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Exploration of the Fundamental Equilibrium Behaviour of Calcium Exchange with Weak Acid Cation Resins

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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 of calcium ions (C_e), 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 superequivalent 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.

Key Words: Calcium; Ion Exchange; Langmuir Vageler; Sodium; Super Equivalent

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

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Abbreviations

Abbreviation	Descriptor
ARE	Average Relative Error
C_e	Equilibrium concentration
C_o	Initial concentration of ions in solution
EABS	Sum of the Absolute Errors
HYBRID	Composite Fractional Error Function
ICP	Inductively coupled plasma
K_F	Freundlich coefficient
K_{LV}	Rate coefficient termed the "half value".
m	Mass of resin
MPSD	Marquardt's Percent Standard Deviation
n_F	Freundlich exponent
NLLS	Non-linear least squares
q_e	Equilibrium loading of ions on the resin
q_{max}	Maximum (monolayer) loading of ions on the resin
SAC	Strong acid cation
SEIX	Super Equivalent Ion Exchange
SNE	Sum of the Normalized Errors
SSE	Sum of the Squares of the Errors
V	Volume of solution
WAC	Weak Acid Cation

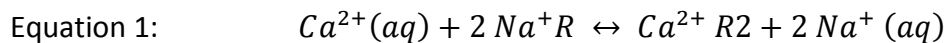
1. Introduction

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] through 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 Equation 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 multiply 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 *et al.*[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/hour for 30 minutes. 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/hour for 30 minutes, 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 triply 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 seconds 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.

2.4. Equilibrium Studies

A range of resin masses were placed into centrifuge tubes with 40 mL of a known concentration of CaCl₂ solution. The samples were agitated on a rotary shaker unit (Ratek

Model RSM7DC) at constant revolutions of 50 rpm for 24 hours at a temperature of *ca.* 19 °C. After equilibrium conditions were achieved the solution was separated from the resin beads and then transferred to a centrifuge to further separate solid from liquid. Calcium concentrations in solution (C_e (mg/L)) were then measured and the equilibrium calcium loading on the resin (q_e (mg/g)) inferred from Equation 2;

Equation 2:
$$q_e = \frac{V}{m}(C_o - C_e)$$

Where: q_e = equilibrium loading of calcium ions on the resin (mg/g); V = volume of solution (L); m = mass of resin (g); C_o = initial concentration of calcium ions in solution (mg/L); and, C_e = equilibrium concentration of calcium ions in solution (mg/L). Sodium concentrations were also measured in solution in order to determine the quantity released from the resin as a consequence of the exchange process. Desorption profiles were either shown where the sodium concentrations were expressed in relation to the mass of resin present (mmol Na/g resin), or in relation to calcium ions in solution under equilibrium (C_e).

3. Background Equilibrium Isotherm Theory

3.1. Langmuir Vageler Model

The Langmuir Vageler model was first reported by Vageler and Woltersdorf [29, 30] and involved the correlation of the starting solution conditions and the equilibrium loading of the species of interest on the sorbent material as illustrated in Equation 3.

Equation 3:
$$q_e = \frac{\left(\frac{VC_o}{m}\right) \cdot q_{max}}{\left(\frac{VC_o}{m}\right) + K_{LV}}$$

Where: q_e = equilibrium loading of calcium ions on the resin (mmol/g); V = volume of solution (L); m = mass of resin (g); C_o = initial concentration of calcium ions in solution (mmol/L); q_{max} is the maximum (monolayer) loading of calcium ions on the resin (mmol/g); and, K_{LV} = a rate coefficient termed the “half value”.

3.2. Competitive Langmuir Model

The Competitive Langmuir expression is different from other sorption models presented here in that it relates more to an ion exchange process as it takes into account the presence of both ions involved in the exchange [31]. Based upon the process in Equation 1 and the law of mass action, the expression in Equation 4 can be derived.

Equation 4
$$q_{e,Ca^{2+}} = \frac{k q_{max} C_{e,Ca}}{C_o + (k-1) C_{e,Ca}}$$

Where, $q_{e,Ca}$ represents the loading of the calcium ions on the resin at equilibrium (mg/g) and $C_{e,Ca}$ is the concentration of calcium ions in solution at equilibrium (mg/L). The system must have a mass balance wherein q_{max} (meq/L) = $q_{e,Na}$ (meq/L) + $q_{e,Ca}$ (meq/L) and C_o (meq/L) = $C_{e,Ca}$ (meq/L) + $C_{e,Na}$ (meq/L).

For the purposes of this paper, wherein the experimental methodology rather than the detailed theoretical exploration is the main focus, it is not necessary to discuss the use of more accurate representations of solutions where activities are calculated rather than molar concentrations.

3.3. Freundlich Model

The Freundlich isotherm expression [Equation 5] has been used in numerous studies of sorption systems. Originally it was an empirical model based upon physical observations, but shown in later years to be based upon fundamental physical principles [32, 33]:

Equation 5
$$q_e = K_F C_e^{1/n_F}$$

Where, q_e = equilibrium loading of calcium ions on the resin (mg/g); K_F = Freundlich coefficient (mg/g (L/mg)^{1/n}); C_e = concentration of calcium ions at equilibrium (mg/L); and, n_F = Freundlich exponent (dimensionless).

3.4 Non-Linear Least Squares (NLLS) Analysis of Equilibrium Data

Isotherm models such as Langmuir and Freundlich have commonly been linearized in published sorption literature, as this promotes ease of use in software packages such as Microsoft Excel or similar. However, this latter procedure violates fundamental assumptions of the least squares process [14]. Consequently, a non-linear least squares (NLLS) fitting approach is more appropriate as described by several authors [34, 35]. Therefore, this paper followed the methodology recommended by Ho *et al.* [36] which used the error functions described in Table 1.

4. Results

4.1. 0.01N Calcium Chloride Solution

Figure 1 **Error! Reference source not found.** shows equilibrium isotherm data for calcium exchange with DOW MAC-3 resin from a 0.01 N solution of calcium chloride. Application of the Langmuir Vageler expression provided a reasonable fit of the data. However, closer inspection of the measured points suggested that the calcium loading actually plateaued at a value of approximately 1.4 mol Ca/kg resin and upon increasing the “driving force” of the exchange process *i.e.* increasing the ratio of calcium ions in solution to the mass of resin present, the calcium loading accelerated. This latter observation was more evident in the corresponding Competitive Langmuir analysis of the equilibrium data [Figure 1 **Error! Reference source not found.**]. It was apparent that the uptake of calcium ions was extremely favourable as the calcium loading rapidly increased at low values of C_e , with a definite plateau noted to develop at C_e values between 7.1 and 86.5 mg/L. The “rectangular profile” of the equilibrium isotherm data was indicative of an exchange process which was practically, almost irreversible [37]. At higher C_e values above 86.5 mg/L, the calcium loading on the resin material exhibited a distinct enhancement which was not consistent with simple Langmuir type sorption behaviour which has the basic premise of a limited number of sorption sites being available [38]. Also shown in **Error! Reference source not found.** was a Competitive Langmuir fit of only the C_e data points up to 86.5 mg/L, which indicated a considerably improved representation of the experimental values, albeit the low range C_e points remained difficult to model adequately. The maximum loading of calcium ions on the resin surface was now estimated to be 58.7 g/kg [Table 1 **Error! Reference source not found.**]. In contrast, the Freundlich model was observed to be inadequate at modelling the equilibrium isotherm, especially at low values of C_e [Figure 1 **Error! Reference source not found.**].

