

a coefficient of variation of 1.2 per cent for both a dilute and a concentrated solution.

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Electrodialysing with a Non-polarizing Membrane

IN the electro dialysis process for demineralizing brackish water, the feed is passed through parallel compartments separated by cation- and anion-exchange membranes arranged alternately. A direct current passed at right-angles to the long, narrow compartments impels the cations and anions to pass through the appropriate, selective membranes, so that alternate compartments become either depleted or concentrated in dissolved salts.

It has been found that when a critical current density is exceeded, the transport of ions to the membrane surface is insufficient to maintain the current, and hydrogen and hydroxyl ions pass through the membrane instead, at a higher voltage¹. The excess energy is dissipated by the splitting of water molecules. Moreover, the pH change caused by hydroxyl ions passing through the anion-exchange membranes induces scale to form in the concentrate compartments, further increasing the electrical resistance and eventually blocking the membranes. In practice, therefore, the current density is maintained at a value of only about 50 per cent of the theoretically critical one. Since the output from an installation is proportional to the current density, this is a serious limitation.

During a recent investigation², a series of commercial ion-exchange membranes were tested in the following cell:

Silver/silver chloride	0.01 N sodium chloride	Membrane	0.01 N sodium chloride	Silver/silver chloride
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Each membrane was clamped horizontally and the current was so arranged that the flow of counter-ions was upward, minimizing convection. The change of voltage with time was noted for constant current.

Fig. 1 is a chronopotentiograph of 'Selemon DMT', a weak-base anion-exchange membrane manufactured for dialysis purposes³. When the solution layer immediately

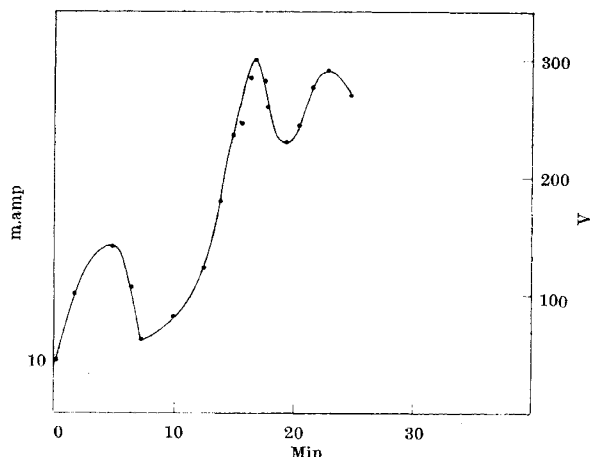


Fig. 1. Voltage-time curve for 'Selemon DMT'

below the membrane became depleted of salt, the resistance rose and hydroxyl ions began to carry an increasing proportion of the current upwards, towards the cathode. Above pH 8-9, however, there was practically no dissociation of the weakly basic groups and the membrane became non-selective. Electrolyte replenished the depleted membrane-solution interface and permeated the membrane, the current being transported by both sodium and chloride ions. The electrical resistance fell accordingly, as did the pH, the functional groups increased their dissociation and the cycle continued. Eventually a steady-state would have been reached.

Suppose such a membrane were used in electro dialysis. An increase in the current density above the critical value would not cause scale and stoppage of the process; instead, the current efficiency would simply decline locally until operating conditions were corrected. This could permit the operating current density to be raised much closer to the theoretically critical value. Only trials in a multi-membrane stack could test the validity of this approach.

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Combined Ion Exchange-Solvent Extraction: a New Dimension in Inorganic Separation Chemistry

Most of the methods at present used for separation of inorganic ions by column chromatography are either based on cation and anion exchange or on partition chromatographic procedures using cellulose, silica gel, 'Kel-F' and various other inert materials as supports for a stationary phase, mostly an aqueous solution, or, as with the reversed-phase techniques, with an organic phase which either acts as an extractant or as a cation or anion exchanger. Common to these methods is the fact that only one mechanism (either ion exchange or solvent extraction) is the decisive factor for effecting the separation. This is especially so in relatively strong mineral acid solutions. Seen from this point of view, these separation techniques are in practically all cases only one-dimensional, that is to say, only one of these principles can be utilized.

Obviously a two-dimensional separation system can be obtained by combining the ion exchange principle with liquid-liquid extraction. This can be achieved by using a solid cation exchanger as the support and a partly non-aqueous system as the mobile phase acting as an extractant for certain metal ions. Consequently, separations which can be achieved under such conditions may be termed "combined ion exchange-solvent extraction" separations (CIESE) because both the principles of ion exchange and solvent extraction are operative simultaneously. The following two separations of large amounts of iron from cobalt and nickel and of uranium from other elements are examples of this CIESE principle.

In the first case, the separation of iron(III) is effected on a column of a 'Dowex 50' cation exchanger using 80 per cent (tetrahydrofuran) (THF)-20 per cent 3 N hydrochloric acid as the eluent. Under these conditions, iron(III) (distribution coefficient $K_d \approx 1$) is removed by washing the resin with this mixture and cobalt is then eluted with 90 per cent THF-10 per cent 6 N hydrochloric acid (v/v) leaving nickel adsorbed on the column. The nickel can finally be eluted with pure aqueous 6 N hydrochloric acid. This separation cannot be achieved on the same resin using pure aqueous 0.6 N hydrochloric acid (same overall acidity as in the THF-hydrochloric acid mixtures) because the K_d -values are 180 (iron), 45 (cobalt),