# Electro-Osmotic Solvent Fractionation: A New Separation Process

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Investigations of organic electrolyte solutions in our laboratories have indicated that the traces of residual water in these solutions are bound to the lithium ions (*1*) and that the transference number of the lithium ions approaches unity in suitable cation exchange membranes in the presence of organic electrolytes (*2*). These observations suggested the possibility of the separation of the residual water from the organic electrolyte by an electro-osmotic process, and affirmative data are reported below.

The electro-osmotic transport of water in porous materials (3) and in ion exchange membranes (*4*) is well known, as is the use of membranes for the separation of a variety of substances (5). No case of solvent fractionation by electro-osmosis has come to our attention.

## EXPERIMENTAL TECHNIQUES

The electro-osmotic experiments were carried out in the cell shown in Figure 1. It contained the electrochemical elements:

$$\begin{array}{c|c|c} \text{Ag/AgCl, 0.1M LiCl in BL} & \text{membrane} & \text{0.1M LiCl in BL, AgCl/Ag} \\ C_0\text{M } H_2O & Li^+ \text{ form} & C_0\text{M } H_2O \end{array}$$

BL = $\gamma$-butyrolactone

Vacuum distilled butyrolactone collected at 61°C. to 65°C. at 1.0 mm. Hg. and analytical grade reagents were used. The cation exchange membranes were converted to the lithium form by leaching with aqueous lithium chloride solutions for three days prior to their equilibration with the various lithium chloride-water-BL solutions for a week. The active membrane area was 2 sq. cm. Each of the electrode compartments of the cell contained 3 cc. of the electrolyte. The silver/silver chloride electrodes contained about 1,000 coulombs of silver chloride and were prepared by pressing 2 sq. cm. silver chloride pellets onto silver screens.

The measurements were conducted at 25 ± 1°C. under constant current conditions, and the concentration of water in the anode and cathode compartments was determined gas chromatographically.

## RESULTS AND DISCUSSION

The passage of current through a cell led to the preferential transport of water from the anode to the cathode compartment, as evidenced by the enrichment of water in the catholyte. The water flux through the membrane was expressed in terms of a transference number defined as the moles of water transported per Faraday of charge transported through the membrane. The experimental results are shown in Figure 2.

The amount of water transferred increased with the water concentration of the solution. The transference number increased from zero in the anhydrous solution to approximately 3 moles/Faraday above 7% (vol.) water in the butyrolactone. The transference number was independent of the current density. It had a value of 2.75 moles/Faraday at 0.5 ma./sq. cm. and 2.63 moles/Faraday at 0.05 ma./sq. cm. in the 10% (vol.) water solutions. The transference number decreased as the salt concentration increased, being 0.96 moles/Faraday in 1.0m lithium chloride and 2.75 moles/Faraday in the 0.1m lithium chloride solutions. This conforms with the behavior of electro-osmotic solvent transport systems where the solvent transport increases markedly with a decrease in the electrolyte concentration (*6*).

The volume changes of the anolyte and catholyte were measured in the 0.1m lithium chloride solution in butyrolactone containing 10% (vol.) water to check the possibility that the state of hydration of the membrane had changed as a result of the transference experiment. The cell was provided with capillary rise tubes and the experiment started from a hydrostatic equilibrium state. The average volume increase of the catholyte equalled the average volume decrease of the anolyte and it amounted to no more than 1% of the total solution volume in any of the experiments. The volume changes were ignored in the calculation of the transference numbers.

A material balance for the 10% (vol.) water solution

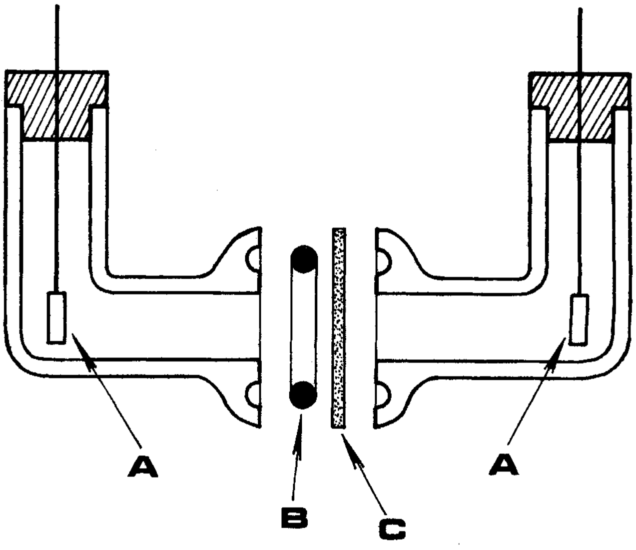

Fig. 1. The electro-osmotic cell: A. silver/silver chloride electrodes; B. "O"-ring seal; C. Ion-exchange membrane.

