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The influence of D-mannitol on the effectiveness of boric acid transport during electrodialytic desalination of aqueous solutions

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ABSTRACT

Previous studies have shown that electrodialytic (ED) desalination can be effective in separating boric acid from salts, and a model for the transport of boric acid during ED desalination has been proposed.

In this study, the influence of D-mannitol on the effectiveness of boric acid transport during ED desalination of aqueous solutions was investigated. The experimental results of periodic desalination were compared with results predicted from a previously proposed model of boric acid mass transport. Both the concentrate and the electrode rinse solution contained lower than predicted amounts of boric acid, especially at high diluate boric acid concentration. This difference was shown to be due to the reaction between monoborate and D-mannitol, which resulted in the formation of mono- and dichelate complexes and therefore significantly reduced the equilibrium concentration of boric acid in the diluate. This phenomenon was observed despite the low *pH* of the diluate. The equilibrium concentration of boric acid in the diluate was calculated using the model for chemical equilibrium. The results were then analyzed with the model for boric acid transport. A good agreement between the predicted and the measurements results was found. The combined model was therefore shown to be accurate in predicting the effectiveness of boric acid transport during ED desalination of mixtures of boric acid and D-mannitol. The effect of D-mannitol was such that it reduced the equilibrium concentration of boric acid in the diluate. This, in turn, reduced the boric acid flux across the membrane. The extent of the above reduction in boron flux can be predicted based on the combined model provided in this work. No evidence of borate complexes and D-mannitol transport across IEMs was observed.

1. Introduction

The average concentration of boron in the Earth's crust is approximately 10 mg/kg [1]. In nature, this element primarily exists in the form of borates or boric acid. Boron compounds are widely used in industry, mostly in glass and ceramics.

According to the WHO [2], most fresh water contains less than 0.5 mg/L of boron. However, this value strongly depends on the presence of boron-bearing minerals near fresh water reservoirs. In addition, the discharge of municipal and industrial effluents into surface waters may affect the boron content. Naturally occurring boron is present in ground waters at a wide concentration range from <0.3 to >100 mg/L. These ground waters include strongly mineralized, naturally carbonized geothermal waters. Considerable amounts of boron are also present in oceans, with an average concentration of 4.5 mg/L [2]. Due to its toxicity, the WHO proposed a guideline value for boron in drinking water of 2.4 mg/L in 2011 [3]. However, in areas with high natural boron levels, local regulatory and health authorities were advised to consider values in excess of 2.4 mg/L by assessing exposure from other sources (e.g., food). Because of the low limit for boron in drinking water, methods to reduce the boron content in drinking waters are required. Moreover, irrigation waters for some plants require even lower concentrations [4,5]. Conventional methods for water treatment, however, do not significantly remove boron. The methods proven to be efficient in reducing the boron content in waters are either adsorption or membrane based [2]. Among the membrane-based methods, reverse osmosis (RO) is the most commonly studied [2,4,5]. The effectiveness of boron removal by RO is strongly affected by the aqueous chemistry of boron species. In aqueous solutions, boric acid, monoborate and polyborates exist. Boric acid, a weak electrolyte with a pK_a of approximately 9.2, dominates in dilute solutions of a *pH* less than 9 [6]. It is, however, poorly rejected by RO membranes [4,5]. In contrast, the monoborate ion exists at $pH>9$ and in dilute solutions. This ion can be removed by RO membranes more effectively than boric acid due to its larger size and discrete charge [4]. Under conditions in which the monobrate ion predominates, however, there is a serious risk of membrane scaling with calcium or magnesium carbonate, hydroxide or combinations of these compounds. Therefore, RO systems cannot be directly operated at high feedwater *pH* due to the possibility of membrane scaling. To mitigate this problem, several

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modifications to RO and its design have been proposed. In general, a cascade design for RO systems in which a fraction of the first stage permeate is treated in the following RO stages (if possible at elevated *pH* values) and the permeates are mixed producing water of the desired quality [5]. This design was successfully applied in the full scale seawater treatment plant in Eliat.

As in the case of RO, the effectiveness of boron removal with ion-exchange membranes (IEMs) is strongly affected by the aqueous chemistry of the boron species. The effectiveness of boric acid removal by electrodialysis (ED) or the electric current efficiency of boron transport in feedwaters at $pH<9$ is poor compared with ionic species [7–12]. In fact, boric acid flux across IEMs is so small that the possibility of boric acid separation from ionic species using ED has been strongly considered [8,9,13–16]. It was reported that it is possible to separate mineral acids [13,14] and salts [8,9,15–17] from boric acid using ED when at low diluate pH. Once separated from mineral salts, boric acid can be concentrated at high pH using other methods i.e. RO as discussed earlier in the text. A model for the transport of boric acid during ED desalination was proposed in [18].

