Study of a New Process for the Efficient Regeneration of Ion-exchange Resins

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Study of a New Process for the Efficient Regeneration of Ion-exchange Resins

N.P. Ganga Nilmini Chandrasekara

A thesis in fulfilment of the requirements for the degree of Doctor of Philosophy

School of Physical, Environmental and Mathematical Sciences

University of New South Wales

Canberra, ACT

Australia

August 2016
Abstract 350 words maximum

Global demand for clean water is becoming a persistent concern and this has stimulated research into efficient and effective desalination and water treatment processes. Ion-exchange (IEX) resins have been used for water purification, but are limited by the continuous depletion of the resins and the need for large volumes of acid and base solutions for their regeneration. This Thesis presents a new chemical/thermal regeneration method and the novel use of mixed-bead and mixed-bed IEX resins for future desalination purposes.

Mixed-bead resins composed of weak-acid and weak-base groups were synthesized and used for sorption studies with saline, followed by regeneration with ammonium bicarbonate (AB) and heating at 80°C. It was found that AB followed by heating provides 100% regeneration of these resins. Unfortunately, the low IEX capacities of polyampholytic resins restrict their commercial applications. However, a novel process was developed for increasing their IEX capacity by exposing Ni\(^{2+}\) and Ca\(^{2+}\) saturated resins to concentrated AB solutions, followed by heating. This was found to increase the IEX capacity by 4−5× with a corresponding increase in observable pore size and Brunauer-Emmett-Teller surface area.

Although these mixed-bead resins could be completely regenerated using AB and heating, this also causes their thermal degradation, so the exhausted resins were also regenerated using AB washing but without heating. This was highly effective and showed an increased IEX capacity when in AB form, with higher selectivity for Na\(^+\) and HCO\(_3\)\(^-\) ions. It was also discovered that mixed-bed resin systems of strong-acid and strong-base resins, can be used to desalt 0.1M NaCl solution, producing about 6× the resin mass of drinking quality water, and this system can also be regenerated using concentrated AB \textit{in situ}. In general, regeneration processes using AB could be applied for mixed-bead and mixed-bed systems in a continuous process, minimizing chemical waste, environmental impact, and costs.

Lastly, a polystyrene based zwitterionic latex was synthesized with a particle size of about 110 nm to study the IEX behaviour of the polyampholytic resins. It was found that Na\(^+\), NH\(_4\)\(^+\), Cl\(^-\) and HCO\(_3\)\(^-\) ions readily exchanged with the surface groups following the Law of Mass Action.

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Publications Arising from this Work


Conference Presentation

Oral presentation: *Polyampholytic resins: advances in ion-exchange properties*, in 2nd EuCheMS congress on Green and Sustainable Chemistry, on 4-7 October 2015 in Lisbon, Portugal.
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UNSW Australia

29th August 2016
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List of Abbreviations and Symbols

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<td>AA</td>
<td>Acrylic acid</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
</tr>
<tr>
<td>AB</td>
<td>Ammonium bicarbonate</td>
</tr>
<tr>
<td>ABCN</td>
<td>1,1’-azobis(cyclohexanecarbonitrile)</td>
</tr>
<tr>
<td>BCE</td>
<td>Bubble column evaporator</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BWRO</td>
<td>Brackish water Reverse Osmosis</td>
</tr>
<tr>
<td>cps</td>
<td>Counts per second</td>
</tr>
<tr>
<td>CSIRO</td>
<td>Commonwealth Scientific and Industrial Research Organization</td>
</tr>
<tr>
<td>Cum.</td>
<td>Cumulative</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>ED</td>
<td>Electrodialysis</td>
</tr>
<tr>
<td>EGDMA</td>
<td>Ethylene glycol dimethacrylate</td>
</tr>
<tr>
<td>EPEI</td>
<td>Ethoxylated polyethyleneimine</td>
</tr>
<tr>
<td>eq</td>
<td>Equivalents</td>
</tr>
<tr>
<td>FO</td>
<td>Forward Osmosis</td>
</tr>
<tr>
<td>HDH</td>
<td>Humidification-dehumidification</td>
</tr>
<tr>
<td>ICI</td>
<td>Imperial Chemical Industries</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>IEX</td>
<td>Ion-exchange</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-red</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>ISE</td>
<td>Ion-selective electrodes</td>
</tr>
<tr>
<td>LTTD</td>
<td>Low-temperature thermal desalination</td>
</tr>
<tr>
<td>LTV</td>
<td>Tube vertical distillation</td>
</tr>
<tr>
<td>MC</td>
<td>Moisture content</td>
</tr>
<tr>
<td>MD</td>
<td>Membrane distillation</td>
</tr>
<tr>
<td>MDC</td>
<td>Multiple distillation columns</td>
</tr>
<tr>
<td>MED</td>
<td>Multi-effect evaporation/distillation</td>
</tr>
<tr>
<td>meq</td>
<td>Milliequivalents</td>
</tr>
<tr>
<td>MSF</td>
<td>Multi-stage flash evaporation/distillation</td>
</tr>
<tr>
<td>NF</td>
<td>Nano-filtration</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>pzc</td>
<td>Net zero charge</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SA</td>
<td>Strong acid</td>
</tr>
<tr>
<td>SB</td>
<td>Strong base</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SWRO</td>
<td>Seawater Reverse Osmosis</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>UPC</td>
<td>Unit product cost</td>
</tr>
<tr>
<td>UPE</td>
<td>Unit product energy</td>
</tr>
<tr>
<td>VC</td>
<td>Vapour-compression distillation</td>
</tr>
<tr>
<td>WA</td>
<td>Weak acid</td>
</tr>
<tr>
<td>WB</td>
<td>Weak base</td>
</tr>
</tbody>
</table>
WHO  World Health Organisations
wt    Weight
wt.%  Mass percentage
XPAA  Crosslinked polyacrylic acid
XPAA-EPEI-XG  Composite resin/sorbent
XRF   X-ray fluorescence spectroscopy
rcf   Relative centrifuge force

**Symbols**

\( a_{H^+} \)  Hydrogen ion activity
\( c_i(x) \)  Ion concentration at distance \( x \) from the charge surface
\( \mu^0 \)  Standard chemical potential
\( ^\circ C \)  Degree Celsius
\( C_{(B)} \)  Bulk ion concentrations
\( C^* \)  Equilibrium sorbate concentration
\( C_0 \)  Final (equilibrium) concentration
\( C_i \)  Initial concentration
\( c_B^{H^+} \) or \([H_B^+]\)  Concentration of hydrogen ions in the bulk solution
\( D \)  Diffusion coefficient
\( dC/dx \)  Ion concentration gradient
\( J \)  Ion flow/flux
\( K \)  Equilibrium constants
\( k \)  Mass-transfer coefficient
\( K \)  Sorption binding constant
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_a$</td>
<td>Ionization constant</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>$p$ and $n$</td>
<td>Freundlich parameters</td>
</tr>
<tr>
<td>$pK_a$</td>
<td>Negative logarithm of the ionization constant</td>
</tr>
<tr>
<td>q</td>
<td>Equilibrium adsorption</td>
</tr>
<tr>
<td>$q_{\text{max}}$</td>
<td>Maximum adsorption capacity</td>
</tr>
<tr>
<td>q</td>
<td>Electric charge of the electron</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperatures</td>
</tr>
<tr>
<td>z</td>
<td>Valency of the ion</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Degrees of ionization of acid group</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Degrees of ionization of base group</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Solution dielectric constant</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Vacuum permittivity</td>
</tr>
<tr>
<td>$\Delta H^0$</td>
<td>Standard enthalpy change</td>
</tr>
<tr>
<td>$\Psi_0$</td>
<td>Surface potential</td>
</tr>
<tr>
<td>$\kappa^{-1}$</td>
<td>Debye length</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>Surface charge density</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Zeta potential</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Fraction of ionized carboxyl groups</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Chemical potential</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

Safe and clean drinking water is vital for life in terms of healthiness, and also for enabling the functions of society. A growing global population, rapid urbanization, demand for higher living standards, emptying of aquifers at faster rates than they are refilled, industrial and farm use of water, and global climate change have all caused increasing water scarcity around the world [1-6]. Therefore, it is currently a challenge to provide safe drinking water for the world’s population.

The Earth’s surface is about 71% water, but oceans (which provide a home for a wide range of plant and animal life) actually hold about 97% of all Earth’s water, with approximately 2% as glaciers or polar ice. Consequently, less than 1% of all the water on Earth is fresh water, required for terrestrial plant, animal and human life. The limits of this water supply are expected to be reached by 2025.

Countries which use water resources for extensive agriculture, such as Greece, and Spain in southern Europe, Israel and Palestine in the Middle East, and Australia, are already suffering from increasing water shortages. Water for agricultural purposes is around 70% of all water use, and for some countries, such as India, it is over 90% [7]. A number of countries around the world are already facing water shortages because of drought, such as Australia, China, Sri Lanka, Syria, Iraq, the United States and even the United Kingdom [7-9]. According to estimates, two-thirds of the world’s population could be living under water stress by 2025[10]. Thirty-three countries will face extreme water stress by 2040, with Bahrain, Kuwait, Palestine, Qatar, the United Arab Emirates, Israel, Saudi Arabia, Oman and Lebanon the most vulnerable countries [11]. Therefore, there is a clear need to develop good practices and find alternative sources of safe drinking water to address the water crisis growing around the world.
There are many methods which could help to address this issue. One approach is protecting existing sources through proper management, and creating permanent measures to stabilize water distribution and access. Other approaches are to create community-based decentralized rainwater collection and distribution systems and to reduce CO₂ emissions to stabilize global precipitation. The establishment of desalination and water-treatment plants [12, 13], and an increase in recycling of water [14] are also likely solutions in the presence of a growing population and rapid urbanization.

According to the International Desalination Association, 18,426 desalination plants were operating in June 2015, producing 86.8 million cubic meters of fresh water per day, providing water for 300 million people worldwide [12]. Water shortages have led to an increase in the use of desalinated seawater to supply drinking water in a number of states in the US [7], as well as in Australia; there are currently desalination plants in Perth, Sydney, the Gold coast, Victoria and Adelaide to ensure water security in times of drought and to supply high-quality drinking water to residents [15]. A water desalination plant [16] was installed on the Thames River at Beckton, East London in 2010, making the prospect of future water restrictions less likely. There are many other desalination plants around the world, with the largest in the United Arab Emirates, Saudi Arabia and Israel; these use a variety of desalination technologies to produce desalinated water.

