxyl form. ○ current density 4 ma/cm^2; ● current density 7 ma/cm^2.

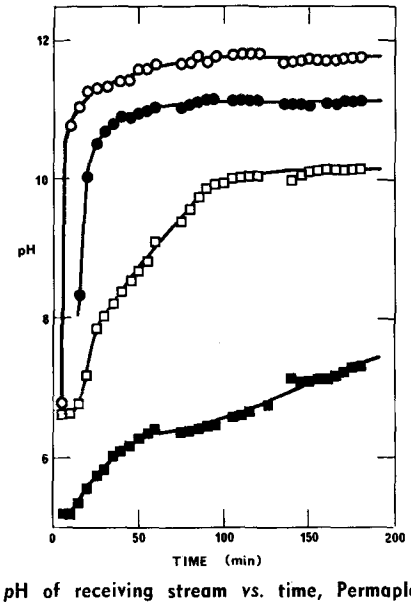

Fig. 5. *p*H of receiving stream *vs.* time, Permaplex A-20, organic matter 0.06 ppm O.A. ○ current density 12 ma/cm^2; ● current density 10 ma/cm^2; □ current density 8 ma/cm^2; ■ current density 5 ma/cm^2.

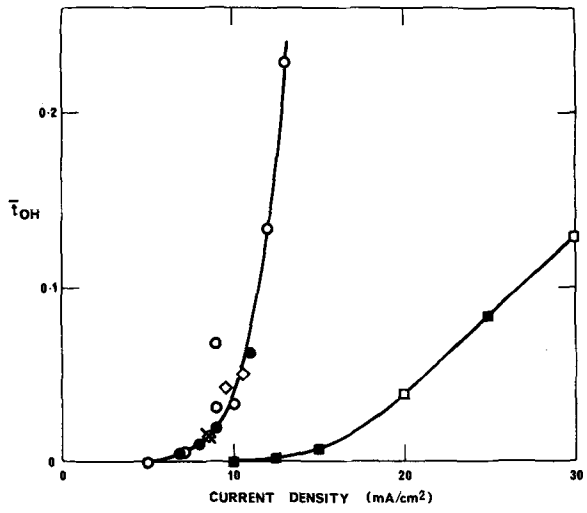

Fig. 6. Hydroxyl ion transference number vs. current density, organic matter 0.06 ppm O.A. ○ Permaplex A-20, after increase in current density; ● Permaplex A-20, after decrease in current density; × Permaplex A-20, three-phase supply; ◇ Permaplex A-20, battery supply; □ T.N.O. A-60, after increase in current density; ■ T.N.O. A-60, after decrease in current density.

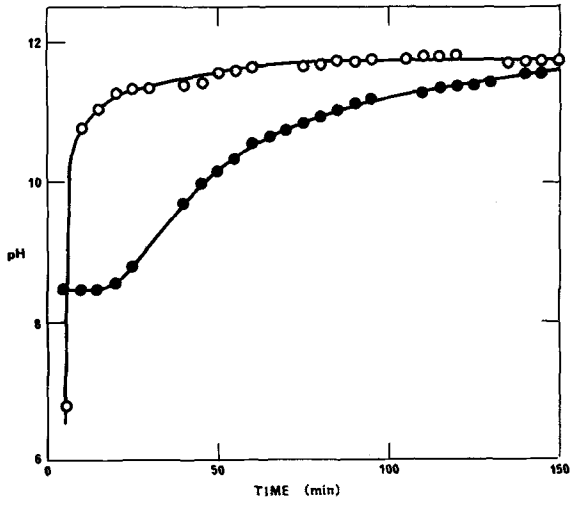

Fig. 7. pH of receiving stream vs. time, Permaplex A-20, organic matter 0.06 ppm O.A. ○ used membrane, 12 ma/cm²; ● new membrane, 45 ma/cm².

work in view of the holdback of only 0.05. Cooke (26) favors an explanation in terms of a variation in δ on the membrane surface. A much smaller variation in δ would be expected in a naturally convective system (26), and hence the criticality observed in this case (7, 8) is explained. Absence of sharp changes could also be explained by nonuniform current distribution due to membrane heterogeneity on a macroscopic (25, 26, 29) or microscopic scale. The latter could result from partial poisoning of the membrane. The absence of sharp changes in flowing systems emphasizes the dangers of using methods dependent on such effects. The rapidity of change is unimportant in the pH method, and in principle the amount of acid required to maintain any desired pH in the receiving stream is directly calculable from data such as is shown in Fig. 6.

