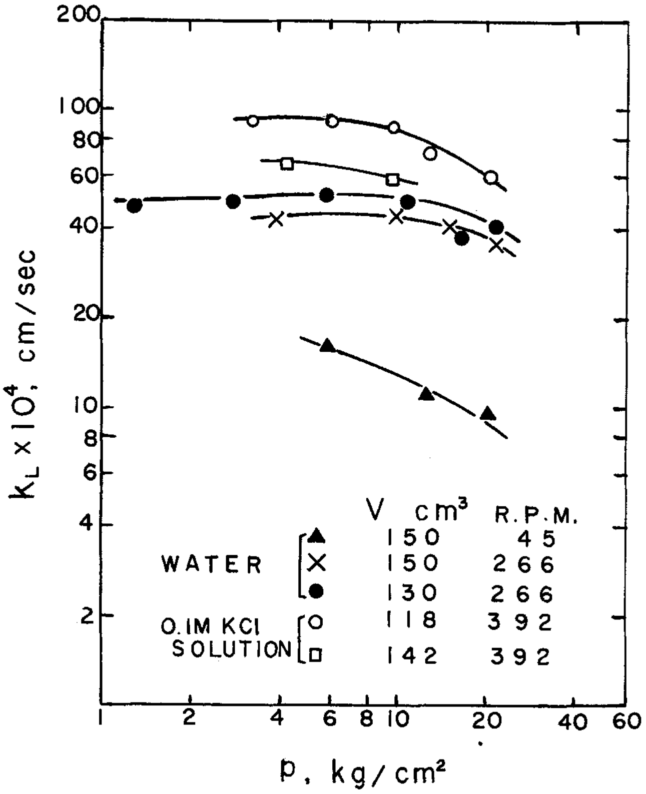

Fig. 1. Pressure dependence of k_L.

gave straight lines, indicating that k_L was constant throughout a single run.

Figure 1 shows the values of k_L which were obtained for absorption of oxygen into a water and 0.1 m. potassium chloride solution at 37.5°C. at three agitator speeds, plotted on logarithmic coordinates against the oxygen pressure. All these data indicate that at pressures above several atmospheres k_L decreases with increasing pressure.

What causes the effect of pressure on k_L is not obvious from the present experiments. The effect of pressure per se on liquid diffusivity is negligible at such moderate pressures used in the present work. Possibly the diffusivity of oxygen in the liquid phase varies with the oxygen concentration in the liquid, which in turn depends on the gas pressure. Another possibility is that the driving potential used in defining k_L may not be appropriate. However, it is more likely that pressure dependence of k_L is due to the change in the surface renewal rate, or in the degree of interfacial turbulence, which in turn could be accounted for by change in surface tension due to the gas pressure. The fact that the pressure effect is more pronounced at lower agitator speeds might support this supposition, see Figure 1. Although no data are available for the effect of pressure on the surface tension of the systems studied, data (*1*) on several gas-liquid systems indicate a variation of surface tension with gas pressure.

It might be mentioned that such pressure dependence of k_L was hardly observed in the physical absorption of oxygen into blood containing oxygen-saturated red blood cells, which was performed in the same vessel. In this case an antifoam agent was added to the blood, which probably changed the surface-tension characteristics of the system.

Such pressure dependence of k_L, as found in the present experiments, may be of practical significance. The aim here is to report the existence of such phenomena and not to clarify its mechanism. Further investigations, theoretical and experimental, are desired.

NOTATION

A = gas-liquid interfacial area, sq.cm.
c = concentration of oxygen in liquid, g.-moles/cc.
c^* = c in equilibrium with p, g.-moles/cc.
k_L = liquid phase mass transfer coefficient, cm./sec.
p = partial pressure of oxygen in gas phase, atm.
p^* = partial pressure of oxygen in equilibrium with c, atm.
t = time, sec.
V = liquid volume, cc.