1.1 Desalination

In simple terms, desalination is a process that removes minerals from saline water. The process can turn both brackish water and seawater into either drinking-quality water or water to suit other domestic purposes.
All naturally occurring water contains dissolved constituents such as sodium chloride, calcium bicarbonate, potassium chloride, magnesium sulfates and many other substances. Water without any dissolved substances tastes flat, but water with too high concentrations of dissolved substances (for example, seawater) tastes unpleasant and cannot be safely ingested. There needs to be a balance in drinking water between these two extremes. Table 1.1 below gives a classification of water sources with their concentration of total dissolved solids (TDS); less than 1,000 ppm is considered as consumable water [17].

**Table 1.1** Classification of water sources according to their concentration of total dissolved solids [18].

<table>
<thead>
<tr>
<th>Water Source</th>
<th>Total Dissolved Solids (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potable water</td>
<td>&lt; 1,000</td>
</tr>
<tr>
<td>Mildly brackish waters</td>
<td>1,000–5,000</td>
</tr>
<tr>
<td>Moderately brackish waters</td>
<td>5,000–15,000</td>
</tr>
<tr>
<td>Heavily brackish waters</td>
<td>15,000–35,000</td>
</tr>
<tr>
<td>Average sea water</td>
<td>35,000</td>
</tr>
</tbody>
</table>

### 1.1.1 Historical Background to Desalination

Desalination has been used for thousands of years, and the Greeks were the first to express philosophical ideas about the nature of water. In the fourth century BCE, the well-known philosopher and scientist Aristotle described evaporation techniques used by Greek sailors for desalinating water [19-21]. They also used sand filters and wool-wick siphons to filter the water. In the first century AD, Romans used clay filters to trap salts, while an Arab chemist in the eight century produced the first scientific paper on desalination. In the nineteenth century there was a huge demand for fresh water to
replenish the boilers of steam ships anchored in harbor, with the first land-based water distillation plant established at Aden. The first desalination patent was granted in 1869 in England. The first large still to provide water for commercial purposes was built in 1930 in Venezuela (Aruba) [19].

Today's sophisticated desalination processes still generally use the concepts and knowledge of distillation or filtration from ancient times to produce billions of litres of water throughout the world.

1.1.2 Desalination Processes

All desalination processes are based on chemical-engineering technology; typically, the feed saline water is subjected to energy applied in the form of heat, pressure or electricity. Two outlet streams are produced, desalinated water and concentrated brine, as shown in Fig.1.1.

![Figure 1.1 Schematic diagram of a typical desalination process.](image)

Most commercial desalination processes use one of two main methods: a thermal (phase-change) process or a membrane process. There are many different desalination technologies at present, with the choice of suitable technology contingent on many factors, such as the quality of the source water, the use of the final water product, the capital cost, energy costs, the required amount of water, plant size and the technical...
resources of the region [22]. All these factors have to be considered prior to establishing a desalination process to attain maximum benefits.

**Thermal Processes**

Distillation is the simplest example of a thermal desalination process; it involves heating of saline water to produce water vapour, which is then condensed to form fresh desalinated water. This water can then be used for domestic purposes (mainly drinking and cooking) and for industrial and agricultural purposes. There are many thermal desalination technologies currently available [23, 24].

- Multi-stage flash evaporation/distillation (MSF)
- Multi-effect evaporation/distillation (MED) or tube vertical distillation (LTV)
- Vapour-compression distillation (VC)
- Low-temperature thermal desalination (LTTD)
- Membrane distillation (MD)
- Humidification-dehumidification (HDH)
- Solar distillation

**Membrane Processes**

These processes use mechanical energy to transport substances between two fractions through a permeable membrane. Often, membrane separation processes do not need heating, so that energy consumption is less than conventional thermal desalination; however, many need expensive specialized membranes and high pressure pumping.
The main membrane processes currently available are [25]:

- Reverse Osmosis (RO)
- Electro dialysis (ED)
- Forward Osmosis (FO)
- Nano-filtration (NF)

*Other Processes*

There are many other desalination processes [23] available currently as below.

- Ion-exchange (IEX)
- Air dehydration
- Capacitive deionization using IEX membranes
- Solar-thermal ionic desalination (hybrid)
- Geothermal desalination
- Crystallisation (freezing and hydration)

Despite the range of desalination technologies in use for desalinating water worldwide, RO and MSF are the predominant desalination processes in use today (see Fig.1.2).

![Figure 1.2](image-url)  
*Figure 1.2 Global desalination capacity by process [26, 27].*
The choice of desalination process is site specific and the economic feasibility of the technology is always a concern. Capital investment, operating costs and product water value are considered prior to the establishment of such technologies. These costs are more significant for developing countries compared to developed countries.

### 1.1.3 Economic Practicality of Desalination Processes

Energy consumption and operating cost are the most important parameters to be considered in the design of a desalination process [13, 28-34]. Therefore, it is a vital to study economic viability; Table 1.2 shows relevant parameters obtained from different studies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>UPC  (US$/m³)</th>
<th>UPE  (kWh/m³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWRO</td>
<td>0.5–1.2</td>
<td>3–4</td>
<td>[13]</td>
</tr>
<tr>
<td>BWRO</td>
<td>0.2–0.4</td>
<td>0.5–2.5</td>
<td>[13]</td>
</tr>
<tr>
<td>MSF</td>
<td>0.8–1.5</td>
<td>10–16</td>
<td>[13]</td>
</tr>
<tr>
<td>MED</td>
<td>0.7–1.5</td>
<td>5.5–9</td>
<td>[13]</td>
</tr>
<tr>
<td>FO</td>
<td>–</td>
<td>&lt;1</td>
<td>[32]</td>
</tr>
<tr>
<td>Solar HDH</td>
<td>0.7</td>
<td>–</td>
<td>[35]</td>
</tr>
<tr>
<td>Solar dew-vaporation</td>
<td>0.3</td>
<td>–</td>
<td>[35]</td>
</tr>
<tr>
<td>VC</td>
<td>–</td>
<td>11–14.6</td>
<td>[23]</td>
</tr>
<tr>
<td>ED</td>
<td>–</td>
<td>2.6–5.5</td>
<td>[23]</td>
</tr>
</tbody>
</table>

Note: SWRO and BWRO are for Seawater Reverse Osmosis and Brackish water Reverse Osmosis, respectively.

However, the leading desalination processes mentioned here cannot be expected to dominate for long, given economic inflation and global demand [13, 30]. Therefore,
most of the technologies have aimed at reducing production costs. Implementation of novel technologies, either from integrating and advancing existing processes or from nascent and emerging technologies will inevitably make desalination less expensive. Novel technologies that show significant potential should be supported.

Possible new technologies are desalination using alternative energy sources [24, 33, 35], low-temperature thermal desalination techniques, advanced IEX resin techniques and hybrid desalination technologies. One such emerging research field is desalination using ion-exchange resins.

Ion-exchange (IEX) resins have been used widely for many years in various water-treatment-related practices, but have not been extensively studied as a desalination technique during the last few decades. This is mainly because of cost of chemical regeneration once the resin is exhausted, which ultimately determines the economic viability of the technique. However, the capital investment, labour and maintenance costs of IEX processes have always compared favourably with other existing systems, such as Reverse Osmosis (RO), membrane filtration and thermal evaporation/condensation [36-39].

1.2 Ion-exchange (IEX) Resins

IEX resins are insoluble polymers with high molecular weights containing charged groups that are able to exchange specific ions or charged groups with a surrounding solution. Generally, they are in the form of small beads [40], 0.3–1.2 mm in diameter, made up from an organic polymer substrate, and available either as a porous or gel polymer. IEX resins attract ions/charged groups by releasing other ions/charged groups; this process is called ion exchange. However, the process takes place without any
permanent change to the IEX material. There are many types of commercial IEX resins available, and they are commonly used for separation and purification purposes.

1.2.1 Historical Background of IEX Resins

The first organic ion-exchanger was discovered in 1935 by Adams and Holmes [41], from observation that crushed phonographic records showed IEX properties. The first IEX resin was synthesized by condensation of phenol or its derivatives with formaldehyde. Since then, ion-exchange technology has advanced rapidly, with developments in the science of polymerization technologies resulting in a vast range of polymeric materials that can meet the need for appropriate resins and techniques for different applications (see Table 1.3).

The original theories and applications related to ion-exchange resin are more than 100 years old, with great changes and momentous inventions since then. Table 1.3, gives a summary of the main chronological developments of resins, but there are lots of other researchers who have contributed in various ways to the development of this technology.
Table 1.3 Chronology of development of ion-exchange resins.