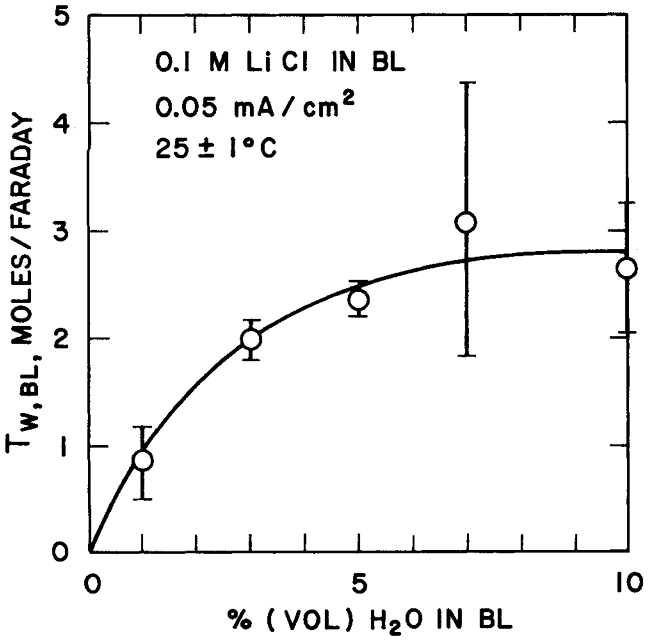

**Fig. 2. The transference of water in a 0.1m lithium chloride solution in butyrolactone.**

showed that the electro-osmotic exudate contained 64% (mole) water which may be compared with 32% (mole) water in the initial solution, that is a molar enrichment factor of two was obtained.

The separation process appeared to depend on the state of hydration of the membrane in a manner similar to that observed for the electro-osmotic transport of water through ion exchange membranes in aqueous solutions (*4*). Although more detailed studies are required to characterize the process adequately, it also appeared to be based on a selective solvation reaction such as:

$$\mathrm{Li}^+\ (\mathrm{BL})_m + n\,\mathrm{H_2O} \rightleftharpoons \mathrm{Li}^+\ (\mathrm{H_2O})_n + m\mathrm{BL}$$

and the subsequent selective transference of the cationic species through an ion-specific membrane. If indeed this is the basis for the separation phenomenon, the electro-osmotic fractionation technique should be applicable to a variety of systems involving solvents or solutes which exhibit differential solvation or complexation with ions which can be extracted selectively through a membrane. An immediate application is the removal of water from γ-butyrolactone which is of interest in the field of organic electrolyte battery technology.

## LITERATURE CITED

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# Heat Transfer to Drag-Reducing Polymer Solutions

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The drag-reducing property of dilute polymer solutions under certain turbulent flow conditions was first recognized and investigated by Toms (*1*). Among the more recent work in this area is that of Metzner and Park (*2*), Hershey and Zakin (*3*), and Virk, et al. (*4*). The usual speculative explanation for this phenomenon is an interaction of viscoelasticity with turbulence. In general, the friction factors for this phenomenon are found to be a function of Reynolds number and of the polymer species, polymer concentration, and pipe diameter. In contrast to these general dependencies, Virk, et al. (*4*), working with a homologous series of polyethylene oxides, have found that the maximum possible drag reduction is limited by a unique asymptote which is independent of molecular weight, concentration, and pipe diameter. Thus the gross flow behavior is bounded by the solvent line and by the maximum drag reduction asymptote. In power law form, these are respectively:

$$f/2 = 0.023\, N_{Re}^{-0.20} \tag{1}$$

$$f/2 = 0.21\, N_{Re}^{-0.55} \tag{2}$$

Although considerable gross flow data exists for momentum transfer, there is little heat transfer data. A heat transfer reduction is anticipated, but no theoretical basis exists for predicting the quantitative relationship between the drag reduction and the heat transfer reduction. For this reason, experiments (*5*) of a preliminary nature were undertaken to examine heat transfer. Data on wall heat transfer were obtained for a pipe flow ranging from 500 to 25,000 in Reynolds number. The solutions used were Newtonian and were of polyethylene oxide and distilled water, as listed in Table 1.

## EXPERIMENTAL METHOD

The wall heat transfer rate was measured electrically. A thin coating ($3 \times 10^{-5}$ in.) of platinum on the inside walls of a 0.117 in. I.D. quartz tube, through which the solution flowed, served both as a resistance thermometer and as a wall heat source. The thermal developing section was 15.2 diam. and the test section, 2.8 diam. The hydraulic developing length to the heat transfer section was 230 diam.

By passing both a large and a small current through the platinum film and measuring the resistance with a Kelvin bridge, one obtained both the wall and upstream temperatures. The large (heating) current was measured by a standard resistor-potentiometer technique from which the heat flux at the wall ($I^2R$) was determined. Finally, the average bulk temperature at the test section was calculated by an energy balance based on the wall heat flux and the upstream temperature.

The wall, bulk, and upstream temperatures ranged between 37 to 39, 25.5 to 26.5, and 24.8 to 25.2°C. respectively. Corrections for variable fluid properties were made only for the