

Conversion of ethylene diamine dihydrochloride into ethylenediamine by electro-dialytic water-splitting

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The feasibility of water-splitting electro-dialysis for the conversion of polyammonium salts into the corresponding amines and acids was demonstrated with the conversion of ethylenediamine dihydrochloride as an example. Two- and three-compartment cells were compared and their current efficiencies ascertained. The former was relatively low in current efficiency, with a roughly linear increase with conversion. The three-compartment cell operated at more than 80% current efficiency over most of the conversion range, with a voltage drop of 2.7 V per repeating unit at 400 A m^{-2} and 25° C .

1. Introduction

Polyamines are extremely useful synthetic compounds, used extensively in the rubber, textile and pharmaceutical industries. Of these the best known are those derived from the straight chain hydrocarbons with an amine group on each terminal carbon atom, $\text{NH}_2 \cdot (\text{CH}_2)_n \cdot \text{NH}_2$. They are most conveniently obtained by the action of ammonia on the corresponding halogen compounds [1]. Solid dihydrohalides are usually formed and the subsequent liberation of free amines is normally done by neutralizing with caustic. Unfortunately, the sodium halides so introduced created a considerable operational problem in the recovery of these free amines by distillation.

Osborn [2] described an amine liberation process by electrolysis in a two-compartment cell separated by an anion-exchange membrane. This process requires electrode reactions to provide hydrogen and hydroxide ions and makes the use of large multiple membrane stacks impossible, which in turn makes large-scale operation expensive. More recently, Dohno *et al.* [3] reported an electro-dialysis process with alternate anion- and cation-exchange membranes in a multi-compartment cell. This process is essentially a double decomposition reaction, converting

diamine dihydrochloride and ammonium hydroxide into the corresponding free amine and ammonium chloride.

Water-splitting electro-dialysis, which allows an electrolyte feed to be converted into the corresponding acid and base, provides an alternative for the liberation of diamines from their salts. As reported by several investigators [4-8], water-splitting is performed using bipolar membranes consisting of an anion-exchange and cation-exchange layer, and at current densities well below the limiting current density for monopolar membrane systems. A comparison [9] of the bipolar membrane process and the more widely known electrolytic process for generating acid and base revealed that the former is not only simpler in construction but also requires less energy.

The feasibility of the water-splitting processes for the present application was demonstrated by converting ethylenediamine dihydrochloride ($\text{en} \cdot 2\text{HCl}$) into its free amine (en). Cells with two and three compartments per repeating unit were compared and their current efficiencies ascertained. Advantages of these processes include: low energy consumption, simplicity in construction, recovery of useful by-product, liberation of free amine in a solution uncontaminated by salt, no requirement of additional chemical reagents.

2. Experimental

2.1. Preparation of bipolar membranes

A good bipolar membrane must combine the properties of low resistance, high mechanical integrity, good chemical stability, high selectivity for counter-ions and fairly high hydraulic permeability. Earlier studies by Gregor *et al.* [8, 10] showed that Ionac membranes MA 3475 and MC 3470 could be fused if a solvent for the matrix polymer of the membranes, dimethylformamide (DMF), was applied to the membrane surface prior to fusing in a heated press. The membrane resistance was reduced by introducing resin particles to increase interfacial contact. However, the membranes thus prepared were not practical due either to a high resistance or an incapability of prolonged operation. Hence in this work a 9.5% solution of linear polystyrene sulphonic acid (L-PSSA) in DMF was used. Also, a swelling time of 1 min was used to enable the solvent to penetrate an appropriate depth into the membrane. The two component membranes were placed together between two pieces of aluminium foil and pressed at 95°C and $1 \times 10^6 \text{ kg m}^{-2}$ for 3 min in a hydraulic press (Pasadena Hydraulic Inc.).

2.2. Cell assemblies

A laboratory cell with a number of polypropylene rings each possessing an exposed inner area of 58.0 cm² and a width of 2.5 cm was used in this study. The electrodes were constructed from 0.01 cm thick titanium coated on one side with $2.54 \times 10^{-4} \text{ cm}$ of platinum, and cemented to the support plates. The rings, together with Asahi Glass membranes AMV and CMV and the bipolar membranes, were assembled as shown in Figs. 1 (three-compartment) and 2 (two-compartment).

