



Physico-chemical local equilibrium influencing cation transport in electrodialysis of multi-ionic solutions



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HIGHLIGHTS

- Electrodialytic removal of solutions containing ternary mixture of electrolytes
- Physico-chemical local equilibria during cation transport
- Theoretically estimated LCD could closely ($\pm 5\text{--}7\%$) predict experimental data.
- Cations with higher charge had low transport number, high adsorption and resistance.

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ABSTRACT

Electrodialysis (ED) of solutions containing ternary combination of electrolytes (NaCl, KCl, CaCl_2 , MgCl_2 , FeCl_3) was carried out. Besides linear velocity of the fluid flowing through the ED cell, physical properties of cations and their interaction with the gel phase of membrane significantly influenced ion transport. The role of concentration polarization was evaluated from limiting current density (LCD) measurement. Theoretically estimated LCD values based on effective diffusivity of each ions and mass transfer coefficients (Sherwood number, Sh correlation) satisfactorily (error $\pm 5\text{--}7\%$) predicted experimental data. Measurement of transport number, adsorption equilibrium, water uptake and membrane resistance were carried out for each composition to understand the role of cations – membrane equilibrium in ion transport. Cations with higher charges showed reduced transport number, higher adsorption and higher resistance over cation exchange membrane (CEM). Water uptake measurement of equilibrated CEM showed negligible difference when cations of similar charges were interchanged while a meager 1.5% variation was noted when cations of different charges were interchanged.

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1. Introduction

Electrodialysis (ED) is an electro membrane process where electric potential gradient is applied across oppositely charged membrane pairs to separate ions from solution. It has diversified itself into several allied fields like reverse ED, bipolar membrane ED, and electro-deionization. ED has been used in production of potable water, pre-treatment of boiler feed water, table salt preparation from sea water (in Japan), heavy metal removal from brackish water, demineralization of food products, production of organic acids (e.g. monocarboxylic acids: formic, acetic, propionic; dicarboxylic: oxalic, malonic, succinic; tricarboxylic: citric, iso-citric, aconitic acid), recovery of important chemicals from fermentation broth of pharmaceutical industries,

where protein separation, fruit juice de-acidification, power generation (using reverse ED), desalting of crude glycerol in biodiesel production, and production of sodium methoxide, acetoacetic ester, methyl methoxy acetate, etc. [1–9].

In ED ion removal efficiency is dependent on several (physico-chemical) phenomena occurring simultaneously e.g. number of ionic species, nature, charge, hydrated size, solubility, transport number, ionic mobility, applied potential, flow hydrodynamics, limiting current, and homogeneity and heterogeneity of the membrane surface [1,10,11]. Experimental and theoretical investigation on removal of single/mono-electrolyte in batch or continuous mode has been extensively studied earlier [12–14]. The presence of multiple electrolytes increases complexity in transport due to the presence of various physical phenomena being simultaneously active and selective transport of ions start working.

Ion transport in ED process occurs in two distinct steps i.e., movement of ions (i) through solution (rate is governed by ionic

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diffusivity of the concerned species) and (ii) through membrane phase (rate is governed by adsorption–desorption equilibrium and mobility of ionic species). Simultaneous existence of mono/di/multi-valent (NaCl, KCl, MgCl₂, CaCl₂, FeCl₃, AlCl₃, etc.) cations bearing different physical properties (charge, size, diffusivity, mobility, electrostatic forces, etc.) creates competition among ions. Competitive nature of ionic species and their transport behavior inside an ED cell was reported earlier by Chapotot et al. [15]. The feed solution considered was containing two electrolytes and cations (monovalent and divalent) transport occurred through strongly charged cation exchange membrane. Ionic adsorption and desorption kinetics were reported by Logette et al. [16] to address selective permeability of Nafion membrane towards different valency cations. Kumar et al. [17] reported transport of various cations (Na⁺, Ca²⁺, Mg²⁺ and Fe³⁺) through silica incorporated cation exchange membrane (CEM) which is more selective towards monovalent ions. Arsalan et al. [18] reported transport number and mobility ratio measurement for three bivalent cations (Be²⁺, Mg²⁺ and Ca²⁺) with PVC-supported strontium–tungstate inorganic precipitated composite CEM.

Very limited number of investigations have so far been reported on removal of multiple multivalent electrolytes through ED technique due to inherent complexities and selective transport through membranes [19–25]. Although electro-dialytic desalination of multi-ionic solution e.g. sea water [26], industrial brackish water [27], black liquor [28, 29], and fruit juices [30] were reported earlier, major focus of those studies were on evaluation of process efficiency in ion removal. Fundamental understanding of physico-chemical and local equilibria influencing ion transport, membrane properties and thereby process efficiency needs to be understood. Kabay et al. [24] reported batch mode electro-dialytic separation of monovalent and divalent electrolytes, where relative removal rates of mono and bivalent cations were compared. Dammak et al. [31] tried to investigate the role of concentrate and diffusion boundary layer on bi-ionic potential occurring due to passage of counter ions through CEM and reported transport and selectivity of counter ion increases with lower water content in the membrane. Geraldies et al. [23] proposed an explicit model based on effective diffusivity and mass transfer coefficient to estimate limiting current density (LCD) during ED of a multi-ionic feed solution. Experimental LCD values match (± 5 –7%) with theoretically predicted LCD. Complexities due to simultaneous presence of three cations become many fold and isolation of role of any single component also becomes challenging. Therefore, the present investigation is focused on understanding cation transport from ternary combinations of electrolytes e.g. NaCl, KCl, CaCl₂, MgCl₂ and FeCl₃ of varying cationic charges in the scope of concentration, flow rate, adsorption equilibrium, transport number, water uptake, and resistance measurements.