Subscript

o = initial value

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Electrodialysis of Monocarboxylic Acid Salts

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In the applications of electrodialysis that have been summarized (*1*), most of the work has been directed toward desalinization and the renovation of municipal and industrial wastewaters for reuse. Little consideration has been given to the transport of organic ions across membranes, particularly short-chain organics whose dimensions would permit ready passage. Of particular interest in wastewater renovation are carboxylic acids, especially the short-chain acids such as formic, acetic, and propionic which are among the highest bio-oxidation products of most naturally occurring organic compounds before final conversion to carbon dioxide and water. In addition there is a need to define in general the behavior of organic compounds in an electrodialysis unit. Extensive theoretical and applied research has been carried out in the general area of membrane transport. Helfferich (*2*) has described transport by diffusion, convection, and electrical transference and has analyzed the effects of film control vs. membrane control. Coupling effects have been studied by Wills and Lightfoot (*3*), and new models of membrane transport have been developed by Kawabe, *et al.* (*4*). Some introductory work has been carried out on transport in a continuous-flow unit (*5*).

The objective of this investigation is to determine experimentally the electrodialytic transport through an

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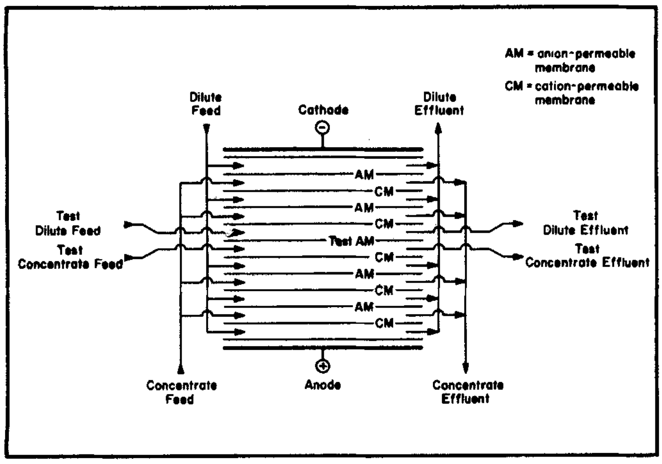

Fig. 1. Schematic diagram of electrodialysis stack.

anion-permeable membrane of monocarboxylic acids and their salts, from formate through valerate. The effects of *p*H induced dissociation and of acid chain length are established on the percent transport of the organic anion and the chloride anion, and on efficiency. The influences of mole fraction carboxylic acid salt and of current density on the percent transport are determined for acetate and butyrate and are compared.

The overall dimensions of the electrodialysis stack, with its plexiglas end blocks, were 16.6 cm. wide, 30.8 cm. high, and 7.0 cm. thick. A schematic diagram of the stack is presented in Figure 1. Five pairs of membranes were used including the anode and cathode compartment membranes; this gave four diluting compartments and five concentrating compartments. Spacers for the stack were cut from 0.077 cm. thick polyvinyl chloride, with two spacers each forming a 0.164 cm. thick diluting or concentrating compartment. Rigid polyproylene screening was fit in the spacer openings to keep the membranes parallel and to increase turbulence in the compartments. Homogeneous, polyethylene base, anion and cation-permeable membranes (AMF series 60) were employed, with an active membrane area of 50 sq. cm. for each. DC power was supplied by an Electronic Instrument Co. model 1064.

The stack was designed especially to permit separate feed to an isolated test cell pair, consisting of a test diluting stream (decreasing in concentration as it passed through the stack) and a test concentrating stream (increasing in concentration as it passed through the stack) separated by an anion-permeable membrane. For the work reported herein, all concentration changes observed occurred due to transport across this test membrane. For each experiment, potassium nitrate solution was pumped to every compartment except the test dilute compartment, and its normality was kept equal to the total normality of the test dilute feed (see Figure 1), about 26 millimole/liter. Thus, nitrate counter-diffused from the test concentrate compartment to the test dilute compartment. The test dilute feed contained potassium chloride and either formic, acetic, propionic, butyric, or valeric acid of reagent grade, the *p*H adjustment was made with hydrochloric acid or potassium hydroxide. The flow rate in the test dilute compartment was approximately 0.90 liters/hr. which produced a superficial velocity of 0.57 cm./sec. Current densities of 0.0, 2.0, 4.0, 6.0, and 8.0 ma./sq. cm. were employed. The stack was purged with the streams and then allowed to equilibrate for several hours. After startup, the stack was operated for about 20 to 60 min. before samples of the test dilute effluent and test concentrate effluent were taken. A detailed description of the entire unit is reported elsewhere (5, 6).