Monoborate is known to create chelated complexes with polyols containing vicinal hydroxyl groups. Among the possible alcohols, D-mannitol is the most commonly used. Its reaction with monoborate has been widely studied [19]. The scheme for these reactions is presented in Fig. 1. In this process, monochelate (structure 1) and dichelate (structure 2) complexes are produced as a result of the reaction between monoborate and D-mannitol at alcohol/boron molar ratio of 1 or more. The reported partial equilibrium product constants for the reactions in Fig. 1 are $\beta_1=616$ and $\beta_2=155$ [19]. This indicates that the mono- and dichelate complexes are thermodynamically favored over monoborate. However, at low *pH,* the amount of monoborate available for complex formation is low. Therefore, at low *pH* values, only small amounts of either monoborate or complexes exist, and boric acid should dominate.

Preliminary reports on the effectiveness of boron removal by RO membranes in the presence of polyols have shown that at high *pH*, the effectiveness of boron rejection was greatly enhanced with the addition of polyols [20,21]. This enhancement was shown to be due to the formation of mono- and dichelate complexes. This effect disappeared as the *pH* decreased. There are, however, no reports on the effect of polyols on the effectiveness of boric acid separation from salts by ED.

2. Objective

The objective of the present work was to investigate the effect of D-mannitol on the effectiveness of boric acid transport during ED desalination. This objective was achieved by comparing the results of periodic desalination of boric acid–D-mannitol mixtures with the results predicted from a previous model of boric acid transport in ED. The observed differences in boron flux were analyzed with respect to the borate complex formation equilibrium. The effect of initial boric acid concentration in the diluate and the type of salt was also investigated.

The results should enable a better understanding of boric acid transport in the presence of D-mannitol. It should also be possible to identify the conditions for ED desalination of waters at a minimum rate of boron transport and effectively separating boric acid and alcohol from salts by ED. In this work, the ability of D-mannitol to minimize flux of boric acid across IEMs during the desalination process was of particular interest. The desalinated boric acid–D-manntiol solution could be effectively concentrated at high *pH* with the use of RO membranes as presented previously in [21].

3. Methods and apparatus

All experiments were conducted in an ED unit as previously described in [16,18]. In this system, it was possible to separate boric acid flux across the cation-exchange membrane (CEM) from the flux across the anion-exchange membrane (AEM). It was also possible to address boron flux to the kind of particular ion as demonstrated in [16,18].

To investigate the effect of D-mannitol on the rate of boric acid transport, 100 cm^3 of diluate samples containing boric acid and D-mannitol were periodically desalinated at 800 mV membrane pair voltage drop. The electric current densities observed varied with the kind of the salt applied; however, never exceeded 90% of the limiting current density. The molar ratio between D-mannitol

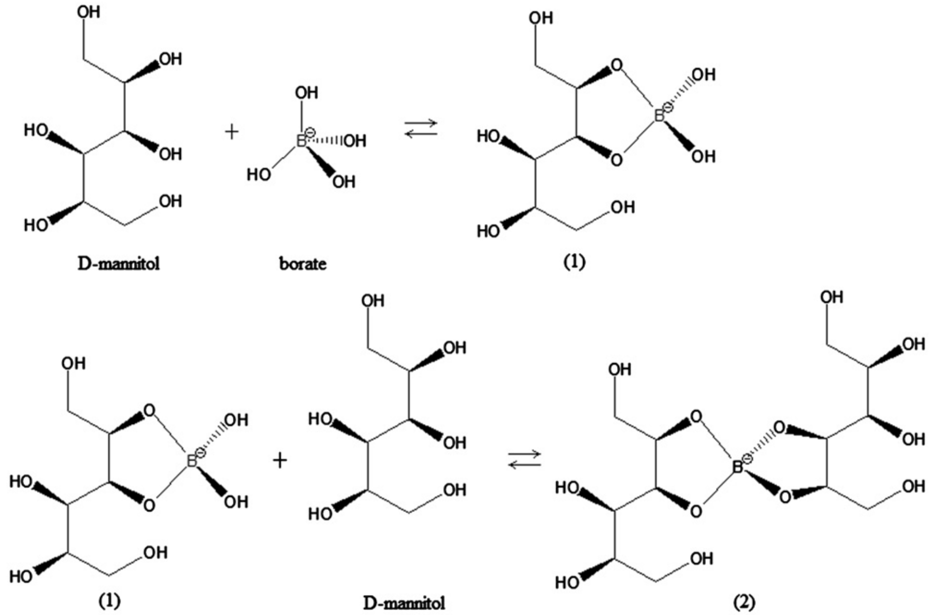

Fig. 1. The scheme for monoborate and D-mannitol reactions at alcohol/boron molar ratio of 1 or higher. Structure (1) represents the monochelate complex while structure (2) represents the dichelate complex.