It was of interest to also examine desorption of sodium ions as the calcium ions were exchanged on the resin surface sites. Figure 2 showed that the Langmuir Vageler and Competitive Langmuir isotherm fits of the measured data for sodium ion desorption were similar in profile to those for calcium uptake [Figure 1 **Error! Reference source not found.**]. The main difference was the magnitude of the sodium ions desorbed compared to calcium ions. A clearer indication of the exchange process which occurred between calcium ions in solution and sorbed sodium ions on the weak acid cation surface was seen by inspection of

Figure 3 which compared the equivalents of sodium released into solution to the amount of calcium removed from solution. Overall, the exchange process appeared to be approximately stoichiometric in nature. There was a discrepancy from ideal behaviour in that slightly less sodium ions were released than expected. This latter deviation may have been due to experimental error, however as will be seen below the behaviour was consistent in several tests and not random in nature. Thus, an underlying physical phenomenon was required to explain the behaviour observed.

4.2. 0.025 N Calcium Chloride Solution

Increasing the solution normality to 0.025 N calcium chloride solution resulted in the equilibrium isotherm profiles illustrated in Figure 4 **Error! Reference source not found.**. The shape of the isotherms recorded were similar to those displayed in Figure 1 when a 0.01 N solution was employed. Again, the initial uptake of calcium ions was rapid and a distinct plateau in the calcium uptake was noted, followed by a rise in the calcium loading as the “driving force” or value of C_e increased. The Competitive Langmuir fit of the data up until a C_e value of 215 mg/L indicated that the maximum calcium ion capacity on the resin was now 53.5 g/kg [Table 2 **Error! Reference source not found.**], which was less than the value of 58.7 g/kg noted when 0.01 N calcium chloride solution was the exchanging solution. Figure 5 **Error! Reference source not found.** displayed the correlation between both sodium ions desorbed and the calcium ions present in the initial solution (Langmuir Vageler plot), and versus the equilibrium concentration of calcium ions in solution (Competitive Langmuir plot). The ejection of sodium ions into solution paralleled the increase in the ratio of calcium ions to resin mass in the initial solution. A small plateau region was evident in the Langmuir Vageler plot [Figure 5 **Error! Reference source not found.**] after which the sodium ion release rate increased. The Competitive Langmuir fit of the data relating to desorbed sodium ions, also indicated the rapid release of these latter species into solution as calcium was loaded onto the resin exchange sites. After a plateau region encompassing a calcium ion equilibrium concentration in solution (C_e) up to 161.4 mg/L, the sodium expulsion from the resin was again enhanced. A graph relating equivalents of calcium loaded on the DOW MAC-3 resin and the quantity of sodium ions released into solution is shown in Figure 6 **Error! Reference source not found.**. As before, the relationship between the amount of calcium ions loaded on the resin surface and the sodium ions desorbed from the resin bead

was approximately linear, with a definite indication that less sodium was released than expected based upon process stoichiometry.

4.3. 0.05 N Calcium Chloride Solution

The normality of the calcium chloride solution was further elevated to 0.05 N in order to examine the impact of increasing solution concentration upon the exchange behaviour of DOW MAC-3 resin. Figure 7**Error! Reference source not found.** presents various model fits of the equilibrium exchange data which mirror those shown in Figure 1**Error! Reference source not found.** and Figure 4**Error! Reference source not found.**. Analysis of the isotherm profiles suggested that they were similar to those already recorded for the 0.01 and 0.025 N calcium chloride solutions. Applying the Competitive Langmuir model to the data for C_e values up to 290.4 mg/L resulted in a prediction for the monolayer exchange capacity of the resin to be 57.2 g Ca/kg of resin [Table 3**Error! Reference source not found.**]. Not unexpectedly, due to the close correspondence between the isotherm profiles noted in Figure 7**Error! Reference source not found.** and those for lower solution normalities, the sodium desorption profiles in Figure 8**Error! Reference source not found.** were remarkably similar to those already commented upon in Figure 2 and Figure 5**Error! Reference source not found.**. Logically, these latter observations should have translated into a similar relationship between calcium ions loaded on the resin and the quantity of sodium ions released in to solution, which was indeed what was seen [Figure 9**Error! Reference source not found.**].

5. Discussion

5.1. Isotherm Profile

Sorption isotherms have been classified by several different types depending upon the profile obtained from experimental equilibrium studies. For example, using the classification of Giles *et al.* [39, 40] the equilibrium curves reported in this study appeared to be consistent with the general “L” type or the subset of “L” which is termed “H”. “L” type isotherms are probably the most common isotherm profiles reported as they are the classic Langmuir pattern wherein a concave curve is observed which related to progressive saturation of surface sites and ultimately formation of a monolayer of sorbed species [37]. “H” isotherms are a variant of the “L” class wherein the initial gradient of the slope is very high and these are often called “rectangular” isotherms. Indeed, the initial stage of the isotherm profiles in this study wherein a rapid increase in the quantity of sorbed calcium ions was observed and a distinct plateau noted, was consistent with the “H” isotherm illustrated by Alberti *et al.* [11]. The subsequent rise in calcium uptake following creation of the plateau in sorption capacity has been noted by Giles *et al.* [39] as the sub-groups 3 and 4 of “L” and “H” class isotherms. The fundamental difference between sub-groups 3 & 4 was the ever increasing uptake of sorbate in sub-group 3 and formation of a secondary plateau in sub-group 4. From the isotherm profiles shown in this study it was difficult to conclusively assign the isotherms to either sub-group mentioned due to a lack of data-points.