Chlorides were analyzed by the argentometric method (7) and the carboxylic acids and their salts were determined by a polarographic method described by Kolthoff (8), using a Sargent, pen recording, strip chart instrument.

Results are presented in terms of the percent transport of a particular anion, defined as

$$\frac{C_{\text{test dilute feed}} - C_{\text{test dilute effluent}}}{C_{\text{test dilute feed}}}\ (100)$$

and in terms of the percent transport of all anions, defined analogously in terms of total concentrations in the test dilute stream which is useful in computing the efficiency of the unit. All concentrations are in units of millimoles per liter.

Figure 2 relates the percent transport of each acid and the percent transport of chloride, at a low *p*H value corresponding to less than 10% dissociation of the carboxylic acid and at a high *p*H value corresponding to greater than 95% dissociation. For each experiment the test dilute feed contained 5.0 millimole/liter of the carboxylic acid and/or carboxylate anion and 21.2 millimole/liter of chloride; the current was 200 ma., corresponding to a current density of 4 ma./sq. cm. First considering the acid transport at low *p*H values, there was a steady decrease as the chain length of the acid was increased until valeric acid for which the transport was essentially zero. The experiment at low *p*H with formic acid requires further discussion as it would appear that the transport was higher than could be expected based on the extent of dissociation of the acid. The test dilute effluent was found to be be about 0.4 *p*H units higher than the test dilute feed (*p*H = 2.4), due to the fact that hydrogen ions have a much higher transport number than potassium ions and were preferentially removed across the cation-permeable membrane under the experimental conditions of low *p*H and high current density. The depletion of hydrogen ions from the cathode side of the anion exchange membrane caused less acidic conditions to occur at the face of the membrane, which in turn brought about a greater degree of dissociation. It is also quite likely that the diffusion of formic acid across the membrane (under a concentration gradient) accounted for a significant fraction of the transport. The same effects probably influenced the transport of acetate and had less influence on the higher-molecular weight acids (6).

At the high *p*H corresponding to greater than 95% dissociation, the transport for each acid was consistently greater than at the low *p*H; however, the increase was far short of the increase in percent dissociation. This could indicate again that ordinary diffusion or diffusion under an electrical gradient (coupling effects) accounted for a considerable fraction of the organic transport, mainly for

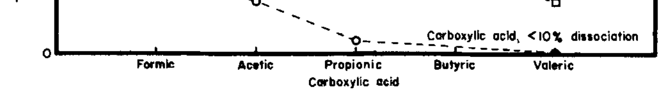

Fig. 2. Percent transport of carboxylic acids and their salts and of chloride.

formic and acetic acids. The transport of propionate appeared to have been anomalously high. At the high pH when the chain length of the acid was increased to that of butyrate, a four carbon acid salt, there was a reduction in transport.

The transport of chloride was not influenced significantly by the presence or extent of dissociation of the organic, until valeric acid was added. It appears that a few hours of exposure to valeric acid were sufficient to foul partially the membrane (producing polarization) and to reduce chloride transport. After the stack was operated for several hours with a potassium chloride feed solution, the membrane recovered its chloride permeability (6).

A comparison of both the chloride and organic total transport to the theoretical total transport, assuming that 96,500 coulombs equivalent transferred the chloride & organic total transport showed efficiencies of about 100%, except for valeric acid or valerate. For the seven experiments with formic through butyric acid (both at high and low pH), the total transport efficiencies ranged from 93.1 to 105.2%. Values greater than 100% were produced by diffusion. With valeric acid at pH 3.7, the efficiency was 63% while at pH 6.9, the efficiency was 65%.