In the assembly shown in Fig. 1, the ethylenediammonium ions ($\text{en} \cdot 2\text{H}^+$) migrate from the feed compartment through the cation-exchange membrane into the base compartment and are neutralized by OH^- to yield the corresponding free amine. Meanwhile, Cl^- in the feed compartment migrates through the anion-exchange membrane into the acid compartment and produces HCl. A large number of membrane cells can be assembled between one set of electrodes. The

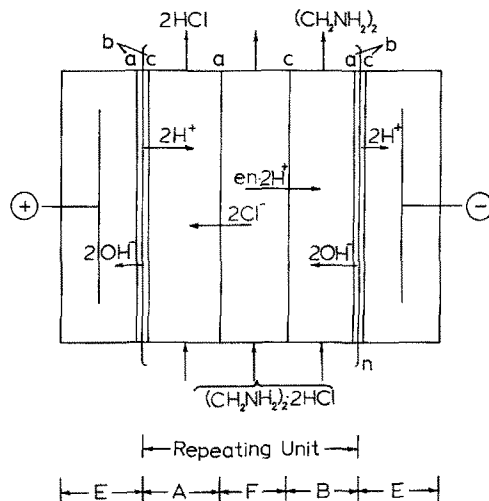


Fig. 1. Three-compartment cell assembly for converting ethylenediamine dihydrochloride into ethylenediamine, A, acid; B, base; E, electrolyte; F, feed; a, anion-exchange membrane; b, bipolar membrane; c, cation-exchange membrane; +, anode; -, cathode.

assembly shown in Fig. 2 represents an attempt to reduce the number of compartments per repeating unit from 3 to 2, thereby reducing capital investment and energy consumption. In this assembly, the feed solution is fed directly into the base compartment. The ethylenediammonium ions, which penetrate the anion-exchange and bipolar membranes only with difficulty, remain in that compartment and are neutralized by OH^- .

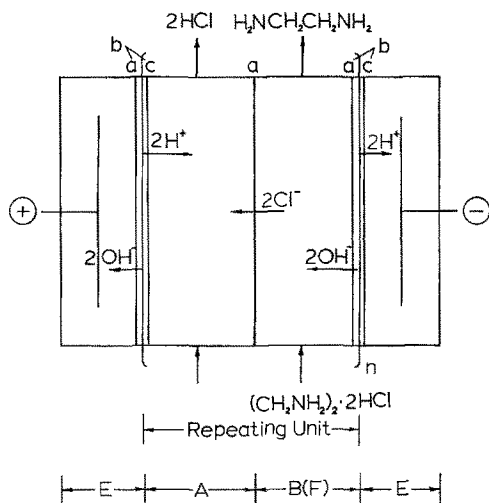


Fig. 2. Two-compartment cell assembly for converting ethylenediamine dihydrochloride into ethylenediamine: A, acid; B, base; E, electrolyte; F, feed; a, anion-exchange membrane; b, bipolar membrane; +, anode; -, cathode.

2.3. Measurement of current efficiencies

The cell and auxiliary equipment were assembled for a batch recirculating operation as shown in Fig. 3. The electrode compartments were supplied by a solution of 0.05 M K_2SO_4 . In each run, the pumps were started and after 15 min constant liquid levels in the risers were reached, along with uniform temperature and composition. Then current was passed at a pre-determined level while the temperature was controlled to $25 \pm 1^\circ C$ and the voltage adjusted to maintain constant current. The concentration of product streams as a function of current passed was determined from collected samples. Differential current efficiencies were ascertained in experiments which were run only until a concentration change of approximately 0.1 M was obtained in the ethylenediamine product stream. Ethylenediamine was estimated by titration with HCl to the methyl red end-point [11]. The ethylenediamine dihydrochloride content was estimated for chloride content according to Volhard [12]. Acid contents were determined by titration with standard base to the phenolphthalein end-point.