<table>
<thead>
<tr>
<th>Scientist</th>
<th>Year</th>
<th>Breakthrough in Field of Ion exchange</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. Griessbach and O. Samuelson</td>
<td>1939–1945</td>
<td>First industrial production of synthetic-resin-based ion-exchangers and application to chromatography</td>
<td>[44]</td>
</tr>
<tr>
<td>G.F. D’Alelio</td>
<td>1942</td>
<td>Invention of sulphonated polystyrene cation exchangers</td>
<td>[44]</td>
</tr>
<tr>
<td>G.E. Boyd, J. Schubert and A.W. Adamson</td>
<td>1942</td>
<td>Demonstration of the applicability of ion exchange for adsorption of fission products in trace amounts</td>
<td>[43, 44]</td>
</tr>
<tr>
<td>C.H. McBurney</td>
<td>1947</td>
<td>Invention of aminated polystyrene polymerization anion exchangers</td>
<td>[44]</td>
</tr>
<tr>
<td>A. Skogseid</td>
<td>1948</td>
<td>Preparation of potassium-specific polystyrene cation-exchanger chelating resin</td>
<td>[44]</td>
</tr>
<tr>
<td>J.A. Marinsky, L.E. Glendenin, and C.D. Coryell</td>
<td>1947</td>
<td>Discovery of promethium, an element found in nature, is attributed to ion exchange</td>
<td>[44]</td>
</tr>
<tr>
<td>M. A. Peterson and H. A. Sober</td>
<td>1956</td>
<td>Development of cellulose ion exchangers</td>
<td>[44]</td>
</tr>
<tr>
<td>Scientist</td>
<td>Year</td>
<td>Breakthrough in Field of Ion exchange</td>
<td>Reference</td>
</tr>
<tr>
<td>-----------</td>
<td>------</td>
<td>---------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>H. Corte, A. Meyer, R. Kunin, E. Matzner and N. Bostnick</td>
<td>1957</td>
<td>Invention of macroporous ion-exchange resins</td>
<td>[44]</td>
</tr>
<tr>
<td>M.J. Hach, J.A. Dillon and H.B. Smith</td>
<td>1957</td>
<td>Introduction of snake-cage resins and ion-retardation process</td>
<td>[45]</td>
</tr>
<tr>
<td>F. Helfferich</td>
<td>1959</td>
<td>New theoretical treatment of ion exchange</td>
<td>[44, 46]</td>
</tr>
<tr>
<td>T.R.E. Kressmann and J.R. Millar</td>
<td>1960</td>
<td>Invention and development of isoporous ion-exchange resins</td>
<td>[44]</td>
</tr>
<tr>
<td>I.R. Higgins</td>
<td>1961</td>
<td>Development of continuous ion-exchange processes</td>
<td>[47]</td>
</tr>
</tbody>
</table>
1.2.2 Types of IEX Resins

Ion-exchange resins can be primarily classified as cation exchangers, anion exchangers or amphoteric exchangers [40, 55, 56]. Cationic IEX resins contain positively charged mobile ions, while anionic IEX resins have negatively charged mobile ions and amphoteric resins have both positively and negatively charged mobile ions. These mobile ions actively participate during the exchange process. These resins are mostly produced from the same basic group of organic polymer matrices, such as cross-linked polystyrene, divinylbenzene, polyacrylic acid and methacrylic acid (Fig. 1.3).

![Cross-linked polystyrene](image)

![Cross-linked polymethaerylate](image)

**Figure 1.3** Basic polymer matrices used for synthesizing resin.

The ionizable/functional groups attached to the hydrocarbon network define the chemical behaviour of the resin, broadly classified as below.
**Strong-acid Cation Resins**

These resins are so named because the chemical behaviour of the resin is similar to that of a strong acid (SA). The resin is highly ionized in both forms of the sulfonate groups, acid (R-SO$_3$H) and salt (R-SO$_3$Na), during the exchange process.

\[
\text{(R-SO}_3\text{H}^+) + \text{NaCl} \rightarrow \text{(R-SO}_3\text{Na}^+) + \text{HCl} \quad (1.1)
\]

The H$^+$ and Na$^+$ forms of the resin are highly dissociative and readily available for exchange over the entire pH range. Further, the SA resin capacity is independent of solution pH [57]. The resins can be used either in hydrogen ion (H$^+$) or sodium ion (Na$^+$) forms depending on the intended application, and after exhaustion, they can be restored to their original active forms by regenerating with a strong acid or sodium chloride solution.

**Strong-base Anion Resins**

Strong-base (SB) resins have highly ionized groups which can also be used over the entire pH range. Mostly, these resins are a quaternary amine product, and are used in the hydroxide (OH$^-$) form for desalination purposes.

\[
\text{RCH}_2\text{N(CH}_3\text{)}_3\text{OH}^- + \text{NaCl} \rightarrow \text{RCH}_2\text{N(CH}_3\text{)}_3\text{Cl}^- + \text{NaOH} \quad (1.2)
\]

When the resin is exhausted, it can be regenerated with concentrated sodium hydroxide (NaOH) to convert it into its OH$^-$ form.

**Weak-acid Cation Resins**

In a weak-acid (WA) resin, carboxylic acid (COOH) usually acts as the ionizable group; WA resins behave similarly to weak organic acids, which are weakly dissociated.

\[
\text{RCOO}^+\text{H}^+ + \text{NaCl} \rightarrow \text{RCOO}^-\text{Na}^+ + \text{HCl} \quad (1.3)
\]
The pH of the solution strongly influences the degree of dissociation of a WA resin, which also determines resin capacity. A typical WA resin has a limited resin capacity at pH values lower than 6.0. These resins show higher affinity for hydrogen ions over SA resins as well as have lower ion-exchange capacities, thus they can be regenerated with lower acid volumes than required for SA resins.

**Weak-base Anion Resins**

These resins are mainly derived from either primary (R-NH$_2$) or secondary (R-NHR$_1$) amine functional groups. Weak-base (WB) resins are like WA resins in that the degree of ionization is strongly influenced by pH; they exhibit minimal IEX capacity at pH values above 7.0.

\[
\text{RNH}_2 + \text{HCl} \rightarrow \text{RNH}_3\text{Cl}
\]  

(1.4)

The depleted WB resins can be regenerated easily using sodium hydroxide, ammonia or sodium carbonate to neutralize the acid absorbed into the resin.

**Amphoteric Resins**

These resins are also known as ampholytic resins. They have both acid and base functionalities and are able to exchange both cations and anions simultaneously. Polyampholytic resins can be formed with SA, SB, WA and WB groups, depending on the requirement [58, 59]. The IEX capacity of such resins depends on the ionizable sites in the resins and is pH dependent. They can exist in cationic, anionic, uncharged and zwitterionic forms. Ampholytic resins cannot be completely regenerated using acid or base; alternative methods are required for their regeneration, as mentioned in Section 1.3.
1.2.3 Applications of IEX Resins

Resins have many uses industrially as well as in research. They are used in water treatment, in the sugar, food, chemical, mining and pharmaceutical industries, and as a catalyst for many reactions. However, these resins have been used more for water purification than for any other purpose.

IEX is a potent technology which produces water of an extremely good quality by softening and demineralizing the water. It has been proven as the best technology for removing most of the trace levels of contaminants when producing ultra-pure water. It can also be used, with suitable improvements, to desalinate seawater [60, 61]. Therefore, it is important to understand the characteristics of IEX resins and the technology required to use them.

1.2.4 Physical and Chemical Properties of IEX Resins

Conventional IEX resins contain a cross-linked polymer matrix with uniformly distributed ion-active sites. These resins are generally either spheres or granules, with the size and consistency set to meet the need of an individual application. The porosity and particle size are controlled by controlling the polymerization conditions during the free-radical polymerization used in the synthesis of resins. IEX resins typically have a density of 1,100–1,400 kg/m$^3$ [40].

The IEX capacity of a resin can be defined in various ways. Usually, it is either the total capacity, which is the total number of sites available for exchange or the operating capacity, which is the number of sites actively participating in the exchange process. Total capacity is expressed as a molar equivalence per unit of dry weight, wet weight or wet volume. Units are equivalents per gram (eq/g) or equivalents per litre (eq/l) of resin. The IEX capacity does not take valence into account; as a result, the unit
“mole” should be avoided (1 eq = 1 mole/valence). The operating capacity of a resin differs from the total capacity due to numerous factors such as the composition of the solution treated, the level of regeneration, the flow rates through the column, working temperatures and the particle-size distribution of the resin.

Swelling of IEX resins primarily occurs due to the hydration of the fixed ionic groups in the polymer network. Conversion to ionic forms with different degrees of hydration also changes the resin volume. For example, hydration of polyvalent ions is lower than monovalent ions.

Ion exchange is a reversible process, and the selectivity of ions towards IEX groups varies with the ionic size and charge of the ion interacting with the IEX groups. Generally the selectivity/affinity is greater for larger ions with higher valencies. Resin selectivity coefficients have been determined for a range of ionic species, relative to the selectivity value 1.00 assigned to H⁺ and OH⁻. For dilute solutions, the order of affinity for some common cation and anion IEXs is given below [40, 44, 62].

**Strong-acid Cation Exchangers:**
Li⁺ < H⁺ < Na⁺ < NH₄⁺ < K⁺ < Rb⁺ < Cs⁺ < Mn²⁺ < Mg²⁺ < Fe²⁺ < Zn²⁺ < Co³⁺ < Cu²⁺ < Cd²⁺ < Ni²⁺ < Cu⁺ < Ca²⁺ < Sr²⁺ < Hg²⁺ < Pb²⁺ < Ag⁺ < Ba²⁺ < Al³⁺ < Fe³⁺

**Weak-acid Cation Exchangers:**
Na⁺ < Mg²⁺ < Ca²⁺ < Ni²⁺ < Co³⁺ < Cu²⁺ < H⁺

**Strong-base Anions Exchangers:**
OH⁻ < F⁻ < IO₃⁻ < HCO₃⁻ < Cl⁻ < Br⁻ < NO₃⁻ < HSO₄⁻ < I⁻ < PO₄³⁻ < CrO₄²⁻ < SO₄²⁻

**Weak-base Anions Exchangers:**
Cl⁻ < MoO₄²⁻ < PO₄³⁻ < AsO₄³⁻ < CrO₄²⁻ < SO₄²⁻ < OH⁻
The degree of cross-linking in a resin depends on the total amount of monomer prior to polymerization. With increased cross-linking, harder, less-elastic resins are produced. Less cross-linking facilitates a higher permeability to ions, higher levels of contained moisture, increased resin capacity on a dry weight basis and higher rates of equilibration. Less cross-linking also reduces physical stability of the resin and its selectivity for various ions but its ability to accommodate larger ions is increased.

1.2.5 IEX Equilibrium and Kinetics

The IEX process can be carried out by either batch or column methods (see Chapter 2 and 4). When the IEX reaches equilibrium, there is no net change in the equilibrated and absorbed ion concentrations in the system. Usually this means that the exchange process has reached maximum absorptivity. However, equilibrium conditions are different for different ions.

There are two types of diffusion that need to be considered during the IEX equilibrium. The first is film diffusion, in which the ions move from the surrounding solution to the surface of the IEX resin. The second is internal diffusion, which involves diffusion of ions from the surface to the interior of the IEX particle (Fig. 1.4).

![Diffusion of ions in the solution into the resin.](image)

**Figure 1.4** Diffusion of ions in the solution into the resin.
Film diffusion is rate controlling at low concentrations and internal diffusion is rate controlling at higher concentrations [46]. In addition, the IEX equilibrium also depends on the IEX particle size, and uniform size particles show greater kinetic performance compared to polydispersed resin beads.