Several studies have reported inflection points in equilibrium isotherm curves, where an increase in ion uptake was noted. For example, Pabalan and Bertetti [25] studied the ion exchange behaviour of various solutions comprising of both mono- and divalent cations with natural zeolite. An important aspect of the latter study was the observation of a strong dependence of the isotherm profile upon solution normality. As the solution normality was lowered the affinity of the zeolite material for the divalent species increased significantly, due to the “concentration-valency” effect. Although, inflections were noted in the majority of isotherms such as those where sodium and strontium ions were exchanged, no discussion was made of this phenomenon. Similarly, Inglezakis *et al.* [41] collected ion exchange isotherms for the exchange of chromium ions from solution with clinoptilolite. The isotherm profile was characterized by an initial increase in sorbate uptake followed by a

distinct plateau and finally a rapid increase in chromium sorption. These authors stated that the exchange process changed from favourable to unfavourable but did not explicitly provide a reason for this behaviour. Bricio *et al.* [42] hypothesised a “double selectivity” model for equilibrium isotherms displaying inflection points, which resulted from exchange of ions with “H⁺” forms of styrene-divinyl benzene resins. The key assumptions were: two different active sites in the resin; distribution of resin capacity related to percentage of divinyl benzene present; and, ion exchange equilibria occurred simultaneously at both types of site. The idea of two distinct types of exchange sites has also been enunciated by Tamura *et al.* [43] for weak acid cation resins. These authors were of the view that one site was located in regions where large pores were present and the other was in the macroporous channels. Limousin *et al.* [37] also discussed several studies regarding the exchange of potassium and calcium ions with 2:1 clays where the isotherms showed a preference for potassium uptake initially and then followed the non-preference curve at higher loadings, thus creating an inflection point. Again, a two site model was fitted to the experimental data.

5.2. Resin Capacity

The resin manufacturer states that the DOW MAC-3 material should uptake 1.9 mol Ca/L or 76.15 g/L which was 101.5 g/kg based upon a packing density of 750 g resin/L and resin supplied in the H⁺ form. The initial procedure used here was to modify the as supplied “H⁺” form of the resin with sodium hydroxide in order to obtain the required “Na⁺” exchanged resin. During this latter exchange process the resin was expected to expand by 70 % and this was the material then weighed for the bottle-point investigation. During the column conditioning of the weak acid cation resin this latter expansion in volume was indeed observed. Consequently, the resin capacity was now adjusted to 1.12 mol Ca/L resin in sodium form, or 1.49 mol Ca/kg resin (assuming packing density of 0.75) which equated to 59.7 g Ca/kg resin. This latter estimate for calcium loading on DOW MAC-3 resin was remarkably similar to the value of 58.7 g Ca/kg resin determined in this study when the exchange capacity calculation was applied for example in Figure 1 **Error! Reference source not found.** to C_e values less than 86 mg/L calcium ions.

Consequently, one must consider what principle explained the increase in calcium uptake post-formation of the plateau region in the equilibrium isotherm plots. One possible explanation was the concept of “superequivalent ion exchange” which has been reviewed in depth by Kokotov [44]. This author elucidated that the inclusion of electrolyte was enhanced when: using solutions of high concentration; the capacity of the sorbate decreased; and, the cross-linking of the resin structure was low. Christensen and Thomsen [45] highlighted the importance of the uptake of co-ions and solvent when working with concentrated solutions during ion exchange processes. This latter situation was comparable to our study when a large concentration of calcium ions in solution was exchanged with a small amount of resin. Christensen and Thomsen [45] for example contacted a calcium loaded resin with a solution of calcium chloride. Evidence was obtained which showed that uptake of calcium chloride salt into the resin structure improved as the solution molality increased. The relative amount of salt included in the resin beads depended upon the Donnan potential [46] and size of the ions involved. Similarly, Soldatov *et al.* [47] examined the non-exchange of various electrolytes with anionic resin and again reported that the inclusion of electrolyte in the resin was promoted by increasing the concentration of the external solution. To account for the sorption degree of electrolytes it was required to include not only Donnan or Nernst distribution effects but also to allow the possibility for formation of hydrated ionic associates.

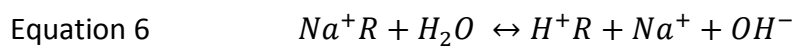
Donnan equilibrium theory predicts that the chloride ions should be excluded from the resin bead at low salt concentrations (“Donnan exclusion”) but progressively be included as the aqueous concentration increased (“Donnan inclusion”) [48].

5.3. Process Stoichiometry

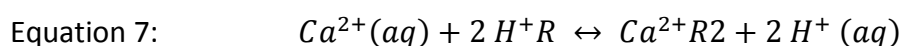
The question of process stoichiometry has to be addressed to gain an insight into the exchange behaviour. For example, in the case illustrated where a sodium loaded resin was placed into a solution containing calcium ions, ion exchange theory dictated that for each calcium ion that moved from solution into the exchanger, two sodium ions should move in the opposite direction. All three plots of calcium loaded on the resin versus the quantity of sodium released suggested an approximately linear relationship over all conditions studied [Figure 3, Figure 6 and Figure 9 **Error! Reference source not found.**], with a slight upward trend noted toward the final stages of the plot perhaps

indicating an increased displacement power of Ca ion at increased driving force conditions. As previously discussed, the plateau region in the isotherm plots appeared to correlate to monolayer exchange of calcium ions with sodium ions on the resin surface.

To gain an insight to the deviation in stoichiometry noted above, an experiment was conducted involving addition of sodium exchanged resin to pure water. The presence of sodium ions in solution following equilibration between sodium exchanged weak acid cation resin and pure water [Figure 10] suggested that partial hydrolysis of the resin surface had occurred according to Equation 6.

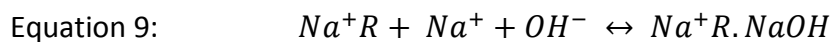
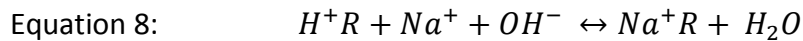


Lehto and Harjula [49] discussed the fact that weak acid cation exchange resins typically exchanged a small proportion of sodium ions on the resin surface with hydronium ions from solution. The concomitant rise in solution pH [Figure 10 **Error! Reference source not found.**] was consistent with Equation 6, and calculations based upon the quantity of sodium ions in solution suggested that the pH should have been in the range 9.8 to 10.2. The latter pH range was in agreement with the measured data and in harmony with the work of Lehto and Harjula [49] which highlighted the significant impact upon pH even a limited degree of hydrolysis can have. Consequently, the hydrolysis effect explains why the calcium-sodium exchange process in this study indicated less ejection of sodium ions from the resin surface than expected, as the exchange process in Equation 7 probably occurred in addition to Equation 1.



Therefore, it was pertinent to inspect for example, the data concerning solution pH during the equilibrium exchange of the 0.01 N calcium chloride solution with DOW MAC-3 resin in this study [Figure 11 **Error! Reference source not found.**]. Notably, the pH values were depressed relative to the situation when the sodium exchange resin was immersed in pure water. This latter behaviour was consistent with two processes, namely exchange of the sodium ions for calcium species which were probably less susceptible to hydrolysis and release of protons (hydronium ions) due to Equation 7.