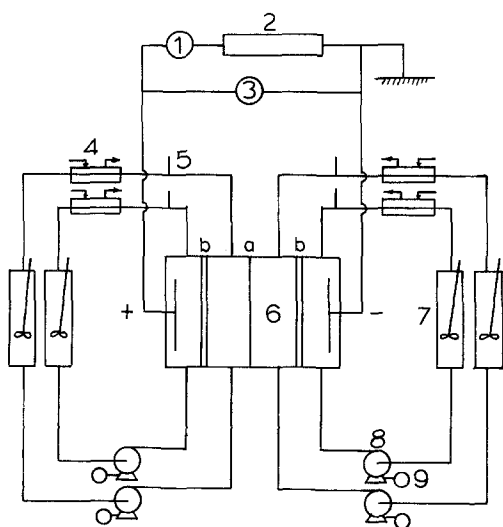


Fig. 3. Schematic diagram of experimental set-up for batch recirculating operation: 1, ammeter; 2, d.c. source; 3, voltmeter; 4, heat-exchanger; 5, thermometer; 6, water-splitting cell; 7, reservoir; 8, pump; 9, voltage regulator.

2.4. Measurement of current-voltage curves

Current-voltage curves of cell assemblies with one repeating unit were first determined. An actual experiment consisted of filling the reservoirs with appropriate solutions, draining air bubbles from the lines and allowing the solutions to circulate at a flow rate of $20 \text{ cm}^3 \text{ s}^{-1}$. As soon as a temperature equilibrium was reached, power was applied. The voltage was raised in steps and the current was measured after a steady state was reached. Current-voltage curves of the assemblies with two repeating units were also determined in the same manner. Subtraction of measurements from cells with one repeating unit from those with two repeating units gave the apparent current-voltage curves per repeating unit.

3. Results and discussion

3.1. Production run

The feasibility of the processes was demonstrated by a run in the cell assembly shown in Fig. 1, in which HCl and $\text{en} \cdot 2\text{HCl}$ was used as a feed solution and 1000 cm^3 of 0.1 M HCl and 250 cm^3 of 0.1 M $\text{en} \cdot 2\text{HCl}$ were used as initial solutions in the acid and base compartments to carry the current. The concentration of product streams as a function of electricity consumption is presented in Fig. 4. Deviations from 100% current efficiency at higher product concentrations can be attributed to

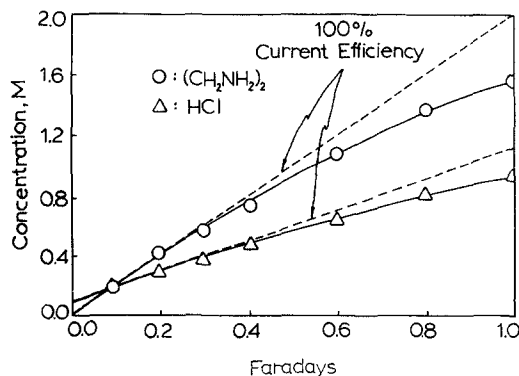


Fig. 4. Production of ethylenediamine and hydrochloric acid as a function of Faradays passed in three-compartment cell assembly. Initial conditions: acid, 1000 cm^3 0.1 M HCl; base, 250 cm^3 0.1 M $\text{en} \cdot 2\text{HCl}$; feed, 1000 cm^3 1 M $\text{en} \cdot 2\text{HCl}$. Operating conditions: current density 200 A m^{-2} ; circulation rate, $20 \text{ cm}^3 \text{ s}^{-1}$.

the decrease in membrane selectivity, which is a strong function of ionic concentrations.

3.2. Current efficiencies

The effect of process conversion upon current efficiency for amine liberation is evident from Fig. 5, where results comparing the two- and three-compartment cell assemblies are presented. The former showed a relatively low current efficiency, particularly at low conversions where the presence of a large amount of the highly dissociated diamine salt substantially decreased membrane selectivity. This assembly showed a roughly linear increase in current efficiency with conversion as a result of transforming the diamine salt into its free amine which is but weakly dissociated ($pK_1 = 10.71$ and $pK_2 = 7.56$ at 0°C). For the three-compartment cell assembly, the current efficiency remained high over most of the conversion range, still being more than 80% at 90% conversion. The loss in current efficiency with conversion in this assembly was due primarily to the diffusional transport of the neutral electrolyte, ethylenediamine, the diffusion coefficient of which, estimated for the present system, was quite small, about $1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This diffusional loss was more pronounced when the concentration of the system was raised but could be substantially reduced by increasing the current density.