The static layer of solution around the resin bead is known as the Nernst film; high flow rates decreases the thickness of this film. The mass-transfer flux of a given ion through the film during the IEX process is given by Fick’s Law [40, 46, 63]:

$$ J = -D \frac{dC}{dx} $$

(1.5)

where J is the ion flow/flux in mol/s.cm², $dC/dx$ is the ion concentration gradient in mol/cm⁴ and D is the diffusion coefficient in cm²/s.

When D is constant, the concentration gradient becomes linear, and the equation can be re-written as:

$$ J = k(C_I - C_0) $$

(1.6)

where k is the mass-transfer coefficient (cm/s), and $C_I$ and $C_0$ are initial and final (equilibrium) concentrations of the specific ion solution in mol/cm³.

Measurements of the mass-transfer coefficients help us to understand the behaviour of a resin, as well as its ability to operate under different temperatures, concentrations and flow rates. Both the Langmuir and Freundlich equations can be used to explain the adsorption behaviour of IEX resins. The isotherms derived from these equations have been used as a benchmark when explaining IEX properties in many research studies [52-54, 64, 65] (See Chapter 2 for further details).
In the column method, ions that are not absorbed by the resin but instead percolate through the column are known as ion leakage. This can be measured as a function of the flow rate of the feed solution and the volume of resin used. However, once the ion leakage is present in the resin bed, it is no longer useful for the process, as most of the resin is saturated with ions and will need regeneration.

1.3 Regeneration Methods for IEX Resins

IEX resins have been used and regenerated by various methods for decades, with acid or base regeneration the most common method. However, the need for large volumes of acid and base solutions for the regeneration process, the cost of chemicals and the resulting acid/base waste has led to the development of new methods of regeneration of IEX resins by other means. The use of electrical energy (electrodialysis), mechanical energy (piezodialysis) and heat energy (the Sirotherm process) have all been studied [66-72]. However, electrodialysis and piezodialysis also use large amounts of energy in their operation, which is expensive, as well as requiring sophisticated cell designs and extensive operational skills.

1.3.1 The Sirotherm Process

The Sirotherm process is an ion-exchange technique for resin beads depleted by salt ions, with a regenerating step for removal of adsorbed ions from the resin using thermal energy, permitting its re-use. During this process, adsorbed salt ions in the resin are exchanged at low temperature with either hydrogen ions or hydroxyl ions in the water, transforming the resin to a usable state (Fig.1.5).
Figure 1.5 Schematic representation of the Sirotherm process in a WA cation IEX resin.

This process to desalinate water was jointly developed in 1972 by the Commonwealth Scientific and Industrial Research Organization (CSIRO) and Imperial Chemical Industries (ICI) Australia, and subsequently used in several desalination plants around the country [73-75].

The process first used a mixture of WA and WB mixed-bed resins, and later resins composed of both WA and WB groups as mixed beads (polyampholytic resins). This process has been used with many different types of mixed-bead resins over the last 40 years [67, 76-79], for example “snake-cage” [45], “plum-pudding” [68, 76] and “composite” resins.

Sirotherm resins are composed of WA and WB groups; thus, during the exchange process, a proportion of Na\(^+\) and Cl\(^-\) ions remain in the solution due to the hydrolysis of the weak-resin salts. Therefore, high-purity deionized water cannot be produced using these resins; they are suitable only for partial removal of salts from solutions with typical salinities in the range of 2000–3000 mg/l [53]. The method discussed in Shimizu’s work on desalination of aqueous solutions employed WA and WB IEX resins, in which the WB groups were converted to a carbonate form, followed by thermal regeneration. This process is also generally effective at sodium chloride
concentrations below 3000 mg/l [80]. The Sirotherm method has been comprehensively investigated to establish an efficient process of desalination.

1.3.2 Further Advances in Sirotherm Resins

The ion-adsorption equilibrium conditions in WA and WB mixed-bed resins vary greatly with temperature, pH and the ionic strength of the solution in equilibrium with the resins [81, 82]. The capacity of such resins to remove salts also depends on the polymeric structure of the resins, the acidity and basicity of functional groups, the ratio of acid to basic groups and the resin affinities for counter ions [64, 66, 80-83]. Titration data have been reported over a temperature range of 20–80°C for carboxylic acid resins and weakly basic amine resins [81]. These studies showed that, when the temperature is raised in a mixed-bed system in equilibrium with a salt solution, there is a noticeable transfer of protons from the base groups to the acid groups in the resin as shown by the titration curves of the resins [82]. That is, when amine resins are heated, they become weaker bases; hence the amine resins have a plateau in the titration curves which moves to lower pH values with increasing temperature. Titration curves of carboxylic acid resins also showed reduced effect with increasing temperature.

The composite resin beads produced combining both the acidic and basic groups in the polymer matrix have a slightly greater adsorption capacity compared to other typical mixed-bed systems [84], but this capacity is lower than for chemically regenerated strong-acid/strong-base resin systems. Another study on chemical/thermal regeneration of IEX resins comprising both weakly acidic and weakly basic groups in the resin matrix found that conversion of weakly basic IEX functional groups to the carbonate form made the resin more likely to maintain a higher desalination capacity [80].
Recent studies [53, 54] on thermally regenerable composite (Sirotherm-type) resins showed that a WA/WB mixed bead resin had a substantially reduced ion-adsorption capacity at higher temperatures. Heating from 30°C to 80°C reduced the capacity by a factor of 8 [53]. Moreover, the presence of a WB group in the mixed-bed resin is known to enhance the ion adsorption properties of the mixed-bed resin [64]. According to Weiss et.al [66], tertiary amines have a higher capacity for salt sorption than primary and secondary amines in conjunction with carboxylic acid groups. The reason for this effect is that the carboxylic acid and tertiary amines have a higher degree of overlapping of their pH titration curves compared to primary and secondary amines. Numerous studies have been carried out on the empirical determination of resin pair behaviour under different temperatures, pH and ionic strengths [66, 81-83]. The prediction of titration-curve behaviour is also useful for resin synthesis design. Experimental studies have been carried out to validate the behaviour of ion-exchange pairs [81].

Ethoxylated polyethyleneimine (EPEI), shown in Fig. 1.6, is considered a good source of tertiary amine groups, as it consists of larger numbers of amine groups than polyethylene amine. Studies on this have been carried out by Chanda et.al [52, 85].

\[
\begin{align*}
&\text{HOCH}_2\text{CH}_2\text{N}^\text{H} \quad \text{HOCH}_2\text{CH}_2\text{N}^\text{H} \\
&\text{R} \\
&\text{HOCH}_2\text{CH}_2\text{N}^\text{H} \quad \text{HOCH}_2\text{CH}_2\text{N}^\text{H} \\
&\text{CH}_2\text{OH} \\
&\text{R=H or continuation of polymer chain}
\end{align*}
\]

**Figure 1.6** Representative formula for ethoxylated polyethyleneimine.
Weiss et al. [83] showed that variation in acid strength can be achieved by varying the cross linkage in the resin. The use of methacrylic acid, acrylic acid or their copolymers during the synthesis of carboxylic acid resins results in enhanced adsorption of counter-cations during the exchange process.

Bolto and Jackson [67] indicated that resin bead sizes in the range 0.3–1.2 mm are ideal for thermally regenerable IEX resins composed of acidic and basic groups together in the porous particles. Further, they showed that the presence of both acid and base groups in the same particle caused ions to be absorbed more rapidly due to the close proximity of the groups. This shortens the diffusion path for the transfer of protons [86]. The “plum pudding” resin structure, which is prepared by embedding microparticles of polyamines and microparticles of polyacids in a water and salt permeable matrix, has been discussed by Bolto et al. [68]. They also described the disadvantage of the presence of a high proportion of inert polymeric matrix material, which tends to limit the thermally regenerable capacity of a particular resin. Therefore, it can be stated that the diffusion of ions through the matrix is the rate-determining step during the IEX process. Here, the matrix behaves as the main diffusion barrier; small particle sizes therefore are used to overcome this.

Shimizu [80] concluded that the particle diameter of the resin beads is a key point, and that it is desirable for the beads to be as small as possible to enhance the rate of exchange; he suggested an optimum size of about 0.5 mm. Generally, the component particle diameters are in the range 0.3–1.2 mm. The smaller sizes are used in fluidized beds but care has to be taken to prevent the dispersion and overflow of fine particles. The larger sizes are generally used in fixed-bed systems, where the size distribution determines the pressure loss across the bed [80].
“No-matrix resins” were introduced as a novel way of enhancing the capacity of thermally regenerable resins, but failed because of internal salt formation in the resin, with no segregation of sites into domains [87].

Synthesis of resins by the encapsulation of microparticles of one polymer have been carried out using the matrix of a polymer of opposite type by Hatch [88], Bolto and Jackson [68]. Later, Chanda et.al [53] used a method with both amine and acid components as polymers. During this synthesis, one polymer was crosslinked to create the polymer particles. The second polymer was then coated onto those particles, followed by crosslinking in order to obtain the best IEX resin for the Sirotherm process.

Syntheses of polyampholytes were reported in the 1950s using free-radical polymerization [58, 89-94] and a study was carried out on their zwitterionic properties [95]. Dissociation constants of WA/WB groups in the resin also play a vital role in such desalting processes. These properties contribute directly to the elution capacity of a resin. A determination of the electrochemical properties of polyampholytic resins [96, 97] and their ionizing groups [98] would therefore help to improve the Sirotherm process. The acid/base behaviour of the polyampholytic resins is different in the individual WA and WB groups. Determination of the isoelectric point (IEP) [99] is also needed to explain the function of such polyampholytic resins. The modified Henderson-Hasselbalch equation can be used here to analyse the acid/base equilibrium of polyampholytes [94, 100-103].

\[
\text{pH} = \text{p}K'_{a_1} + \log(\alpha / 1 - \alpha) \quad (1.7)
\]

\[
\text{pH} = \text{p}K'_{a_2} + \log(1 - \beta)/\beta \quad (1.8)
\]
where \( pK'_{a1} \) and \( pK'_{a2} \) are the ionization constants of acid and base groups, respectively, and \( \alpha \) and \( \beta \) the degrees of ionization of acid and base groups, respectively, of the polyampholytes.

