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Cooperative sorption of weak and strong electrolytes in microporous adsorbents

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ABSTRACT

Sorption of pure electrolytes and binary electrolyte mixtures in non-ionic microporous adsorbents was studied in batch and fixed-bed systems. Hypercrosslinked polystyrene (HCPS) and densely crosslinked dextran gel (G10) were used as adsorbents and the studied model systems were $HCl/CaCl_2$/HCPS at 25 °C and Na_2-tartrate/NaOH/G10 at 50 °C. The results were explained in terms of cooperative sorption and the experimental data were correlated using a generalized Donnan equilibrium model together with Pitzer model for evaluation of the ion-ion and ion-adsorbent interactions. Moreover, a model was included for partial ion dehydration at high concentrations.

Non-linear sorption observed at very low and high concentrations of pure electrolytes was explained by electrostatic exclusion and partial ion dehydration. In binary mixtures, a more complex behavior was observed because of cooperativity and good separation of the electrolyte mixtures was obtained in the fixed-bed experiments involving pulse feed and elution with pure water. In the $HCl/CaCl_2$/HCPS system, selective uptake of HCl was enhanced by increasing the total electrolyte concentration. This trend can be explained by taking into account both size exclusion of $CaCl_2$ and the non-ideal behavior of the electrolyte mixture. Separation of Na_2-tartrate and NaOH was dominated by size exclusion of the tartrate anion and well-defined separation is possible even at very high column loading. Moreover, the observed splitting of Na_2-tartrate to NaH-tartrate and NaOH can be explained on the basis of cooperativity. The results suggest that the proposed model applies equally well to materials having rigid microporous structure and to densely cross-linked gels.

1. Introduction

Separation of ordinary electrolyte solutions containing e.g. mineral acids and their salts is usually thought to require materials that carry fixed ionic groups to bind the ions from the solution. The use of the ion exchange resins is well-established in water treatment and purification or fractionation of salt solutions. Conventionally, separation of the species contained in the solution is based on *competition*. This means that some or all of the solution components compete for same ion exchange or adsorption sites present in the solid. Consequently, uptake of a given component is *negatively* affected by the others. One major drawback of ion exchange is high consumption of regeneration chemicals. This is particularly true with materials that are tailored to obtain high selectivity for a given component.

In some cases, presence of other species may enhance sorption of a given component and the competition is accompanied or replaced by *cooperation*. This means that some physico-chemical interactions or restrictions give rise to a *positive* influence on sorption of the target component by one or several components existing in the studied mixture. The term cooperative adsorption has been used for a long time and it usually refers to systems giving rise to S-type isotherms, where strong lateral interactions between adsorbed species are present [1]. When the term is used in the sense of this study, the solution-side interactions are dominant while interactions with the adsorbent may be negligibly weak. The simplest case of cooperativity stems from interactions in the bulk solution; the activity coefficient of the target component increases because of the other components and the driving force for sorption increases. Salting-out of uncharged species at high electrolyte concentrations is a typical example and it is observed in protein separation and purification, fractionation of molasses and, more recently, of biomass hydrolysates [2].

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The objective of this study is to show how cooperative sorption induced by non-ionic microporous adsorbents can be used for separation of electrolyte mixtures. Conventionally, separations based on molecular size are applied only on substances, which have large difference in their molar masses. Separation of simple electrolytes like HCl and NaCl stems from the tendency of the common anion to distribute evenly between the bulk liquid and the pore-filling liquid. Equivalent amount of cation is required and the smaller H^+ is preferred in the pore liquid, while Na^+ concentrates in the bulk solution [3,4]. Ultimately, the method can be used to split a neutral salt into its parent acid and base as shown by Davankov et al. [5]. Adsorbent-induced cooperativity has recently been utilized in fractionation of organic acids from wood pulping chemicals [6]. Densely cross-linked polymer gels have been found effective to obtain clear-cut fractionation of the organic electrolytes from the inorganic components. In both cases the benefits of cooperative sorption are obvious. Separations efficiency tends to increase with solution concentration and/or adsorbent loading, which is opposite to what is normally observed in competitive sorption. Moreover, actual capacity of the solid separation medium in the separation process is high and no chemicals other than water are needed to run the process.

Phase equilibrium of electrolytes in solid/liquid systems is usually described using the Donnan equilibrium condition [7], where the chemical potential of each ion is assumed equal in both phases. This relationship forms the basis for cooperative sorption and several explanations have been put forward to explain the low activity coefficients of e.g. acids in the resin phase [8–10]. Alternatively, size exclusion and its contribution in the chemical potential of the ions have been considered [11,12]. For small ions like H^+ and OH^- this contribution is negligible but for ions with size approaching the pore size, the chemical potential increases rapidly. It is thus possible to obtain separation of electrolytes even when there are no specific interactions between the ions and the resin. An analogous phenomenon can be observed in nanofiltration [13], where the pore size of the membranes lies in the same range as in the above-mentioned microporous materials.