Mention has been made in the literature of effects due to periodic changes in current (47, 48). It seemed desirable to ascertain whether the periodicity of current that results from full wave rectification of single phase a.c. was affecting our data. A few experiments were therefore carried out with full wave rectification of three phase a.c., where the amplitude of the ripple is much less, and with a battery source. Figure 6 indicates that there was no significant difference in the hydroxyl ion transference number with the three types of power supply.

Although the T.N.O. A-60 membrane used for the data in Fig. 6 was new, the Permaplex A-20 membrane had previously been in contact for three runs with solutions which had not been subjected to precautions to reduce organic matter. Further runs were therefore made with a series of new Permaplex A-20 membranes using solutions in which the organic matter had been reduced to 0.06 ppm O.A. The surprising result was that under these conditions the critical region was much higher at 35-40 ma/cm². Furthermore the phenomenon of an upward pH drift reappeared and steady values were not obtained within the period of the runs. The difference between the two conditions is illustrated in Fig. 7. For the first 150 min of operation, at least, hydroxyl ion transport through a new membrane at 45 ma/cm² was less than that through the used membrane at 12 ma/cm². A steady pH was reached with the used membrane after 80 min, but such was not achieved after 150 min with the new membrane.

The following points have now emerged. The critical current density region of new unpoisoned Permaplex A-20 membrane under our specified flow conditions is much higher than might be suspected from the literature. The critical region is, however, very sensitive to the condition of the membrane in that even an influent with as little organic matter as 0.06 ppm O.A. caused steady deterioration during the short time of a run. Further a few hours running with an influent containing 0.7-1.5 ppm O.A. which is by no means an excessive level, *i.e.*, the condition of the used membrane, reduces the critical current density approximately fourfold. The apparently steady, reproducible and reversible conditions obtaining for the data on Permaplex A-20 in Fig. 6 must have occurred because the amount of organic matter accumulated by the membrane during the runs was small relative to the amount already on the membrane at the start of this series.

Further work served to confirm the above interpretation. Runs were carried out in which current density was varied so as to maintain a constant concentration of alkali in the receiving stream. A new membrane was used for each run. Figure 8 shows that a much faster reduction of current density was necessary when the organic matter in the influent solution was 0.7-1.5 ppm O.A. than when it was 0.06 ppm O.A. However, even with an influent containing only 0.06 ppm O.A. of organic matter a fairly rapid reduction in current density was necessary. Obviously it was de-

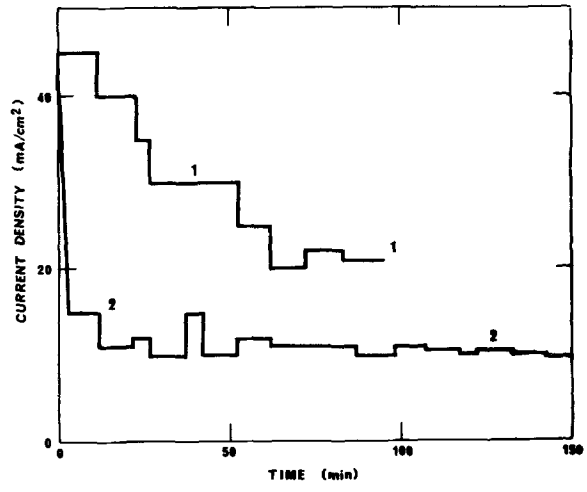

Fig. 8. Current density vs. time, receiving stream alkalinity 0.0027N, new Permaplex A-20. 1, organic matter 0.06 ppm O.A.; 2, organic matter 0.7-1.5 ppm O.A.

sirable to show that no reduction in current density was required when organic matter was completely absent from the influent solutions. In spite of considerable effort we were unable to produce solutions of this purity on the scale required. By the use of activated carbon (Chlorosorb, British Carbo Norit Union) columns (4 in. diameter x 18 in.) after the DeAcidite FF trap columns the influent organic matter was halved to 0.03 ppm O.A. (49), but pH drift indicating membrane poisoning still occurred with this solution.