Many theoretical models have been introduced to determine the dissociation constants of the ionizing groups, which highlight the effects of the microstructure of copolymers on the acid-base equilibrium of the polyampholytes \([58, 94, 100, 102, 104-106]\). Changes in temperature also affect the dissociation constants of the acidic and basic groups of Sirotherm resins, so that adsorption by the IEX resins varies with temperature. In such cases, the van’t Hoff equation can be used to calculate the equilibrium constants for the resins at working temperatures by relating them to the known equilibrium constants at a reference temperature.

The van’t Hoff equation can be presented as:

\[
\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

(1.9)

In this equation, \( K_1 \) is the equilibrium constant at absolute temperature \( T_1 \), \( K_2 \) is the equilibrium constant at absolute temperature \( T_2 \) and \( \Delta H^0 \) is the standard enthalpy change.

### 1.4  Chemical and Thermal Regeneration of IEX Resins

The recovery of regeneration chemicals is important because of the need for large volumes of acid and base solutions for the regeneration of depleted IEX resins. Many groups have tried to develop suitable methods using a variety of techniques. Kadlec et.al \([107]\) used weakly acidic cation exchangers at raised temperatures, 80–150°C during the desalination process to recover ammonium ions. A weakly basic IEX resin containing amine functional groups has been used to capture carbon dioxide, then
regenerated by heating in water at temperatures greater than 50°C [108]. This Thesis also discusses the feasibility of regenerating the resin by heating when it is exposed to ammonium hydrogen carbonate (IUPAC), referred to as ammonium bicarbonate (AB). Shimizu [80] introduced a desalination process using WA and WB resins, and used carbonic acid and ammonium sulfate solutions for their regeneration. The passing of heated water at 50–100°C through the resin converted the resin back into its initial state.

IEX resins can be used as a feasible and practical method for extracting carbon dioxide from seawater, with the carbon dioxide captured by strong-base anion exchange resins in the form of bicarbonates [108, 109]. Many studies have been carried out using anion and cation exchange resins for water desalination followed by regeneration with carbon dioxide [110-114]; the Carix process [115, 116] is a good example. In these studies it was demonstrated that exposure of strong base IEX resins in a pH-neutral form (e.g. regenerated with Cl⁻) to a solution of bicarbonate ions resulted in a reduction in the pH of the solution. This indicates that the basic bicarbonate ions were removed from the solution by the IEX resin. This pH change affects the adsorption of ions, resulting in less extraction of carbon dioxide [109]. Ammonium bicarbonate (AB) can be used to overcome this problem by maintaining the pH of the system. Evidence from the use of AB for forward osmosis supports the suitability of AB as a regenerant for IEX resins [36, 117].

Chemical and thermal regeneration followed by a desalination process with IEX resins can be introduced as a cyclic adsorption process [80, 118]. Most importantly, such processes do not require special treatments such as neutralization, precipitation or separation of the resulting concentrated waste water, which is crucial in acid-base regeneration. Commercial mixed beds are present as an intimate mixture of cationic and anionic resin beads, while regeneration is carried out using acids and bases after the two
resins have been separated [40, 119]. It would be advantageous to have one specific regenerant which could be used for IEX resin regeneration, saving time and also eliminating additional steps.

Ammonium bicarbonate decomposes in solution above 60°C [36], so the energy required for regeneration is less than for other desalination processes. Therefore, chemical/thermal regeneration of IEX resins could be incorporated during the desalination of salt water by IEX resins. Blow down of steam is common in most power plants, and waste heat generated from many other industries can also be utilized in the desalination process. Solar energy can also be used in countries where it is sunny throughout the year. Based on these considerations, IEX resins, together with novel regeneration techniques, could be eminently suitable for efficient desalination.

1.5 Research Aims and Thesis Outline

The purpose of this research is to develop a novel method for desalination of seawater or brackish water using IEX resins, then regenerating the resin *in situ* with the aim of recycling and re-using the regenerant solutions. Regeneration of ion-exchange (IEX) resins thermally and recovery of regenerants has been shown to be possible in our recent studies [120, 121]. Strategies to regenerate IEX resins with re-use of regenerants have so far not been realistic, but the problem has yet to be tackled effectively. Polyampholytic resins composed of both acid and base groups, and a combined chemical-thermal regeneration potentially provides a good solution for this problem. This strategy enables the desalination of saline water, the regeneration of depleted IEX resins and the re-use of the regenerants, providing a complete water treatment process, without wasteful use of acids and bases. Combining desalination and regeneration, this
new strategy aims to provide a more efficient desalination process, in which energy consumption and chemical waste are much reduced compared to existing technologies.

**Chapter 1** gives a general overview of the importance of and current research on the desalination of saline water using ion-exchange resins. Generally speaking, the intrinsic properties of IEX resins make them a potential candidate for a number of applications, especially in desalination. Previous studies on emerging technologies in desalination, together with various types of IEX resins, have been described, and their limitations discussed. The potential for desalination applications using IEX resins is considered in this chapter.

In further exploration of this process, the thesis chapters are divided into three parts. The first part of the study, contained in Chapters 2 and 3, concentrate on the synthesis of polyampholytic IEX resins, their behaviour and ion exchange capacity. **Chapter 2** describes the synthesis of a polyampholytic resin consisting of weak-acid and weak-base groups, equilibrium studies with saline water and regeneration ability of the resin in an ammonium bicarbonate (AB) solution in a batch system. **Chapter 3** introduces the use of divalent ions (Ca$^{2+}$ and Ni$^{2+}$) to enhance IEX capacity of these polyampholytic resins and explains the possibility of pore expansion inside the resin.

The second part of the thesis, Chapters 4 and 5, focusses on a study of IEX (mixed-bead and mixed-bed) resins in continuous-flow systems for desalinating water, followed by regeneration without heat. **Chapter 4** investigates the possibility and efficiency of using mixed-bead resins for desalination of saline water and regeneration with AB, the affinity of the active sites of the resins for counter-ions and the behaviour of the resin during the exchange process. **Chapter 5** explains the use of commercial mixed-bed resins for desalination with a novel regeneration process, which offers a complete, effective desalination and regeneration technology.
The third part, Chapter 6, presents an IEX model to explain the IEX behaviour of a polyampholytic resin using polystyrene polyampholytic latex, which has both weak-acid and weak-base surface groups. This chapter gives details of the synthesis of a polyampholytic latex colloid, of equilibrium studies with zeta potential measurements and of adsorption data with saline and AB solutions. Finally, Chapter 7 contains a summary and conclusions of our findings and examines the potential of IEX resins for commercial desalination processes.
Chapter 2. Study of a New Process for the Efficient Regeneration of Ion-exchange Resins


2.1 Introduction

Mixed-bed, ion-exchange (IEX) resins have been used for many years to remove scale-forming ions such as Ca$^{2+}$ and Mg$^{2+}$ from feed water and to produce distilled water from tap water. They can also be used for the desalination of fairly concentrated brackish water without the need for high pumping pressures, extensive pre-treatment or high thermal-energy input. However, the IEX process is limited by the depletion of the resin and the need for large volumes of acid and base solutions for their regeneration.

Desalting using ion exchangers requires the continuous removal of the adsorbed salt ions with large volumes of mineral acids and bases. For example, it has been found that for the removal of 1 equivalent of salt, 1.2–3 equivalents of mineral acid and 1.3–2 equivalents of base have to be used [107]. Because of this, such desalting processes have high operating costs, create substantial volumes of by-product saline waste and require large amounts of acid and base solutions.

The Commonwealth Scientific and Industrial Research Organization (CSIRO) in Melbourne, Australia therefore developed the “Sirotherm” process [66] in which the resins are regenerated by heat energy. It was originally based on the use of a physical
mixture of weakly basic (WB) and weakly acidic (WA) IEX resin beads, and later employed for resins containing both WA and WB components within each bead, in a so-called ‘plum-pudding’ structure [67, 68]. These resins are thermally regenerable, that is they are capable of removing salts from an aqueous solution by sorption at ambient temperatures; whereas, at higher temperatures their sorption capacity is significantly reduced [81].

A thermally regenerable composite resin of crosslinked polyacrylic acid and ethoxylated polyethyleneimine was used for water desalination more recently by Chanda et. al. [53, 54]. This type of resin, also used in the present study, can be regenerated thermally, with no apparent loss of capacity, for up to 10 cycles of operation [53]. However, total regeneration cannot be achieved from this thermal process; but it is proposed here that integration of a re-usable chemical regenerant with the Sirotherm process could enable higher resin recovery.

Concentrated solutions of ammonium bicarbonate (AB) have been used as a draw solution in Forward Osmosis (FO), which was developed [37] to overcome the high pumping pressures required in Seawater Reverse Osmosis (SWRO). An aqueous solution of a concentrated mixture of dissolved ammonia (NH₃) and carbon dioxide (CO₂) can be used to produce a draw solution of concentrated ammonium bicarbonate, which can then be completely decomposed, in solution, by heating to above 60ºC [36] to produce the pure, desalted-water product. The gases (NH₃ and CO₂) can then be collected, either by column distillation or membrane distillation (MD) [37, 122], and used for a new draw solution. Ammonium bicarbonate is used in the current work as a regeneration solution, in combination with heat, to remove adsorbed ammonium and bicarbonate ions from a specifically designed resin.
The process studied in this work is based on the “Sirotherm process” [66, 77] together with the addition of a regenerating solution, which can completely regenerate the IEX resin, and can then be itself almost completely regenerated through a relatively low-temperature, chemical decomposition reaction. This regeneration process does not require large quantities of acid or base. The regeneration solution is thermally decomposed into gases and, since the resin also has a substantially reduced capacity at higher temperatures, the combined effect offers a potentially more useful and efficient process. As a result, in this work, a novel combined process of thermal and chemical mixed bead IEX regeneration was developed and evaluated.

Since IEX resin processes can be considered to include both adsorption and absorption processes, the more general term ‘sorption’ was used in this study. In order to understand the regeneration mechanisms, three different protocols were followed. These were a distilled-water wash; distilled-water wash and heating at 80±1°C; and regeneration using AB followed by heating at 80±1°C.