The additional uptake of calcium ions after monolayer exchange was postulated to be due to inclusion of calcium ions from the calcium chloride electrolyte at high ratios of calcium in solution to resin mass. Consequently, it can be deduced that inclusion of electrolyte in the resin beads concomitantly resulted in the expulsion of non-exchanged sodium ions already present within the resin pores. The source of these non-exchanged sodium ions was presumably from the sodium hydroxide used in the initial resin regeneration stage as shown in Equation 8 and Equation 9.



Despite the fact that extensive rinsing with purified water was completed following the sodium hydroxide regeneration procedure until the effluent solution pH stabilized, evidently some sodium hydroxide was retained within the resin structure. In order to ascertain whether sodium chloride entered the resin beads or simply sodium ions from the external solution, the concentration of chloride ions in the equilibrium solutions was measured [Figure 12Error! Reference source not found.]. The data suggested that the quantity of chloride present in the bulk solution remained reasonably constant. This evidence indicated that the chloride ions were unable to enter the resin pore structure despite evidence showing a super ion exchange taking place, which was in accord with Donnan exclusion theory. Consequently, a charge balancing anionic species must have been present inside the resin bead in order to maintain electroneutrality. The only possibility appeared to be hydroxide ions from inclusion of some of the sodium hydroxide regenerant.

5.4. Experimental Procedures

As shown in the results section the equilibrium isotherms can be complicated. Evidence has been presented which showed that changing the solution concentration or amount of resin used had consequences on the data produced. As outlined by Lehto and Harjula [49], with ion exchange a common mistake was the labelling of equilibria as “isotherms” since ion exchange required not only conditions of constant temperature but also constant solution normality. Moreover, the equilibrium data obtained was representative for only the specific experimental conditions used to produce the data. Indeed, it can even be the case that only a portion of the ion exchange equilibrium isotherm curve was measured as often test

conditions were chosen arbitrarily. Lehto and Harjula [49] have noted the difficulty in choosing appropriate ratios of solution to sorbent material present for ion exchange processes. The Langmuir Vageler equation which has not been the subject of significant attention in previous literature, was shown in this publication to be a critical method for normalizing the experimental conditions employed in relation to generation of isotherm plots. The “driving force” used in the bottle-point technique needed to be at least 2 mmol Ca^{2+} ions in the initial solution relative to resin mass for a plateau in the sorption profile to be observed. Increasing the exchange “driving force” to 2.5 mmol Ca^{2+} ions per gram of resin resulted in an inflection point as calcium was loaded at an increased rate. When all three Langmuir Vageler plots were overlaid, as shown in Figure 13**Error! Reference source not found.**, it was observed that a perfect overlap of measured data was present up until a “driving force” of 1.27 mmol calcium ions per g of DOW MAC-3 resin. Consequently, for the current experimental conditions it could be concluded that the “driving force” was a key experimental parameter.

6. Conclusions

This study has demonstrated that even well-known and long established ion exchange processes such as water softening can exhibit relatively complex behaviour. We have shown that an arbitrary choice of experimental parameters for isotherm generation, which is inherent to a substantial quantity of published literature, could be potentially responsible for incomplete data sets and a source of misinterpretation of the true situation. In this respect, the “driving force” employed in the exchange process was demonstrated to be a key factor and that application of the Langmuir Vageler expression was useful in analysing the impact of varying the ratio of calcium ions in the initial solution to the resin mass, to the final equilibrium loading of calcium ions on the resin. The Langmuir Vageler equation although known for the past 80 years has been relatively ignored until now. Nevertheless, its employment to interpret equilibrium data in conjunction with traditional isotherm models such as Langmuir and Freundlich appears justified, even essential. Evidence was obtained which suggested that in addition to ion exchange between calcium ions in solution and sodium ions on resin sites, at high driving force conditions calcium ions could also enter the resin beads and exchange with sodium ions present due to inclusion of sodium hydroxide. The isotherm profiles obtained in this paper highlighted the impact of

experimental parameter choice and the benefit of measuring all ions in solution, including the anionic species in this case, in order to gain a comprehensive process understanding. Assumptions that a simple ion exchange process is occurring should not automatically be assumed, as we have shown both structural and non-structural ion exchange processes can occur. Correspondingly, the history of the resin used for testing purposes should be evaluated as it is likely that salts are present within the pore structure of the resin beads. The need to consider hydrolysis effects was also found to be of significance when studying weak acid cation resins, and incorporation of this latter process allowed more accurate determination of ion exchange stoichiometry conditions.

7. Acknowledgements

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Figures

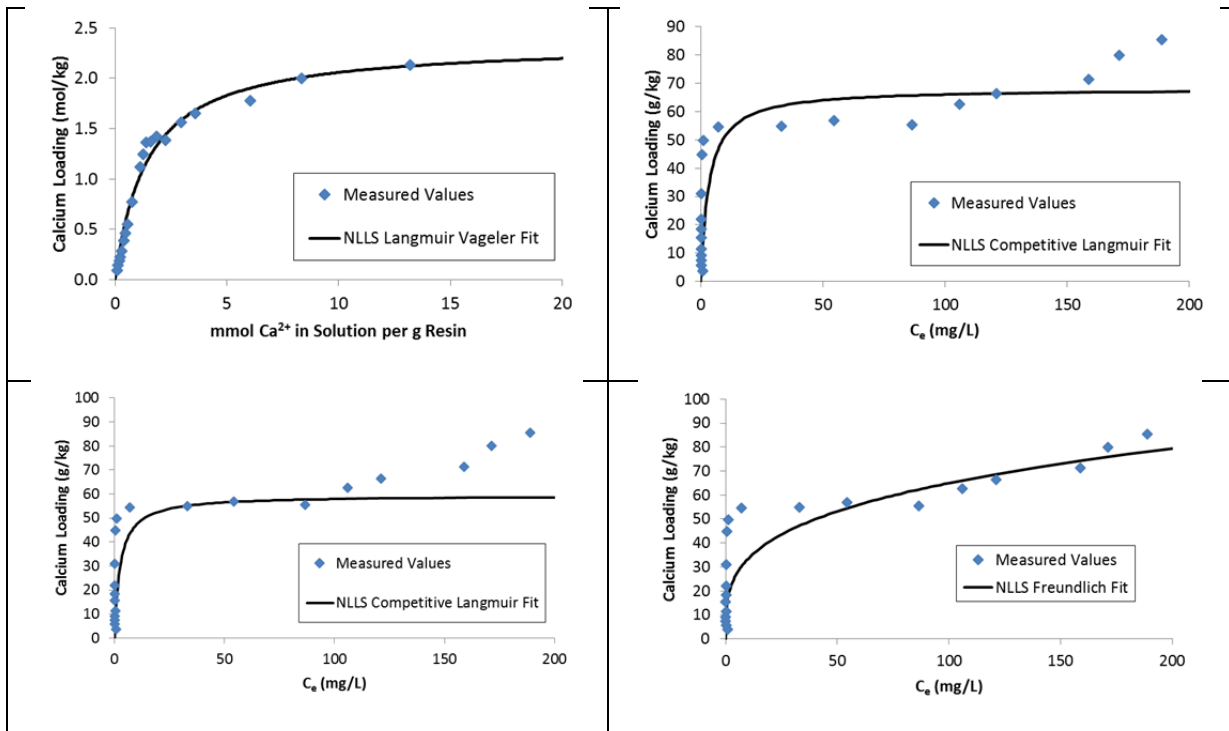


Figure 1: Model fits for exchange of calcium ions from a 0.01 N calcium chloride solution with DOW MAC-3 weak acid cation resin