In this study, we provide a general approach for cooperative sorption of electrolytes in microporous adsorbents. Only non-ionic adsorbents are considered here but the treatment is equally valid for ionic materials with microporous structure. For this purpose, the approximate thermodynamic equilibrium model reported earlier [10,11] is reformulated to include mixing, electrostatic and steric effects in a thermodynamically consistent way. Moreover, a quantitative treatment is proposed for the partial dehydration of the ions at high electrolyte concentrations and its influence on electrolyte sorption. To the best of our knowledge, this has not been done before. The proposed model is tested against static and dynamic experimental data measured for binary HCl/$CaCl_2$ and NaOH/Na_2-tartrate aqueous mixtures using hypercrosslinked polystyrene (HCPS) and densely crosslinked dextran gel (G10) as microporous adsorbents.

2. Experimental

Separation of the Na_2-Tar/NaOH system was studied by Hellsten et al. [6]. The adsorbent was Sephadex G-10 (G10, Sigma-Aldrich), which is a homogeneous gel composed of cross-linked dextran. The properties are listed in Table 1. The break-through profiles were measured in a 97 mL bed for pure Na_2-Tar and for mixtures of the two electrolytes at 50 °C. Here new data for the equilibrium uptake was measured. In the equilibrium experiments, the resin was equilibrated overnight at 50 °C with solutions containing different amounts of Na_2-Tar and NaOH. After removal of the resin, the solution composition was analyzed using HPLC (HP 1100, Agilent/HP) for Na_2-Tar and potentiometric titration for NaOH. Details of the HPLC analysis are given elsewhere [6].

Table 1
Properties of the water-swollen adsorbents.

	HCPS	G10
Average particle size, μm	400	110
Pore size, nm	2–3	–
Permanent porosity, -	0.58	–
Density[a], kg/L	0.47	0.32
Polymer volume fraction, -	–	0.30
Water content, L/kg	1.23	1.65

[a] Polymer content in the swollen resin. Estimated from the water sorption data.

The experimental data for the $CaCl_2$/HCl system were taken from the papers of Davankov and co-workers [3,4]. Hypercrosslinked polystyrene (HCPS, Purolite) was used as the adsorbent and the properties are given in Table 1. The equilibrium data consist of uptake curves of both electrolytes from pure and mixed solutions at 25 °C. Break-through experiments were made in a column with a bed volume (BV) of 44 mL. The flow rate during the feed pulse and water elution was 1.35 mL/min.

3. Theory

3.1. Phase equilibrium model

The thermodynamic equilibrium condition for component i can be written as shown in Eq. (1). Here μ is chemical potential and the subscripts mix, sw, el and st refer to mixing, swelling, electrostatic and steric contributions, respectively. Quantities with over-bar refer to the solid phase. It is assumed here that the standard values of μ are identical in the two phases. Moreover, a is activity, V_m is partial molar volume, z is valence and E_D is Donnan potential. $\mathfrak{F}$ is Faraday constant and R and T have their usual meanings. Only isothermal systems were considered here and the temperature dependency of the parameters discussed below was neglected.

$$\begin{gathered}\Delta\mu_i = \mu_i - \overline{\mu}_i = \Delta\mu_{i,mix} + \Delta\mu_{i,sw} + \Delta\mu_{i,el} + \Delta\mu_{i,st} = 0 \\ (i = \text{ions, molecules, water}) \\ RT\ln\frac{\overline{a}_i}{a_i} + V_{m,i}\pi + z_i\mathfrak{F}E_D - RT\ln K_{st,i} = 0\end{gathered} \tag{1}$$

The swelling pressure, $\pi = \overline{p} - p$, is present in gel-type solids and it is due to entropy decrease stemming from limited expansion of the crosslinked polymer chains. A non-Gaussian network model shown in Eq. (2) has been found suitable to evaluate π in ionic and non-ionic materials [14]. Here ψ_p is the polymer volume fraction, and L^{-1} is the inverse Langevin function. Parameters K_{el} and n_{stat} depend on the degree of cross-linking and they can be evaluated from the existing swelling pressure data. The correction factor d_c is assumed equal to 1.0 [14]. The swelling pressure is assumed to vanish in materials containing permanent pore structure and the pressure of the pore fluid is taken equal to that of the bulk solution.

$$\begin{aligned}\pi &= \frac{1}{3}K_{el}\psi_p^{2/3}n_{stat}^{1/2}L^{-1}(w) \\ w &= \left(\psi_p\right)^{-1/3}n_{stat}^{-1/2} \\ \psi_p &= \frac{\rho_w V_{m,R}\overline{m}_R}{1+\rho_w\left(V_{m,R}\overline{m}_R + \sum_{ions} V_{m,j}\overline{m}_j\right)}\end{aligned} \tag{2}$$

The steric contribution is due to entropy decrease stemming from sterically hindered entrance of an ion or a molecule in a