An additional series of 45 experiments was carried out with acetate and butyrate at pH 7.6 and 9.0, respectively, to insure virtually 100% dissociation. The mole fraction acetate in the test dilute feed was 0.34, 0.51, or 0.67 to 0.68, with the rest being chloride; the mole fraction butyrate in the test dilute feed was 0.32, 0.38, or 0.68, with the rest being chloride. The total molarity of the test dilute feed averaged 27.5 millimolar. A new AMF series 60 anion-permeable membrane was placed in the test-cell pair, because the membrane used in the previous series had been operated for some time (5). Results in terms of percent total transport of chloride plus acetate or butyrate are given in Figure 3. Polarization effects (hydrolysis and OH^- transport) were evident at a current of 300 ma., indicating a transition from membrane control to film control, and severe polarization occurred at 400 ma. The dotted line was drawn by assuming that 96,500 coulombs transported an equivalent; a comparison between the curve drawn through the averages of each group of points and the line gives the efficiency of the electrodialytic transport process. The transport at zero current and efficiencies greater than 100% were produced by ordinary diffusion. There was virtually no effect of mole fraction organic in the test dilute feed on the percent total transport. Comparing acetate to butyrate, at the same current, the percent total transports averaged slightly (1 to 2%) higher with acetate.

The percent transports of chloride and of the organic species are given in Figure 4. The curves are drawn through the averages of each group of points. For chloride, polarization effects became evident at 400 ma., while for acetate and butyrate an increase in current from 300 to 400 ma. brought about no change in the percent transport. In comparing the two curves, the selectivity (transport of one species compared to another) was about unity at zero current and then steadily became slightly more favorable for chloride as the current was increased. This may have been influenced by the transition in the controlling mode of transport from membrane to film control. In comparing the selectivities at zero current and at 400 ma. it is evident that the relative diffusivities of chloride and of the organic species were different in the membrane phase than in the solution phase.

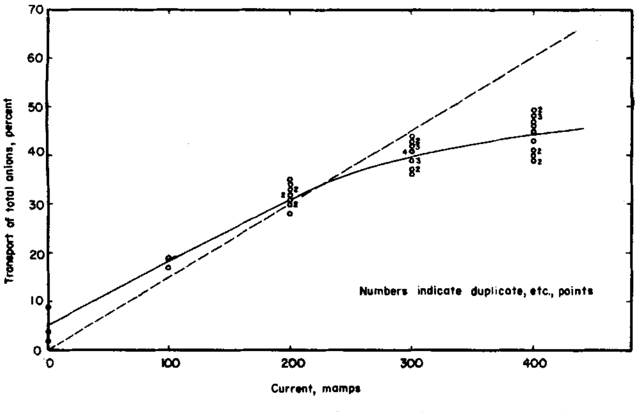

Fig. 3. Percent total transport of chloride plus acetate or butyrate versus current density.

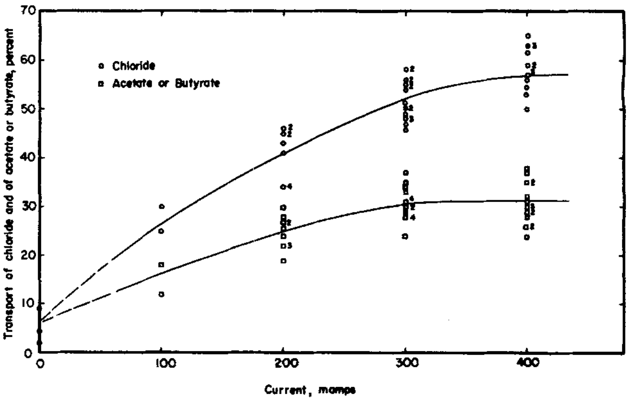

Fig. 4. Percent transport of chloride and of acetate or butyrate versus current density.

There was no effect of the mole fraction of either organic species in the test dilute feed on the percent transport of that species. There was a slight but consistent effect that as the mole fraction of chloride in the test dilute feed was increased, the percent transport of chloride decreased. There was no effect on chloride transport in changing from acetate to butyrate. The percent transport of acetate was slightly greater than that of butyrate: the average at 200 ma. was 25% for acetate vs. 23% for butyrate; at 300 ma., 33 vs. 29% and at 400 ma., 32 vs. 30%. For the sake of clarity, only a single curve is drawn for the organic data on Figure 4. A previous study (5) indicated a sharper distinction between acetate and butyrate, also as evidenced in Figure 2. Also, the percent transport of butyrate was lower (5) than shown on Figure 4, perhaps due to a partly fouled membrane in the test-cell pair.

ACKNOWLEDGMENT

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