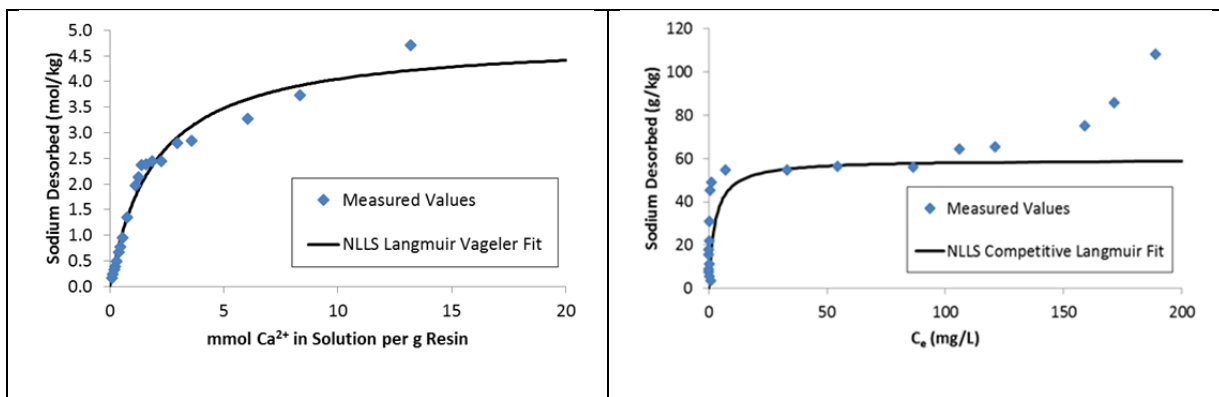


Figure 2: Model fits for desorption of sodium ions during exchange of calcium ions from a 0.01 N calcium chloride solution with sodium loaded DOW MAC-3 weak acid cation resin

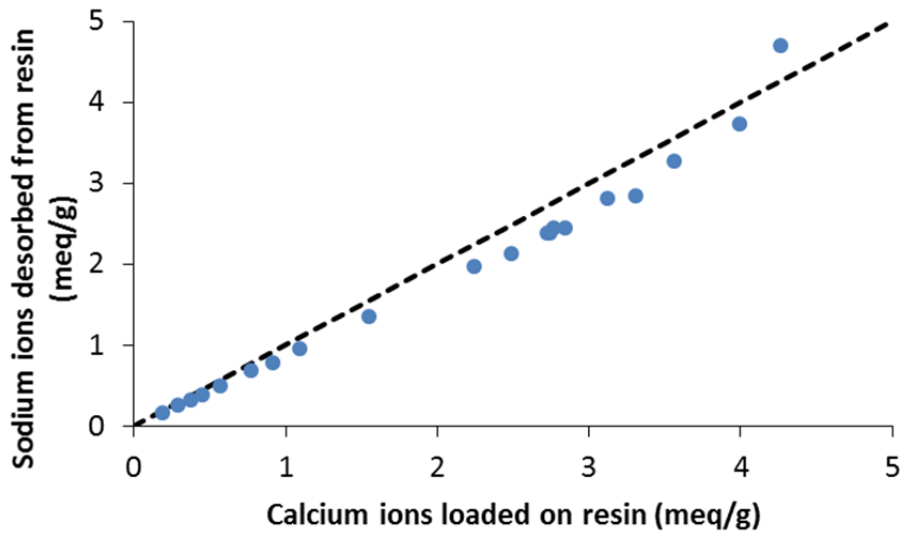


Figure 3: Stoichiometry of calcium ion exchange with sodium ions on DOW MAC-3 resin at a solution normality of 0.01N; dashed line shows ideal stoichiometric exchange

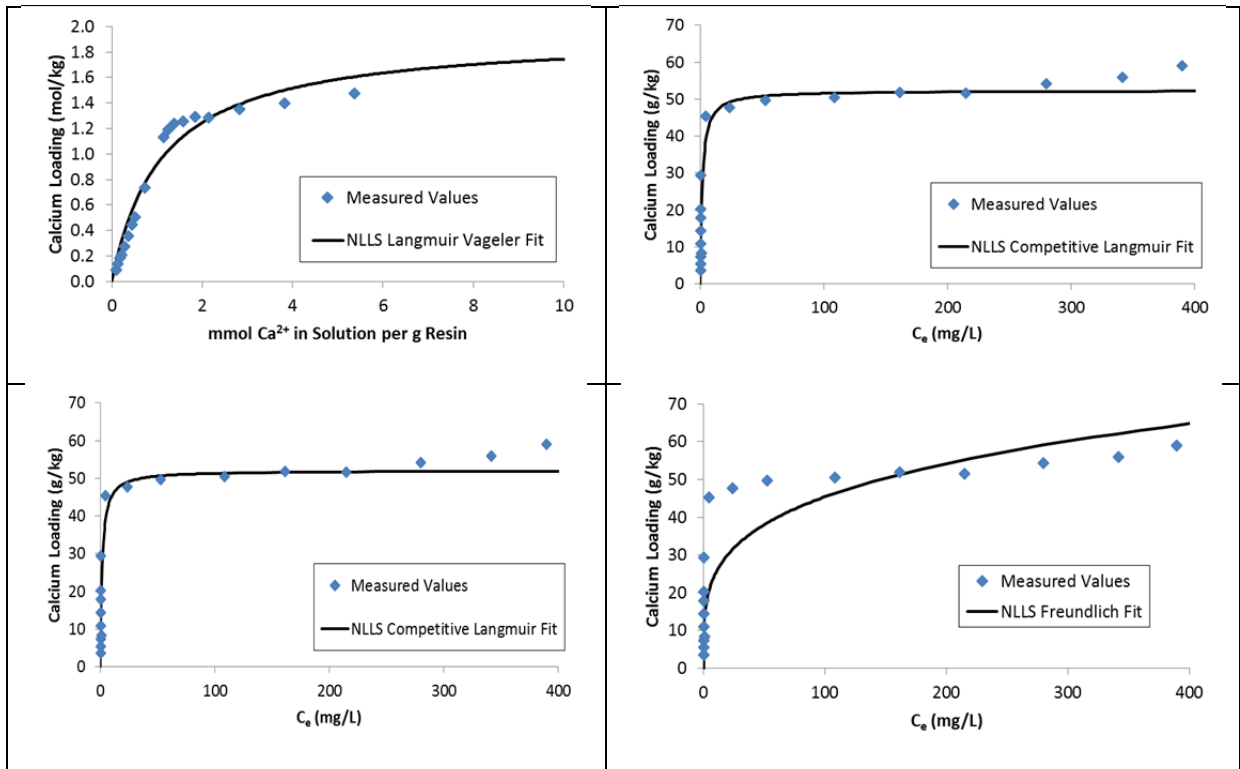


Figure 4: Model fits for exchange of calcium ions from a 0.025 N calcium chloride solution with DOW MAC-3 weak acid cation resin