2.2 Materials and Methods

2.2.1 Materials

Acrylic acid (AA), ethylene glycol dimethacrylate (EGDMA) (crosslinking agent) and 1,1’-azobis(cyclohexanecarbonitrile) (ABCN) (initiator) were used to make crosslinked polyacrylic acid (XPAA). 80% ethoxylated polyethyleneimine (EPEI) in 37% aqueous solution and 25% glutaraldehyde (crosslinking agent) were used during this synthesis. All chemicals were used as received from Sigma-Aldrich, Australia as reagent grade.

Ammonium bicarbonate (99%) was obtained from May & Baker, Dagenham, England, and 98% sodium chloride from Sigma-Aldrich, Australia was used as
purchased. Sodium, chloride and ammonium ion standard solutions, of 100 ppm and 1000 ppm, were obtained from Hach Pacific Pty Ltd, Australia.

### 2.2.2 Resin Synthesis

The composite resin designated as (XPAA-EPEI-XG) was synthesized by free-radical copolymerization according to previously published procedures [53], [120], as outlined schematically in Fig. 2.1.

![Schematic diagram of the method used for the preparation of the resin XPAA-EPEI-XG](image)

**Figure 2.1** Schematic diagram of the method used for the preparation of the resin XPAA-EPEI-XG by copolymerization with acrylic acid (AA), ethylene glycol dimethacrylate (EGDMA), followed by reaction with ethoxylated polyethyleneimine (EPEI) and crosslinking with glutaraldehyde.
The WA/WB, mixed-bead, IEX resin was synthesized by copolymerisation of 76 wt.% of acrylic acid and 24 wt.% ethylene glycol dimethacrylate with 0.4 wt.% of 1,1’-azobis(cyclohexanecarbonitrile) initiator in a number of 10 ml sealed glass tubes, filled to half capacity with a nitrogen atmosphere. The reaction mixture was de-oxygenated by bubbling with nitrogen gas for 10 minutes, ensuring the removal of oxygen from the reaction system prior to sealing, as oxygen inhibits the free radical polymerization [123, 124] during the reaction, and also to obtain a better polydispersity index in the polymer. The mixtures were then heated in a water bath to 85°C for an hour, the glass tubes then broken and immersed in distilled water to facilitate the solid product detaching from the glass. The polyacrylic acid (PAA) obtained was wet ground to less than 1.2 mm in size and partially dried. The product was then sifted using standard laboratory test sieves, of 250 µm and 1.18 mm, manufactured by EndeCotts, London, England, to obtain particles of diameter in the range 0.3–1.2 mm. The PAA (100 g) was then refluxed with 10 wt.% ethoxylated polyethylenimine in 500 ml methanol with constant stirring for 6 hours. The EPEI-coated polymer was again crosslinked with 10 wt.% glutaraldehyde for 3 hours and the final product, brown in color, kept in boiling water for an hour to remove any free EPEI, followed by repeated washing with distilled water. Four batches of this mixed-bead IEX resin were synthesized (see Fig. 2.3) to ensure reproducible composition.
Structures of the initiator and the cross linking agents used in this study are as follows:

![1,1’-azobis(cyclohexanecarbonitrile)](image)

![Ethylene glycol dimethacrylate](image)

![Glutaraldehyde](image)

**Figure 2.2** Chemicals used during the syntheses of resin XPAA-EPEI-XG.

![Photographs of a synthesized composite resin sample (XPAA-EPEI-XG); (a) physical appearance and (b) magnified image.](image)

**Figure 2.3**

2.2.3 Analysis

2.2.3.1 Determination of Moisture Content

The moisture content of the resin samples was measured after partial drying with porous filter paper, followed by slow ‘natural’ drying in a laminar-flow cabinet at room
temperature for 10 minutes. The samples were then placed in an oven at 104°C for 18 hours, and the moisture content then measured.

2.2.3.2 Determination of Sodium Chloride Concentrations

The concentration of NaCl in solution was determined by measuring the Na⁺ and Cl⁻ ion activity using ion-selective electrodes (ISE) (HQ440d-Hach). In these studies, known concentrations of Na⁺/Cl⁻ ions were measured using sodium and chloride ISE’s, with output in millivolts (mV) and calibration plots obtained. The sodium standard concentrations used for calibration were 10, 23, 69, 92, 100 and 115 ppm; the chloride standard concentrations used were 10, 17.7, 35.4, 70.9, 100, 106.3, 141.8, 177.2 and 212.6 ppm. The unknown concentrations of Na⁺/Cl⁻ ions in the samples were measured in mV, and the concentration of the samples in ppm found from the calibration plots. Each measurement was taken after 10 minutes of immersion of the ISE electrode in the sample solution. All the measurements were taken at 20.8±0.2°C.

2.2.3.3 Determination of Functional Groups in the Resin

The presence of amine and carboxylic groups in the resin sample was examined with the KBr disk method using an infra-red (IR) spectrometer made by Shimadzu, IR Prestige-21. The pellets were prepared using finely ground mixed-bead resin, with approximately 5 mg of sample and 100 mg of KBr. The infrared absorbance was scanned 10 times at a resolution of 4 cm⁻¹ in the range 400–4500 cm⁻¹.

Presence of carboxylic groups and amine groups were also analyzed from acid/base titrations and pH measurements using a pH-PC 700, Eutech instruments.
2.2.3.4 Determination of Resin Morphology

Resin morphology was studied with a Hitachi TM3000 scanning electron microscope (SEM) using the bulk-sample analysis technique. The resin beads were mounted on a specimen stub using conductive tape and the images observed at a beam energy of 5 kV, with 2000× magnification and a 30 µm micromarker.

2.2.4 Ion-exchange Studies of the Synthesized Resins

2.2.4.1 Equilibrium Studies with Saline

The synthesized resin was used for equilibrium studies by immersion in a series of NaCl solutions (in the range 0.1−0.5 mol/l (M), at pH 5.6) in tightly stoppered tubes at 20°C. These were mechanically shaken for 15 hours. In each sorption study, 0.8 g of the wet resin was immersed in 10 ml of the NaCl solution. Initial and final concentrations of the Na⁺/Cl⁻ ions were measured for each sample, and the extent of sorption calculated. These equilibrium studies of the mixed-bead resin in saline were performed twice at each concentration to ensure the accuracy of the results.

2.2.4.2 Resin Regeneration

In the regeneration studies, the mixed-bead resin in State 1 (Fig. 2.4) was exposed to 0.5M NaCl solution and equilibrated for 15 hours at 20°C. The resin was then converted into State 2 (Fig. 2.4). The exhausted resin was then washed in distilled water several times until the rinse water had an electrical conductivity of distilled water, which was within 1.04−1.09 µS/cm. The washed resin was partially dried in filter paper, then stored as a wet solid (with moisture content (MC), of about 40 w/w%). It was then equilibrated with 0.5M NaCl for 15 hours at 20°C and the extent of sorption and the percentage of regeneration obtained from the residual chloride concentration in the equilibrated solution.
Figure 2.4 Schematic diagram of the functional groups on the IEX resin used in this study in various process states.

The washed, exhausted resin (0.8 g) in State 2 was heated to 80±1°C for an hour in 2 litres of distilled water with continuous stirring. The resin sample was then washed several times, collected in filter paper, patted dry and stored as a wet solid (MC about 40 w/w%). It was then equilibrated with a solution of 0.5M NaCl for 15 hours at 20°C. The extent of sorption and the percentage of regeneration were calculated by measuring the residual chloride concentration of the sorbate in the equilibrated solution.

The washed, exhausted resin in State 2 was immersed in 2M ammonium bicarbonate solution for 15 hours at 20°C and then washed several times in distilled water until the rinse water had a conductivity of distilled water, which was within 1.04–1.09 µS/cm. The sample was then heated in 2 litres of distilled water for an hour.
with continuous stirring at 80±1°C. The resin sample was then washed several times in distilled water, collected in to a filter paper, patted dry and stored as a wet solid. Samples were then equilibrated with a range of NaCl solutions for 15 hours at 20°C and the extent of sorption and the percentage of regeneration were calculated by measuring the residual chloride concentration of the sorbate in the equilibrated solution. All the regeneration procedures used above were performed twice to ensure accuracy of the results.

2.3 Results and Discussion

2.3.1 Physical, Chemical and Structural Properties of the Resin

The resultant wet resin solid product (XPAA-EPEI-XG) had a particle diameter in the range 0.3–1.2 mm and a moisture content of about 40%. The synthesized resin was stored as a wet resin product for analysis.

The FTIR spectrum shown in Fig. 2.5 reveals the presence of carboxylic and amine groups in the XPAA-EPEI-XG; some of the basic properties of the synthesized mixed-bead resins are recorded in Table 2.1. The carboxylic acid content and the amine content in the resin are given in Table 2.1.
Figure 2.5 IR spectrum of the composite sorbent (XPAA-EPEI-XG), composed of copolymerization with acrylic acid (AA), ethylene glycol dimethacrylate (EGDMA), ethoxylated polyethyleneimine (EPEI) and crosslinked with glutaraldehyde.

Table 2.1 Basic physical and chemical properties of the mixed-bead resins used in these studies.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>40%</td>
</tr>
<tr>
<td>Particle diameter (mm):</td>
<td></td>
</tr>
<tr>
<td>Wet</td>
<td>0.30–1.2</td>
</tr>
<tr>
<td>Dry</td>
<td>0.25–1.1</td>
</tr>
<tr>
<td>Carboxylic content (meq/g) dry</td>
<td>1.3–1.5</td>
</tr>
<tr>
<td>Amine content (meq/g) dry</td>
<td>3.7–4.0</td>
</tr>
</tbody>
</table>

The morphology of the synthesized resin shows a well-established porous structure, as seen in the SEM image in Fig. 2.6.
Figure 2.6 SEM image of a typical WA/WB XPAA-EPEI-XG mixed-bead resin produced as described in the text. This image shows the typical pore structure of the resin, with pores of around 1 µm.

2.3.2 Sorption Isotherms

A typical equilibrium sorption isotherm obtained for NaCl using a sample of the mixed-bead resin (XPAA-EPEI-XG) is illustrated in Fig. 2.7, for the adsorption of both Na⁺ and Cl⁻ ions. The maximum NaCl sorption density was typically about 0.5 mmol/g (dry wt).