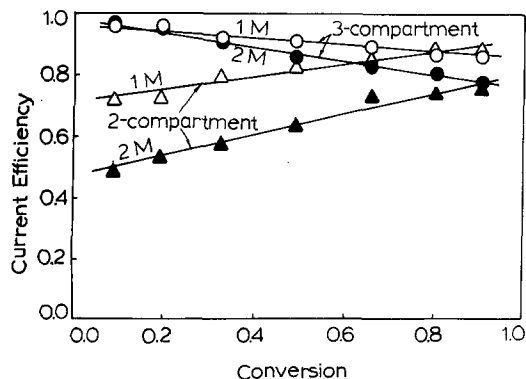


Fig. 5. Current efficiency versus ethylenediamine dihydrochloride conversion: \circ three-compartment cell assembly; feed, 1 M en-2HCl; \bullet three-compartment cell assembly; feed, 2 M en-2HCl; \triangle two-compartment cell assembly; feed, 1 M en-2HCl; \blacktriangle two-compartment cell assembly; feed, 2 M en-2HCl. Operating conditions: acid, 0.1 M HCl; current density, 200 A m^{-2} ; circulating rate, $20 \text{ cm}^3 \text{ s}^{-1}$.

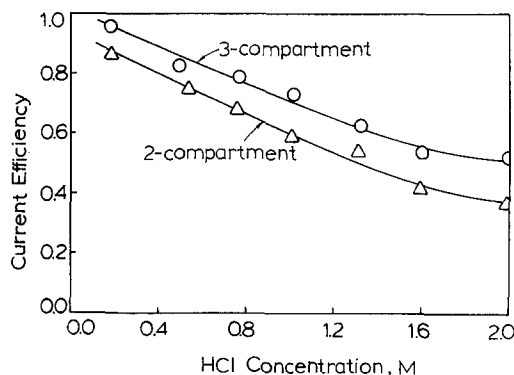


Fig. 6. Current efficiency versus hydrochloric acid concentration: \circ three-compartment cell assembly; \triangle two-compartment cell assembly. Operating conditions: base, 0.5 M en and 0.1 M en-2HCl; feed 0.5 M en-2HCl; current density, 200 A m^{-2} ; circulation rate, $20 \text{ cm}^3 \text{ s}^{-1}$.

Fig. 6 shows the effect of HCl concentration on the efficiency of the amine conversion. With the three-compartment cell assembly, there are two principal sources of loss in current efficiency. When the HCl concentration was high in the acid compartment, the high transport number of H^+ as compared to that of Cl^- across the anion-exchange membrane resulted in a substantial leakage of H^+ into the feed compartment, where it competed with en- 2H^+ transport and reduced the amount of en formed per Faraday. Secondly, the heterogeneous Ionac membranes making up the bipolar membrane have a relatively large 'leak' in concentrated solutions, so HCl diffusing to the left from the acid into the base compartment lowered current efficiencies for both acid and base formation. Similar sources of loss are present in the two-compartment cell assembly. It is evident that, in the absence of more highly selective membranes, one must limit the acid concentration in product streams. If necessary, the acid can be concentrated further in a separate device by conventional electrodialysis.

3.3. Current-voltage curves

The power requirements of these systems are set, to a large extent, by the cell voltages required. Current-voltage curves of the two- and three-compartment cell assemblies are shown in Fig. 7. Doubling the current density will double the output of the system while roughly quadrupling the energy consumption. The optimum current

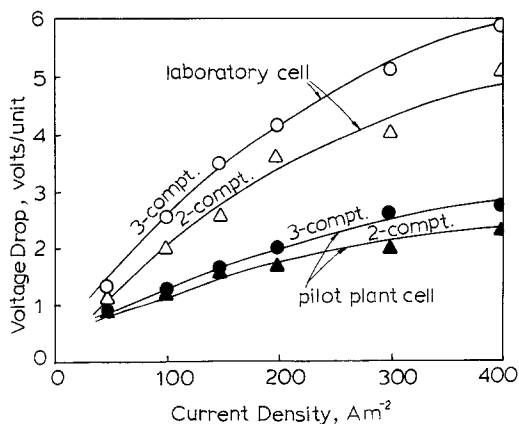


Fig. 7. Voltage drop per repeating unit versus current density. \circ and \bullet laboratory and pilot plant cell for three-compartment cell assembly, respectively; acid, 0.5 M HCl; base, 0.5 M en and 0.1 M en·2HCl; feed, 0.5 M en·2HCl; \triangle and \blacktriangle laboratory and pilot plant cell for two compartment cell assembly, respectively; acid, 0.5 M HCl; feed, 0.5 M en·2HCl and 0.5 M en. Operating conditions: circulation rate, 20 cm³ s⁻¹, temperature, 25° C.

