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Exploration of the fundamental equilibrium behaviour of calcium exchange with weak acid cation resins

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HIGHLIGHTS

- Detailed understanding of the behaviour of ion exchange resins for water softening
- Demonstration of the usefulness of the Langmuir–Vageler expression
- Observation of partial hydrolysis of weak acid cations in aqueous solution
- Evidence for super-equivalent ion exchange behaviour
- Suggestion that dissolved salts remain in the interior of the resin beads

ARTICLE INFO

ABSTRACT

This study evaluated the complexity of calcium ion exchange with sodium exchanged weak acid cation resin (DOW MAC-3). Exchange equilibria recorded for a range of different solution normalities revealed profiles which were represented by conventional "L" or "H" type isotherms at low values of equilibrium concentration (C_e) of calcium ions, plus a superimposed region of increasing calcium uptake was observed at high C_e values. The loading of calcium ions was determined to be *ca.* 53.5 to 58.7 g/kg of resin when modelling only the sorption curve created at low C_e values, which exhibited a well-defined plateau. The calculated calcium ion loading capacity for DOW MAC-3 resin appeared to correlate with the manufacturer's recommendation. The phenomenon of super equivalent ion exchange (SEIX) was observed when the "driving force" for the exchange process was increased in excess of 2.25 mmol calcium ions per gram of resin in the starting solution. This latter event was explained in terms of displacement of sodium ions from sodium hydroxide solution which remained in the resin bead following the initial conversion of the as supplied "H^+" exchanged resin sites to the "Na^+" version required for softening studies. Evidence for hydrolysis of a small fraction of the sites on the sodium exchanged resin surface was noted. The importance of carefully choosing experimental parameters was discussed especially in relation to application of the Langmuir–Vageler expression. This latter model which compared the ratio of the initial calcium ion concentration in solution to resin mass, *versus* final equilibrium loading of the calcium ions on the resin; was discovered to be an excellent means of identifying the progress of the calcium–sodium ion exchange process. Moreover, the Langmuir–Vageler model facilitated standardization of various calcium–sodium ion exchange experiments which allowed systematic experimental design.

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1. Introduction

Ion exchange is a technology which spans many fields, from analytical research purposes to industrial streams, and beyond to natural processes such as the exchange of minerals in soils [1,2]. The exchanger medium comes in various forms, such as naturally occurring zeolite materials [3,4] to industrially synthesised ion exchange resins [5–7]. Regardless of the type of exchanger, ion exchange is understood to occur at a stoichiometric ratio; that is, one ion of a certain charge in solution migrates into the exchanger phase and replaces ions of equivalent charge resident on the exchanger surface. The process of ion exchange has been studied primarily by three experimental methodologies;

kinetic [8], equilibrium and column studies [9,10]. Common to all three approaches is the use of numerous models to describe the sorption process, some of which are generalized for both adsorption and ion exchange systems [11]. Thus, there can at times exist confusion [12], a lack of fundamental understanding [13], and insufficient experimental rigour [14]. Consequently, our research group has focussed upon developing a systematic approach to investigating the basic experimental procedures used in ion exchange. For example, equilibrium isotherm studies of singly charged ions with strong acid cation resins have revealed the pitfalls of failing to comprehend the impact of experimental conditions such as bottle-point method used and solution/resin ratio [15].

This paper extends the study of ion exchange equilibria to situations where multiply charged ions are involved. One of the oldest ion exchange processes known and also a very common industry application is the softening of water using materials such as zeolite A [16] or synthetic resins [17]. Zeolite is used as a detergent builder as it is more environmentally benign when compared to phosphate based materials [18]. Costa et al. [19] studied the synthesis of zeolite 4A using kaolin as a starting material, with the aim of preparing more cost effective detergent builders. Similarly, Ma et al. [20] attempted the synthesis of zeolite 4A using bentonite clay. Recently, Xue et al. [16] improved the softening performance of zeolite 4A, especially magnesium removal, by enhancing the mesoporosity. Hoffmann and Martinola [17] reviewed the application of various synthetic ion exchange resins to softening of water. Ghergheles et al. [21] reported a study using a cationic resin to soften geothermal water which successfully softened the water to the point of suitability for household use. The concept of hybrid ion exchange-reverse osmosis water treatment plants has also gained interest in relation to development of high water recovery units [22]. For example, Venkatesan and Wankat [23] modelled ion exchange softening pre-treatment of brackish water prior to reverse osmosis operation and noted an improvement in water recovery from 36 to 90% without the appearance of precipitation. Lipnizki et al. [24] also advocated the combination of ion exchange softening processes with reverse osmosis treatment of wastewater.