In another series the effect of deliberately poisoning a Permaplex A-20 membrane for various times was studied. Poisoning was carried out at 5 ma cm^{-2} by passage of a 0.01*N* solution containing 0.85 ppm O.A. Reasonably reproducible results were obtained only if the poisoning was followed by a 6-hr conditioning run carried out at 5 ma cm^{-2} with the 0.06 ppm O.A. influent solutions, before proceeding to the standard pH runs. Even then the results after the longest poisoning of 16 hr were very scattered. For this work the normal compartment filling was omitted, and the membrane was supported by rigid plastic strips (2 mm wide) spaced parallel to the direction of flow and with centers 1.0 cm apart. The results shown in Fig. 9 clearly demonstrate the extreme sensitivity of Permaplex A-20 to poisoning by organic matter. After six or more hours poisoning it appears from Fig. 9 that there is substantial hydroxyl ion transport at any current density. This behavior is similar to that shown by bipolar membranes (50) and could result from acidic groups of the organic matter that are free, *i.e.*, in excess of those participating in bonds with the membrane, causing the surface to become cation selective. Cooke (26) has made similar comments.

The T.N.O. A-60 membrane was unaffected by 20-hr poisoning runs. While this cannot be extrapolated to long-term performance it does represent a remarkable difference from the sensitivity of Permaplex A-20. Other differences which may be related to the same prime cause are the ready attainment of steady-state conditions with new T.N.O. A-60 membranes and a lower critical current density region. The structure of the two membranes is of course quite different. Cooke and van der Walt (15) have provided evidence that with Permaplex A-20 the diffusion layer is not entirely irradicable by stirring as it is with a homogeneous A.M.F. membrane. This may be due to the Permaplex A-20 being of the heterogeneous type (19) or to its fabric reinforcement (32). A few runs with a new homogeneous A.M.F. membrane showed that this also was different to the T.N.O. A-60 membrane. The A.M.F. membrane showed a critical current density region as high as 45-50 ma cm^{-2} and the same upward drift of pH with influent solution containing 0.06 ppm O.A., indicating sensitivity to organic poisoning. We, therefore, think that the lower critical current density region and the short term insensitivity to poisoning of T.N.O. A-60 are not due to its homogeneous structure,

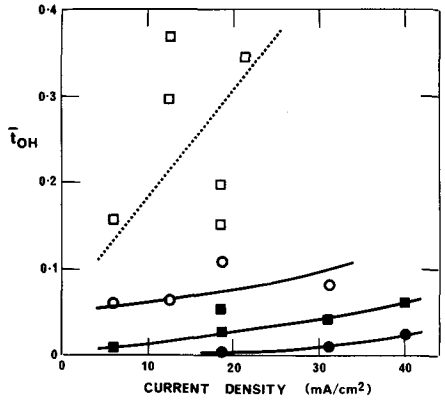

Fig. 9. Hydroxyl ion transference number *vs.* current density, Permaplex A-20. ● after poisoning for 0 hr; ■ after poisoning for 2 hr; ○ after poisoning for 6 hr; □ after poisoning for 16 hr.

but rather that it was partially poisoned at the outset of the work. Obviously this is only supposition, and the nature of the poison is unknown although it may be remarked that the membrane was stored with a T.N.O. C-60 membrane from which a little polystyrene sulfonate may have been leached. Cooke (26) has shown that polystyrene sulfonate poisons anion-selective membranes. Although the present paper has dealt only with poisons introduced with the water it is clear there must be absolutely no tendency for the cation-selective membrane to shed soluble polymeric anions which would poison anion-selective membranes. Wegelin (51) noted that homogeneous membranes were less resistant than heterogeneous membranes to the effects of poisoning by a polluted water from the Rhine.