The sorption isotherms show the classical behaviour of a “Sirotherm” resin, having both WA and WB groups in the same bead. The sorption values obtained were fitted well with both Langmuir and Freundlich isotherms, with the former model fitting the data more closely.
Figure 2.7 Equilibrium sorption isotherm of NaCl on XPAA-EPEI-XG resins at 20°C at a sorbent loading of 0.8 g (wet resin)/10 ml of equilibration solution. Each solution was equilibrated with the resin over 15 hours with continuous stirring. Typical error for the sorption measurements about ±0.01 mmol Na\(^+\) or Cl\(^-\) per gram of (dry) resin sorbent.

With \( q_{\text{max}} \) the maximum sorption capacity (meq/g dry sorbent) and \( K \) the sorption binding constant (l/meq), the Langmuir isotherm can be written as

\[
q = \frac{q_{\text{max}} KC^*}{1 + KC^*}
\]  

(2.1)

where \( q \) is the equilibrium sorption (meq/g dry sorbent) and \( C^* \) is the equilibrium sorbate concentration (meq/l) in solution.

The Freundlich isotherm can be written as

\[
q = p(C^*)^n
\]

(2.2)

where \( p \) and \( n \) are Freundlich parameters, and \( q \) and \( C^* \) are the same as defined above.
The values were determined by least-squares fit of the adsorption data; a summary is presented in Table 2.2.

**Table 2.2** Langmuir and Freundlich isotherm parameters for sorption of NaCl on mixed-bead resins.

<table>
<thead>
<tr>
<th>isotherm</th>
<th>parameter</th>
<th>units</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_{\text{max}}$</td>
<td>meq/g dry sorbent</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>$K$</td>
<td>l/ meq</td>
<td>$3.17 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Correlation coefficient</td>
<td></td>
<td>0.998</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$p$</td>
<td></td>
<td>$9.22 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td></td>
<td>0.646</td>
</tr>
<tr>
<td></td>
<td>Correlation coefficient</td>
<td></td>
<td>0.976</td>
</tr>
</tbody>
</table>

**2.3.3 Simple Thermodynamic Model of Mixed-bead Resin Ion-exchange Processes**

The solution ionization properties of the WA (carboxylic) and WB (amine) groups in a typical WA/WB mixed-bead resin, where the groups are in close proximity, can be modelled using a suitable amphiprotic molecule, such as glycine. The $pK_a$ values as a function of temperature for the two ionizable groups on the amino acid glycine have been measured in aqueous solution [125, 126]. In this amino acid, the carboxylic (COOH) group is a stronger acid and the amine (NH$_2$) a weaker base than the corresponding individual components in solution. When the temperature was increased from 25°C to 75°C; the COOH groups became slightly more ionized but the NH$_2$ groups became significantly less ionized (Table 2.3).
Table 2.3 Ionization constants of glycine in aqueous solutions with temperature.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$K_a$(COOH)</th>
<th>$pK_a$(COOH)</th>
<th>$K_a$(NH$_3^+$)</th>
<th>$pK_a$(NH$_3^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>4.47×10$^{-3}$</td>
<td>2.35</td>
<td>1.66×10$^{-10}$</td>
<td>9.78</td>
</tr>
<tr>
<td>75°C</td>
<td>4.79×10$^{-3}$</td>
<td>2.32</td>
<td>1.00×10$^{-9}$</td>
<td>9.00</td>
</tr>
</tbody>
</table>

However, the degree of ionization depends critically on solution pH. At pH values in the range 5–8, both groups remain almost fully ionized, even though the ratio of NH$_2$ groups ionized is reduced by a factor of 6 with the increase in temperature, as shown in Fig. 2.8.

![Ionization behaviour of COOH groups and NH$_2$ groups on the glycine molecule in solution with pH and temperature.](image)

**Figure 2.8** Ionization behaviour of COOH groups and NH$_2$ groups on the glycine molecule in solution with pH and temperature.

By comparison, there is no significant change in ionization of the COOH groups with temperature. Thus, it appears that the change in ionization of the amine groups


works as a driving force for the reduction in mixed-bead resin capacity with increasing temperature, presumably by proton exchange.

At higher pH values, greater than 8, the available number of protonated amine groups is significantly reduced, and so the effect of an increase in temperature on total ionization levels is greater. For example, at around pH 8, protonated amine to non-protonated ratios change from 60:1 to 10:1 as the temperature is increased from 25°C to 75°C. It appears that deprotonation also tends to reduce the CO$_2^-$/COOH ratio.

Primary, secondary and tertiary amines alone in aqueous solution behave in a similar manner with temperature, as summarized in Table 2.4. These ionization constants for primary, secondary and tertiary amines at 80°C were calculated using the van’t Hoff equation, based on experimental values [127-129] obtained at 25°C.

Table 2.4 Ionization constants of secondary and tertiary amines in aqueous solution with temperature.

<table>
<thead>
<tr>
<th>Base</th>
<th>$pK_a$ at 25°C</th>
<th>$pK_a$ at 80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylamine</td>
<td>10.63</td>
<td>9.08</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>10.94</td>
<td>9.48</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>10.72</td>
<td>9.51</td>
</tr>
</tbody>
</table>

Measurements of pH taken during the equilibrium resin sorption studies, over a range of NaCl concentrations, were found to be reduced by less than 0.1 from the initial pH values of around 5.6. This small increase in hydrogen-ion concentration is negligible, which shows that this type of resin has more-or-less similar sorption capacities for both Na$^+$ and Cl$^-$ ions.
2.3.4 Resin Regeneration

The variation in electrical conductivity with the volume of rinse water (distilled) was measured during the consecutive washings of the exhausted resins. Typical results are given in Fig. 2.9. The subsequent sorption equilibrium studies showed that only a fraction of the exhausted sites were regenerated by distilled-water washing at room temperature. The density of available or accessible anionic (carboxylic) and cationic (amine) binding sites was found to be about 0.5 meq/g (dry wt) for each of the mixed-bead resins produced. By comparison, the total number of sites available was estimated from the reaction scheme to be about 9 and 2 meq/g (dry wt) for cationic and anionic exchange groups, respectively. These results indicate that there were far more inaccessible amine groups in the polymer matrix.

![Conductivity decrease on sequential washings of the resin (0.8 g wet weight) with distilled water. After about 1 litre, the conductivity approached that of the distilled water (about 1.0 µS/cm).](image)

**Figure 2.9** Conductivity decrease on sequential washings of the resin (0.8 g wet weight) with distilled water. After about 1 litre, the conductivity approached that of the distilled water (about 1.0 µS/cm).
The accessible sites presumably have both functionalities (WA/WB groups) present in close proximity in the mixed-bead resin, and they can be readily regenerated either with distilled water, heat or chemical/thermal regeneration techniques. The accessible sites can be divided into easily exchangeable and less readily exchangeable sites. Thus, only sites which are easily exchangeable contribute to the reversible regeneration when exposed to excess distilled water. Therefore, the less readily exchangeable sites determine the limiting factor for the capability of regeneration of the mixed-bead resins. The percentage regeneration through distilled-water washing at room temperature was typically found to be about 40%, as shown by T1 in Fig. 2.10.

Figure 2.10 Equilibrium sorption isotherm of NaCl on new and regenerated XPAA-EPEI-XG resins at 20°C at a sorbent loading of 0.8 g (wet resin)/10 ml of equilibration solution. Each solution was equilibrated with the resin over 15 hours with continuous stirring. Equilibrium ion adsorption for three different regeneration methods was also studied. T1 was measured after washing with distilled water at room temperature (22°C). T2 was measured after distilled-water washing, then heating to 80±1°C. T3 was measured after equilibration with 2M ammonium bicarbonate solution, then heating to 80±1°C. Typical error for the adsorption measurements about ±0.01 mmol Na⁺ or Cl⁻ per gram of (dry) resin sorbent. [130]
Sodium and chloride ions will be physisorbed, electrostatically, onto oppositely charged groups on the IEX resin; washing with distilled water should remove these adsorbed ions, replacing them with hydronium and hydroxide ions. The change in $pK_a$ values of the WA and WB groups with increase in temperature in the mixed bead resins where the WA and WB sites are in close proximity appears to facilitate the reduction in ion adsorption capacity. This process also facilitates the regeneration of the resin. In the current study, it was found that the percentage resin-site regeneration on heating to $80^\circ C$ was about 80%, as shown by T2 in Fig. 2.10.

Using the analogy with glycine protonation in aqueous solution, it might be expected that, although there is a $6\times$ drop in the ratio of protonated amine groups to unprotonated on raising the temperature, in the pH range 6–8 almost all the carboxylic acid sites and amine sites will be ionized. Hence, the reduction in IEX capacity with temperature of these WA/WB resins is hard to explain. It is possible that the polymer matrix of the resin plays a role in this process, given the fact that the IEX capacity of these resins at room temperature is already much below the number of functional groups expected from the polymer synthesis composition (see Table 2.1). The apparent reduction in access to the majority of sites at room temperature may increase further as the temperature rises. These effects may be related to the close proximity of the WA and WB sites in the same beads and to configurational changes in the polymer matrix on heating.

### 2.3.5 Regeneration using Ammonium Bicarbonate

The solution ionization behaviour of ammonium bicarbonate was studied by measuring electrical conductivity versus concentration of the salt. The results obtained show that this salt has a high degree of ionization in solution, at a level similar to other typical
salts [131] such as potassium nitrate (KNO₃), potassium chloride (KCl) and ammonium chloride (NH₄Cl) (see Fig. 2.11).

![Conductivity vs Concentration Graph](image)

**Figure 2.11** Electrical conductivity with concentration for several common salts at 25°C.

The estimated degree of ionization of AB is about 80% compared to the conductivity values obtained for the different concentrations of potassium nitrate. Thus, it can be expected that washing the depleted resins with concentrated AB solution should effectively displace adsorbed NaCl at low temperatures, around 20–25°C.