The fundamental representation of the softening process is shown in Eq. (1).

$$Ca^{2+}(aq) + 2Na^+R \leftrightarrow Ca^{2+}R2 + 2Na^+(aq). \tag{1}$$
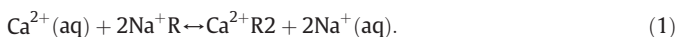
However, the assumption of simplicity may not necessarily be correct, since, as noted in Helferrich [2], any ion exchange process is inevitably coupled with the process of adsorption. Moreover, when multiple charged ions are present in solution their exchange behaviour is highly dependent upon the solution normality. For instance, Pabalan and Bertetti [25] studied the exchange of various solutions of alkali and alkaline earth cations with clinoptilolite. A strong relationship between the solution normality and shape of the equilibrium isotherm was reported. In general, with increasing dilution the zeolite material exhibited a preference for the higher charged species, which was referred to as due to the "concentration–valency" effect.

Surprisingly, for such a common industry application, we have found relatively few fundamental sorption equilibrium studies in the open literature regarding water softening by synthetic resins. Jiang et al. [26] reported the exchange of calcium and magnesium ions by a chelating resin, and provided examples of kinetic and equilibrium behaviour. However, these authors did not examine weak acid cation resins with carboxylic acid functional groups, or use non-linear least squares (NLLS) fitting procedures to interpret the data. Instead, they linearized relevant equations and introduced known errors associated with this approach [14]. Enterazi and Tahmasbi [27] also used linearized isotherm models, did not investigate the influence of solution normality and only considered a strong acid cation (SAC) resin. Yi et al. [28] obtained isotherm data for calcium and magnesium exchange with a chelating resin, but did not evaluate the impact of solution normality or compare

different isotherm models with the aim of determining which fits the data optimally.

Therefore, the aim of this publication was to examine the equilibrium exchange behaviour of calcium with a commercially available weak acid cation resin comprising of carboxylic acid functional groups. Particular focus was upon the methodology for generating sorption isotherms, relevant equations to use, impact of solution normality and appropriateness of non-linear least squares fitting procedures.

2. Experimental

2.1. Resins

The resin used was termed MAC-3 and supplied by DOW Water & Process Solutions. This resin was characterized by a weak acid cation functionality through carboxylic acid groups, a polyacrylic macroporous structure, and a stated exchange capacity of 3.8 eq./L. The resin was initially received in the "H$^+$" form and as such required conversion to the desired "Na$^+$" form. The transformation procedure was as follows: A quantity of wet resin in the "H$^+$" form was placed into a clear u-PVC ion exchange column of 0.05 m diameter and subsequently rinsed with purified water at a rate of 15 L/h for 30 min. A 4% (w/v) solution of NaOH was then used to convert the resin to the "Na$^+$" form, again at a flow rate of 15 L/h for 30 min, at which point conductivity and pH measurements of the outlet solution had stabilised. Finally, the resin was again rinsed several times with water to remove any residual NaOH species present. In addition, the bed was 'lifted' between each rinse through a brief period of running the rinse water counter-current in order to settle the resin beads evenly and prevent channelling.

2.2. Chemicals

Aqueous solutions were prepared using triple distilled water to which appropriate amounts of salt were added. Analytical reagent grade calcium chloride was supplied by Rowe Scientific.

2.3. Analysis

Samples were analysed using a Perkin Elmer Optima 8300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for integration times of 0.15 s with 10 replications. Samples were diluted to a concentration between 1 and 100 mg/L using a Hamilton auto-dilutor with 10 mL and 1 mL syringes. A certified standard from Australian Chemical Reagents (ACR) was diluted to form multi-level calibration curves. An external reference was used to monitor instrument drift and accuracy of the results.

Table 1
Summary of error functions used for non-linear least squares (NLLS) analysis of equilibrium exchange data.

Error function	Equation
Sum of the squares of the errors (ERRSQ or SSE)	$\sum_{i=1}^{p}\left(q_{e,calc}-q_{e,meas}\right)_i^2$
Hybrid fractional error function (HYBRID)	$\frac{100}{p-n}\sum_{i=1}^{p}\left[\frac{(q_{e,meas}-q_{e,calc})_i^2}{q_{e,meas}}\right]_i$
Marquardt's percent standard deviation (MPSD)	$100\left(\sqrt{\frac{1}{p-n}\sum_{i=1}^{p}\left[\frac{q_{e,meas}-q_{e,calc}}{q_{e,meas}}\right]_i^2}\right)$
Average relative error (ARE)	$\frac{100}{p}\sum_{i=1}^{p}\left|\frac{(q_{e,calc}-q_{e,meas})}{q_{e,meas}}\right|_i$
Sum of the absolute errors (EABS)	$\sum_{i=1}^{p}\left|(q_{e,calc}-q_{e,meas})\right|_i$