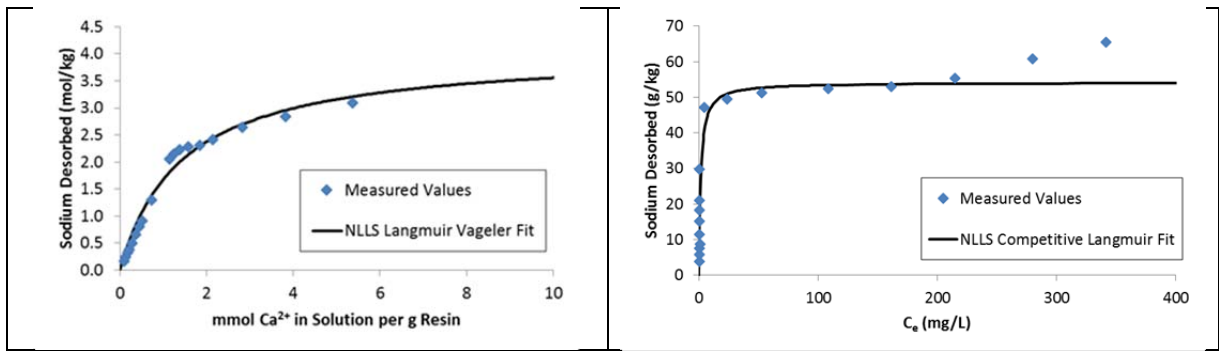


Figure 5: Model fits for desorption of sodium ions during exchange of calcium ions from a 0.025 N calcium chloride solution with sodium loaded DOW MAC-3 weak acid cation resin

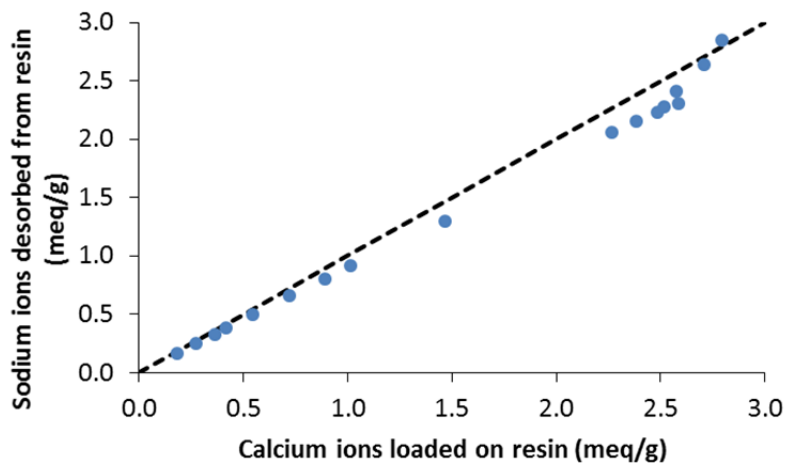


Figure 6: Stoichiometry of calcium ion exchange with sodium ions on DOW MAC-3 resin at a solution normality of 0.025 N; dashed line shows ideal stoichiometric exchange

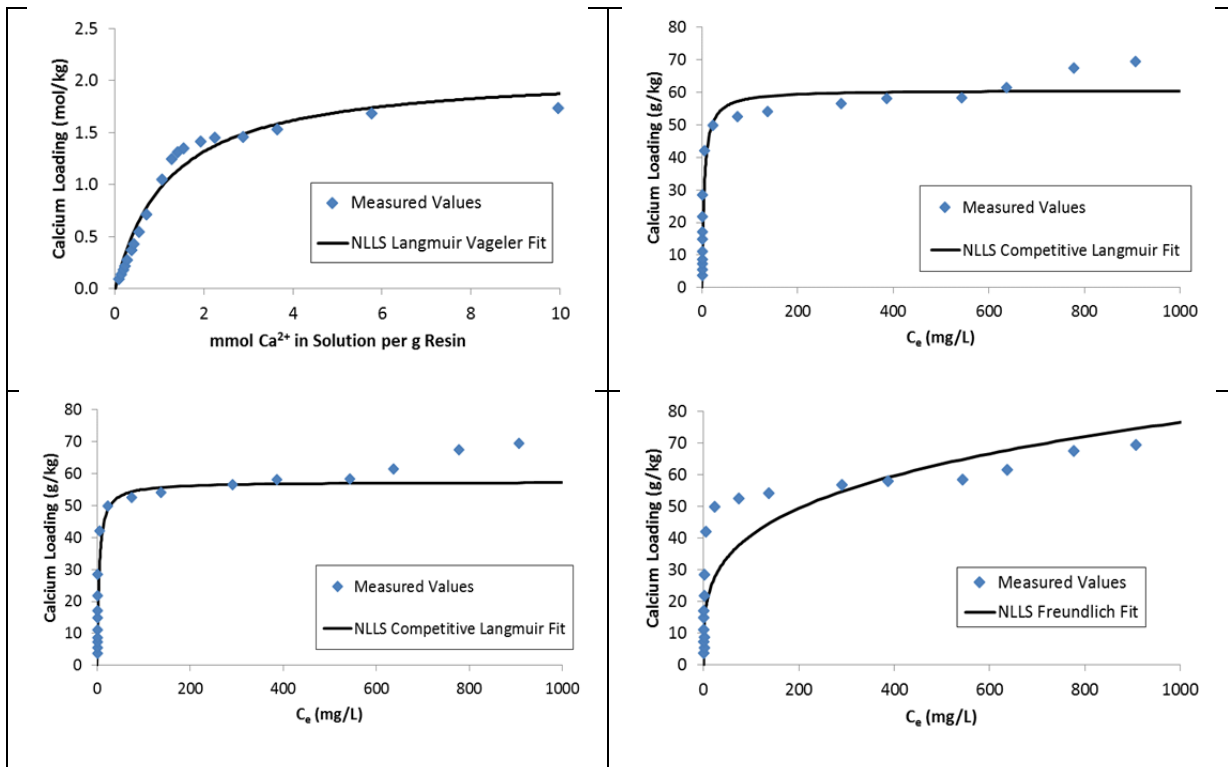


Figure 7: Model fits for exchange of calcium ions from a 0.05 N calcium chloride solution with DOW MAC-3 weak acid cation resin