2. Theory

Rectangular flow channel is the most preferred geometry for ED apparatus. Ion transport through this ED apparatus is very much influenced by the hydrodynamics of the rectangular channel between membrane pair. Differences in mobility of ions in solution relative to that through membrane matrix cause concentration gradient at the membrane–solution interface. This is known as concentration polarization and becomes the source of resistance to ion transport and limits the passage of ions through interface. Once concentration of ions approaches zero near membrane surface in the diluate compartment it is known as the limiting current (LC) situation. This current per unit membrane area is defined as the limiting current density. Current density above limiting value leads to water splitting and considerable amount of applied potential gets used up producing H⁺ and OH⁻ ions from electrolysis of water. Therefore, ED operations are usually performed at 80% of the limiting current density (LCD) to make it energy efficient [32–37]. For a single salt solution the LCD, i_{lim} is approximated by integrating

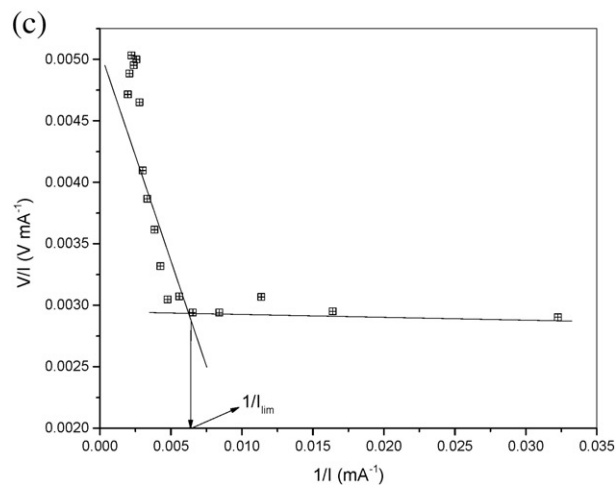
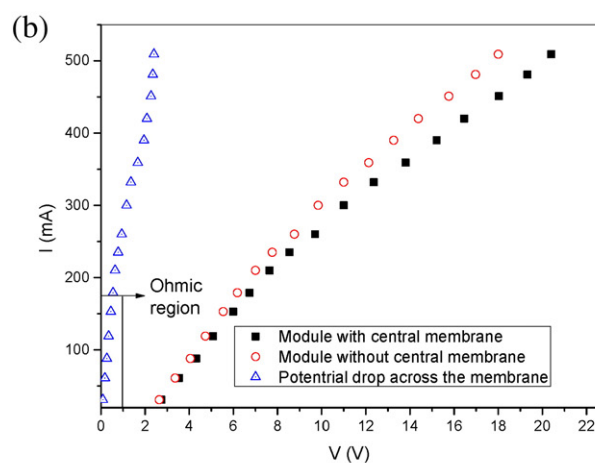
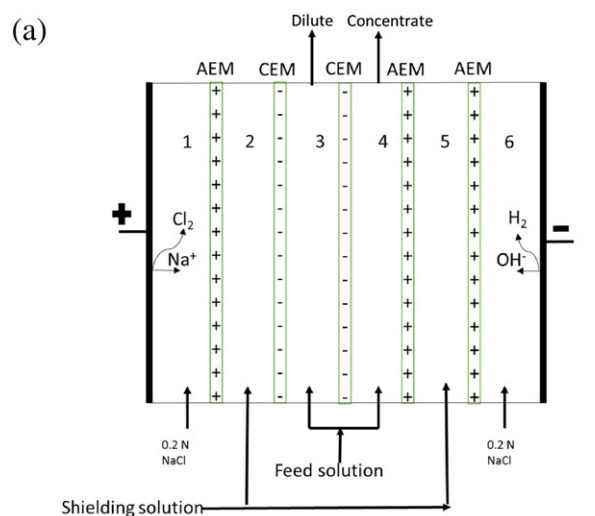


Fig. 1. (a). Electro-dialysis module used. (b). Current versus voltage, (I/V) plot for experiment A1 at $Re = 255$. (c). Plot of V/I , vs. mA^{-1} against $1/I$, mA^{-1} to estimate limiting current density, LCD for experiment A1 at $Re = 255$.

Nernst–Planck equation with appropriate boundary conditions [38]:

$$i_{lim} = \frac{Fz_j C_{j,b} D_j}{\delta(t_{j,m} - t_{j,b})} \quad (1)$$

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