General comment on organic poisoning.—Information on the deleterious effects on strongly basic anion-exchange resins of organic matter, tenaciously absorbed from water, accumulated during the 1950's (45, 46, 52-54). Similar problems would be expected with anion-selective membranes which in the main have similar structure and functional groups. One might anticipate even greater difficulties as there is no frequent regeneration procedure and the additional force of electrical potential is present to drive the organic matter into the membrane. It is thus surprising that prior to about 1962 there is hardly a mention of undesirable effects due to organic matter. Analyses of waters to be treated do not contain figures for organic matter. Resistance to organic fouling is not a specified membrane requirement. Even in major works there is no discussion related to organic matter in water sources. Since 1962 there has been a gradual awakening (12, 13, 18, 37, 44, 55, 56) although comments are mostly limited to unsupported statements. Even in 1963 Wilson (24), studying polarization to explain the failure of the Free State Geduld plant to meet design predictions, did not appear to give any consideration to organic poisoning of the membranes. Few authors (26, 29, 51) have provided positive information on organic poisoning.

Although the precise nature of organic matter in water varies with location and season, much is known in general terms (57). It is sufficient for the present purpose to note only that these materials, collectively termed humic and fulvic acids, have acidic groups of pK value about 4 (46, 58) and a range of molecular weights which includes a fraction capable of penetrating, albeit slowly, the interior of ion-exchange materials (26, 45, 46). There is no sparsity of acid groups in the molecules. Unpublished work at the Permutit laboratories indicates equivalent weights of around 100. Van der Waals' forces between the organic acids and the organic framework of the ion-exchanger (46) probably contributes to the tenacious binding, and in this respect the performance of the new inorganic membranes (59, 60) would be interesting.

Organic acids adsorbed on an ion-selective membrane can effect the critical current density region in three ways. First, as already mentioned, they can provide a surface of acid groups which is cation selective and results in a membrane of bipolar character (50). Second, the adsorption of a species of zero or low mobility on the most accessible membrane sites must result in the counterions having to reach less accessible sites before being subjected to the selective influence of the membrane. This is equivalent to an increase in δ in Eq. [2]. Finally the heterogeneous distribution of low mobility species in the membrane will divert current to paths where such species are relatively few, thus causing nonuniform current distribution on a microscopic scale.

The results obtained with new Permaplex A-20 membranes and indicated with homogeneous A.M.F. membranes show that, with properly designed compartments and suitable hydrodynamic conditions, i_c/c

values of about 4000 amp cm equiv^{-1} may be achieved. This value corresponds to a value of δ of 0.0008 cm which seems reasonable. Previous workers have reported much lower critical i_c/c values. For example at our linear flow rate, Cowan's formula for filled compartments (41) yields a figure of 340 amp cm equiv^{-1}, and Mandersloot and Hicks (61) obtained about 400 amp cm equiv^{-1}. One is tempted to suspect the influence of organic poisoning. Seko (44) on the other hand found no critical polarization up to 1000 amp cm equiv^{-1} which was the highest value he studied. A critical value of 4000 amp cm equiv^{-1} leaves ample scope for the choice of an economically optimum current density. We conclude, therefore, that the main limitation to electrodialysis is not polarization *per se* but poisoning of the anion-selective membrane which reduces the critical current density region to an economically unattractive level.

Conclusion

The measurement of *p*H changes at the anion-selective membrane is advocated for determination of critical current density regions.

Organic acids in the feed water, even in very small concentrations, drastically reduce critical current density.

For unpoisoned membranes the critical i_c/c values are much higher than has previously been appreciated and leave scope for an economic choice of current density.

The main limitation on electrodialysis is not polarization *per se* but poisoning of the anion-selective membranes.

Acknowledgments

The authors thank, S. K. Ahsanuddin for his persistent and careful experimental work, the Directors of The Permutit Company Ltd. for permission to publish, and one of them (FLT) thanks the Directors of The Ever Ready Company (Great Britain) Ltd., for permission to present the paper at the Boston Meeting of The Electrochemical Society.

Manuscript submitted May 31, 1968; revised manuscript received *ca.* Sept. 10, 1968. This paper was presented at the Boston Meeting, May 5-9, 1968, as Paper 236.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1969 JOURNAL.

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