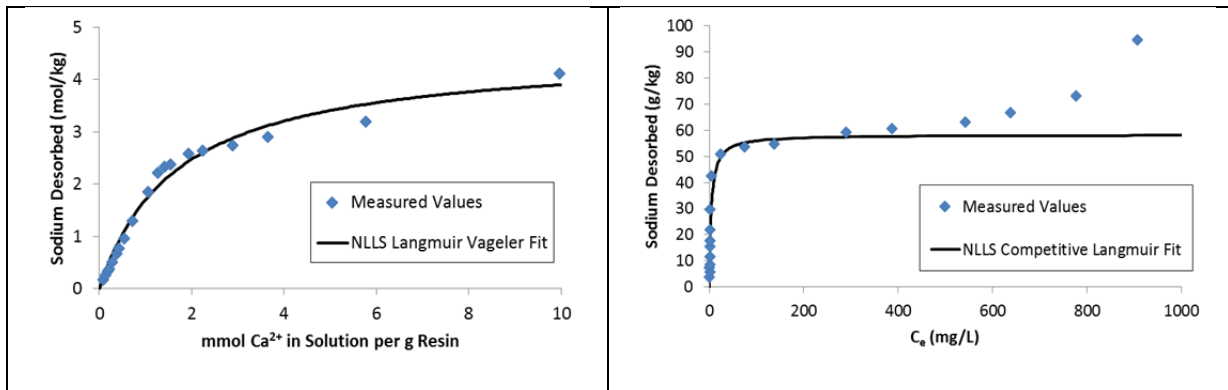


Figure 8: Model fits for desorption of sodium ions during exchange of calcium ions from a 0.05 N calcium chloride solution with sodium loaded DOW MAC-3 weak acid cation resin

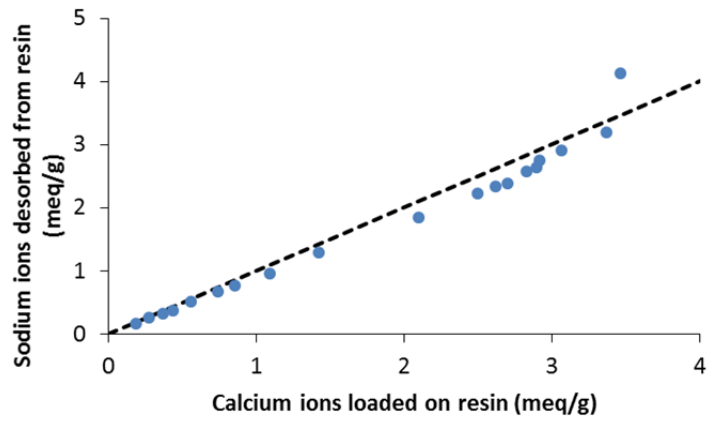


Figure 9: Stoichiometry of calcium ion exchange with sodium ions on DOW MAC-3 resin at a solution normality of 0.05 N: dashed line shows ideal stoichiometric exchange

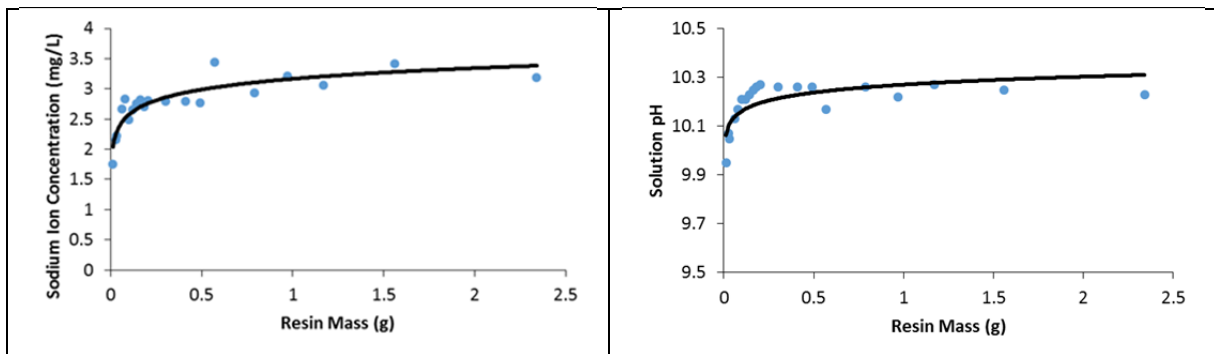


Figure 10: Equilibrium data for DOW MAC-3 weak acid cation resin in pure water

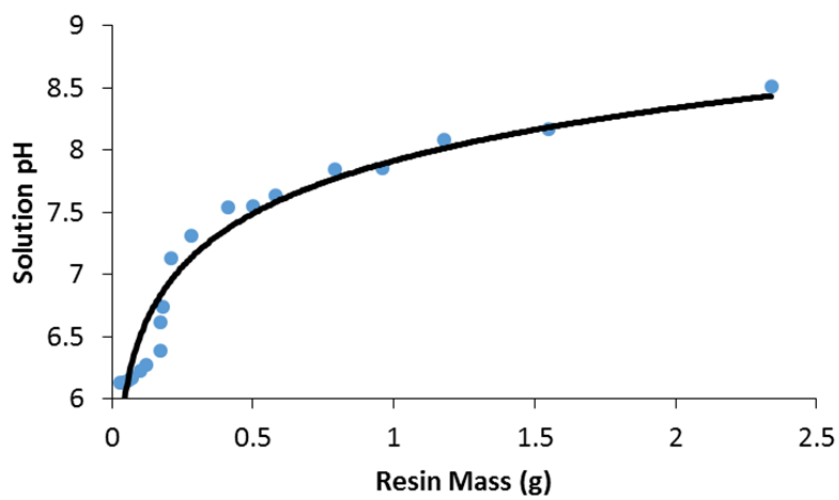


Figure 11: pH as a function of DOW MAC-3 resin mass in a 0.01 N aqueous solution of calcium chloride