density is a compromise between amortized investment in membrane equipment, which decreases as the current density increases, and energy consumption, which increases with current density. The voltage drop in commercial cells would be considerably lower because the laboratory cell used has cell spacings of the order of 2.4 cm. To demonstrate this, results obtained from a small pilot plant facility [10] are also shown in the same figure. At a current density of 400 A m⁻², the voltage drops of the two- and three-compartment cells were observed to be 2.2 V and 2.7 V at 25° C, respectively. A large portion of these voltage drops was actually due to the voltage drop across the bipolar membrane, which is a key factor in determining the economic viability of the water-splitting processes.

The current-voltage curve of the bipolar membrane was measured in a two-compartment cell with 0.5 M HCl on the acid side and 0.1 M en·2HCl and 0.5 M en on the base side. The voltage drop across the bipolar membrane was taken as the difference between the voltage drop measured with the membrane in place and the average value when either the acid or the salt solution was present in the cell without the membrane. This result is shown in Fig. 8, which was characterized by a rapidly rising potential at low current den-

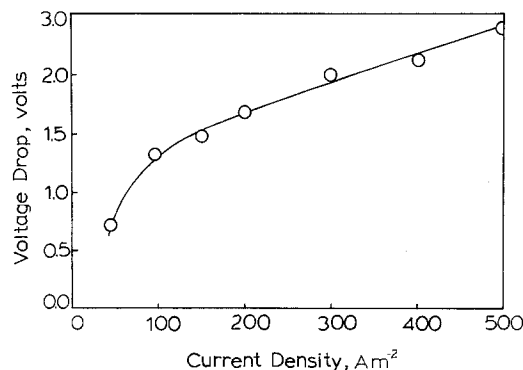


Fig. 8. Voltage drop of bipolar membrane versus current density. Operating conditions: acid, 0.5 M HCl; base, 0.1 M en·2HCl and 0.5 M en; circulation rate, 20 cm³ s⁻¹; temperature, 25° C.

sities and an apparent linear region at higher current densities. A detailed analysis of the bipolar membrane current-voltage curve following Gregor *et al.* [8] showed that the inter-membrane distance was of the order of 10 nm. This inter-membrane gap is a critical property of bipolar membranes. At a current density of 400 A m⁻², the IR-drop across the two component membranes of these bipolar membranes was 0.4 V. For water-splitting, the reversible or minimum potential is 0.83 V to produce acid and base at unit activity. Thus, if the inter-membrane gap could be reduced to zero, one could in theory operate bipolar membranes made from Ionac membranes at 1.23 V as compared to 2.35 V at 500 A m⁻² for the membrane used in this study. Obviously, better methods of cementation can reduce the inter-membrane distance and result in a reduction in the membrane voltage. More recently, Liu *et al.* [13] reported a bipolar membrane voltage of 1.1 V at 1000 A m⁻², but no details were presented.

4. Conclusions

This study has shown that water-splitting electro-dialysis may well be technologically feasible and also economically sound for the conversion of polyammonium salts into the corresponding free amines. A comparison of the two- and three-compartment cell assemblies showed that the former is superior in its low cell voltage but

inferior in its low current efficiency. A practical process may be a combination of the two assemblies with the conversion carried out in the three-compartment cell assembly; base streams from this assembly are then fed into the two-compartment cell assembly to liberate the trace of polyammonium salt which is presented in the base streams to reduce ohmic drops. Significant reductions in operating power requirements are foreseen through modifications in cell design, membrane preparation and method of operation. These modifications will promote higher efficiency and will also mean lower capital investment for cells and rectification equipment. A pilot plant study of this process is the obvious next step.

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