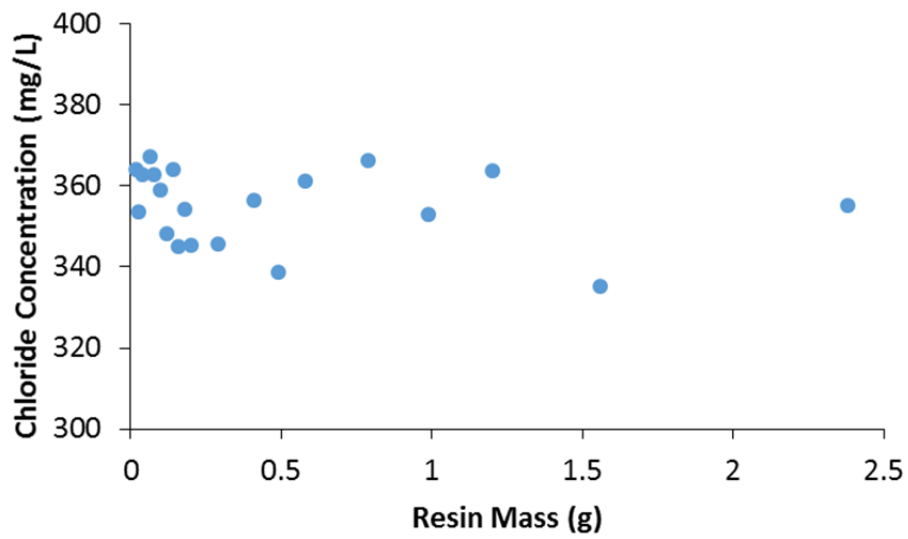


Figure 12: Solution concentration of chloride ions as a function of DOW MAC-3 resin mass in a 0.01 N aqueous solution of calcium chloride

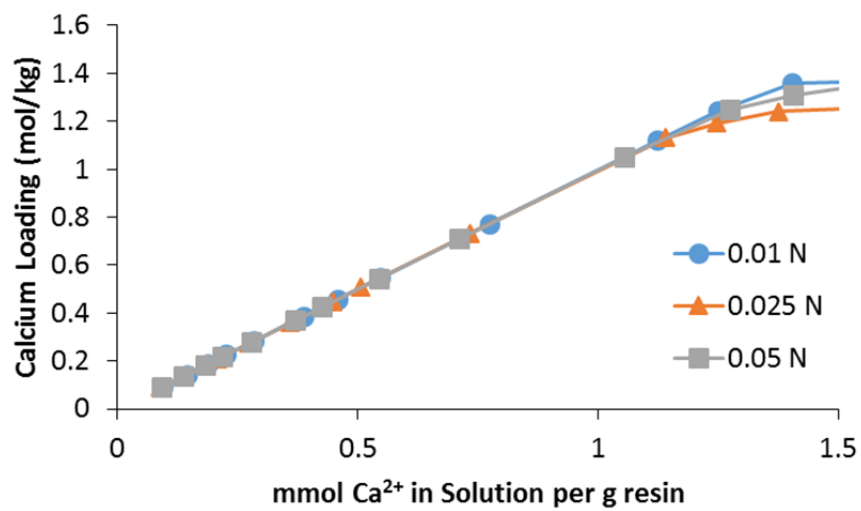


Figure 13: Comparison of Langmuir Vageler fits of equilibrium data for various solution normalities

Tables

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)	$\sum_{i=1}^p (q_{e,calc} - q_{e,meas})_i^2$
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)	$\sum_{i=1}^p q_{e,calc} - q_{e,meas}) _i$

Table 2: Non-linear least squares (NLLS) fit of Competitive Langmuir & Freundlich isotherm data for calcium exchange from a 0.01 N CaCl₂ solution with a sodium loaded DOW MAC-3 weak acid cation resin. Numbers in bold indicate minimum error values and minimum sum of normalized error values.

	SSE	HYBRID	MPSD	ARE	EABS
q _{max} (g/kg)	54.0	58.7	63.5	66.9	56.1
K _L	671.5	89.0	28.8	17.9	1063.6
SSE	2139	4330	6193	6924	2474
HYBRID	2025	929	1071	1161	2880
MPSD	221	88	71	72	265
ARE	72	54	52	51	81
EABS	127	193	230	243	105
SNE	3.25	2.74	3.11	3.30	3.79

	SSE	HYBRID	MPSD	ARE	EABS
K _F	28.2	17.2	9.0	16.5	26.0
n _F	5.2872	3.4624	2.4395	3.4432	5.0057
SSE	2438	3757	6432	3989	2531
HYBRID	1278	728	973	733	1075
MPSD	161	87	64	84	145
ARE	68	44	49	44	61
EABS	174	195	258	198	171
SNE	4.05	3.88	4.85	3.89	4.80

Table 3: Non-linear least squares (NLLS) fit of Competitive Langmuir & Freundlich isotherm data for calcium exchange from a 0.025 N CaCl₂ solution with a sodium loaded DOW MAC-3 weak acid cation resin. Numbers in bold indicate minimum error values and minimum sum of normalized error values.

	SSE	HYBRID	MPSD	ARE	EABS
q_{\max} (g/kg)	53.2	53.5	53.9	52.2	52.1
K_L	544.9	349.2	231.5	353.1	536.2
SSE	521	669	985	701	535
HYBRID	320	232	279	234	301
MPSD	75	49	42	49	71
ARE	35	28	30	28	34
EABS	75	82	96	81	74
SNE	4.3	4.2	4.8	4.2	4.8

	SSE	HYBRID	MPSD	ARE	EABS
K_F	20.64	13.99	9.80	9.76	20.33
n_F	5.48	3.91	3.10	3.23	5.60
SSE	1170	1699	2598	2619	1197
HYBRID	660	381	481	486	650
MPSD	110	59	46	46	109
ARE	56	37	34	33	55
EABS	117	133	161	153	113
SNE	4.2	4.0	4.6	4.3	4.9

Table 4: Non-linear least squares (NLLS) fit of Competitive Langmuir & Freundlich isotherm data for calcium exchange from a 0.05 N CaCl₂ solution with a sodium loaded DOW MAC-3 weak acid cation resin. Numbers in bold indicate minimum error values and minimum sum of normalized error values.

	SSE	HYBRID	MPSD	ARE	EABS
q_{max} (g/kg)	56.0	57.2	57.7	56.7	54.8
K_L	421.2	266.0	178.7	171.6	535.9
SSE	459	649	1057	1143	510
HYBRID	319	229	277	292	447
MPSD	71	48	41	41	88
ARE	33	28	27	26	37
EABS	60	76	90	91	57
SNE	3.48	3.23	3.73	3.84	4.07

	SSE	HYBRID	MPSD	ARE	EABS
K_F	18.63	11.72	7.72	7.98	18.22
n_F	5.11	3.68	2.94	3.11	5.09
SSE	1348	2020	3167	3133	1358
HYBRID	712	403	512	510	679
MPSD	112	58	45	45	109
ARE	56	38	35	34	54
EABS	126	151	187	172	122
SNE	4.1	4.0	4.6	4.2	4.8