On heating to 80°C, the combination of reduced IEX capacity of the resin and decomposition of the adsorbed AB produces an efficient regeneration. This process was found to produce about 100% regeneration of the WA/WB resin used in this study, as can be seen from the sorption data in Fig. 2.10. These results suggest that this type of resin, combined with AB regeneration followed by heating and water washing, offers an efficient and complete resin regeneration.
As discussed earlier, it is possible that configurational changes in the polymer matrix on heating bring the WA and WB groups closer together, which both reduces exchange capacity and facilitates AB decomposition. As shown in Fig. 2.12, proton transfer can assist, at higher temperatures (80°C), in NH₄⁺ and HCO₃⁻ ion desorption and in the decomposition of AB, enhancing the mixed-bead resin regeneration. This process enables the sorption capacity of the resin to be returned to close to its original value without the need for acid and base washing. In addition, the emitted gases, carbon dioxide and ammonia, can be readily collected and re-used to generate the AB solution, which offers the potential for use in both batch and continuous commercial processes.

**Figure 2.12** Schematic diagram of the mechanism proposed for the reduction of ionized sites in the mixed-bead resin followed by regeneration by ammonium bicarbonate with temperature.

### 2.4 Conclusions

A mixed-bead resin (XPAA-EPEI-XG) was synthesized in order to study alternative methods for regeneration without the use of conventional acid and base washing. The resin contained WA and WB groups in the same resin beads. Once the resin was exhausted by exposure to NaCl solutions, it could be partially regenerated by washing in excess distilled water. These results suggest that about 40% of the ions bound to the
resin were weakly held, probably by electrostatic forces. These results also suggest that there are two types of active binding sites employed during the IEX process in the resin: some which are accessible and easily exchangeable; and some which are accessible but less readily exchangeable. The accessible, less readily exchangeable binding sites could be exchanged using concentrated salts such as ammonium bicarbonate. Then, it appears that a significant configurational change occurs at elevated temperatures in the polymer matrix which both reduces exchange capacity and causes the complete decomposition of the adsorbed AB. This process can be used to completely regenerate this type of resin, without the need for acid and base washing. In addition, the decomposition gases can be collected and used to regenerate the AB solution. These results suggest that use of this salt could be efficient because it readily displaces NaCl from this type of resin and completely decomposes at relatively modest temperatures.
Chapter 3. Enhanced Ion-exchange Capacity of Polyampholytic Resins

This chapter is based on the published journal article: N.P.G.N. Chandrasekara and R.M. Pashley, Enhanced ion exchange capacity of polyampholytic resins. Separation and Purification Technology, 2016. 158: 16-23.

3.1 Introduction

Ion-exchange (IEX) resins are commonly available as cationic or anionic resins but not as polyampholytic resins. This is probably because sequential acid and base washing cannot produce complete regeneration of polyampholytic resins with chemically attached anionic and cationic groups in close proximity. However, we have recently shown that these resins can be completely regenerated by washing with concentrated ammonium bicarbonate (AB) solution followed by heating [120]. Even so, the low IEX capacities of polyampholytic resins still restrict their commercial applications.

These composite polyampholytic resin beads have lower IEX capacities than the two kinds of strong-acid (SA) and strong-base (SB), individual IEX resins available commercially. Therefore, it is important to increase the IEX capacity of these mixed bead resins because, if their sorption capacity is increased, they could be used more widely, with AB regeneration, to reduce chemical waste.

There are many factors that affect the IEX capacity of mixed-bead resins composed of weak-acid (WA) and weak-base (WB) groups, such as temperature, pH and ionic strength of the solution, polymeric structure of the resins, the acidity and the basicity of functional groups, the ratio of acid/base groups and the resin’s affinities for counter ions [81, 82]. Consequently, numerous studies [64, 66, 80-83, 86] have been
carried out to synthesize resins with enhanced IEX capacity taking into account all these factors.

The methods used for chemical synthesis of these resins can also affect their IEX capacities. Therefore, the polyampholytic resins used in this study have been synthesized and studied under conditions where better IEX capacities can be achieved, as discussed in the Introduction (Section 1.3.2 in Chapter 1) and the earlier experimental procedures (Section 2.2.2 in Chapter 2). Chanda et al. [52, 85] enhanced the IEX capacity of polyampholytic resins by introducing ethoxylated polyethyleneimine (EPEI), which is considered a good source of tertiary amine groups. A similar type of resin was used in the current study.

The IEX capacity of a resin depends upon the affinity of a counter-ion for that resin [81]. A resin containing carboxylic groups will exchange protons with cations in the normal manner. However, carboxylic groups coordinate preferentially with divalent metal ions [132]. In general, divalent cations have a stronger affinity for carboxylic groups than monovalent cations. For this reason, exposing a polyampholytic resin to divalent cations, followed by regenerating with AB, may activate less active exchanging groups, increasing the activity of the resin for other ions after regeneration. If so, this method may enhance the IEX capacity of mixed-bead resins.

In the present work, the monovalent and divalent cation-sorption capacity of a typical polyampholytic resin was studied, both before and after regeneration, using a combination of washing with concentrated ammonium bicarbonate solution and heat regeneration. The AB solutions used here can be re-formed on collecting the decomposition gases, NH₃ and CO₂ [37, 122]. In order to understand the regeneration mechanisms, three different protocols were followed. These were a distilled-water
Chapter 3  

Enhanced IEX Capacity of Polyampholytic Resins

wash; distilled-water wash and heating at 80±1°C; and regeneration using AB followed by heating at 80±1°C.

3.2 Materials and Methods

3.2.1 Materials

The synthesized composite IEX resin (XPAA-EPEI-XG), was produced as described in Section 2.2.2 in Chapter 2, and was used in this study. The resin had a particle diameter in the range 0.3−1.2 mm and a moisture content of about 40%.

Ammonium bicarbonate (99%) was obtained from May & Baker, Dagenham, England, 98% nickel (II) chloride and 99% calcium chloride dihydrate were obtained from Sigma-Aldrich, Australia. These salts were used as purchased. Sodium nitrate, nickel nitrate and calcium nitrate standard solutions (1000 ppm) were obtained from Ajax Finechem, Australia, and also used as supplied.

3.2.2 Analysis

3.2.2.1 Determination of the Concentration of Nickel, Calcium and Sodium Ions

The concentrations of nickel, calcium and sodium ions in solution were analysed by atomic absorption spectroscopy (AAS) using a Varian SpectrAA-400 (test methods followed were ASTM D1886-03, D511-03 and D4191-03). In these studies, calibration plots were obtained for the nickel, calcium, and sodium metals. The calibration plot for nickel was obtained by six-point calibration from 1 ppm to 6 ppm, for calcium five-point calibration from 1 ppm to 5 ppm, and for sodium five-point calibration from 0.3 ppm to 1.5 ppm. Then, using the calibration plots, the concentrations of the nickel, calcium and sodium ions were measured for each sample, and the extent of sorption then calculated.
The concentrations of nickel and calcium retained in the resin were measured by energy-dispersive X-ray fluorescence spectroscopy (XRF) using a Shimadzu EDX-800HS. In this study, either intensity (cps/µA) or peak height was measured for known concentrations of nickel/calcium, and the calibration plots obtained. The nickel standards of 58.6 ppm, 117.2 ppm and 586 ppm were prepared by mixing finely ground polyampholytic resin with NiCl₂. Ca²⁺ standards of 32 ppm, 80 ppm, 160 ppm were prepared using finely ground polyampholytic resin with CaCl₂. Calibration graphs were plotted for both Ni²⁺ and Ca²⁺ content in the resin. Then, the unknown concentrations of Ni²⁺/Ca²⁺ in the samples were found using the calibration plots.

3.2.2.2 Determination of Resin Morphology

Resin morphology was studied with a Hitachi TM3000 scanning electron microscope (SEM) using the bulk sample analysis technique (see Section 2.2.3.4 in Chapter 2), images were observed at 5 kV beam energy, with 2,000× magnification and a 50 µm micromarker.

The pore volume of the resin was monitored by measuring the Brunauer-Emmett-Teller (BET) surface area using a Micrometrics TriStar 3000. In this study, samples were vacuum dried at 80°C in a vacuum compartment and used for adsorption/desorption studies with nitrogen gas and finally, the BET surface area was obtained.

3.2.3 Ion-exchange Studies of the Mixed-bead Resins

3.2.3.1 Equilibrium Studies with Solutions of Nickel and Calcium Ions

Equilibrium studies of the mixed-bead resins were carried out by immersion in a series of NiCl₂ and CaCl₂ solutions (in the range 0.0001M to 0.05M, at pH 5.6) in tightly stoppered tubes at 20°C, with continuous mechanical shaking for 15 hours 1.0 g of the
wet resin was used in each sorption study. Here the resin samples were immersed in 25 ml of the NiCl₂/CaCl₂ solutions to determine the sorption levels. The extent of sorption was calculated using the initial and final concentrations of nickel and calcium for each sample. These equilibrium studies were performed twice for the mixed-bead resins with the metal-ion solutions at each concentration to ensure the accuracy of the results.

3.2.3.2 Resin Regeneration

The synthesized mixed-bead resin was used in regeneration studies following the previously published procedure [120]. In this study, the mixed-bead resin in State 1 (Fig. 3.1) was exposed to 0.01M NiCl₂ / 0.01M CaCl₂ solutions and equilibrated for 15 hours at 20°C. After this time, the resin was converted into State 2 (Fig. 3.1). The resulting ‘exhausted’ resin was then repeatedly washed in distilled water at room temperature (RT-20°C) until the rinse water had an electrical conductivity of distilled water, which was within 1.04–1.09 µS/cm.
Figure 3.1 Schematic diagram of the functional groups on the WA/WB polyampholytic resin used in this study in various process states.

The distilled water washed resin was then partially dried on filter paper and stored as a wet solid (with a moisture content (MC) of about 40 w/w %). These washed resin samples were then re-equilibrated with 0.01M NiCl₂ / 0.01M CaCl₂ for 15 hours at 20°C and the extent of sorption determined. The percentage regeneration was calculated by measuring the residual nickel/calcium concentrations in the equilibrated solutions.
Samples (each of about 1 g) of the exhausted and distilled-water washed resin in State 2 were heated to 80±1°C for an hour in 1 litre of distilled water, with continuous stirring. The resin samples were then repeatedly washed in distilled water at room temperature, partially dried on a filter paper and stored as a wet solid (MC about 40 w/w%). This resin was equilibrated again with a solution of 0.01M NiCl₂ / 0.01M CaCl₂ for 15 hours at 20°C. Then the residual nickel/calcium concentrations of the sorbate in the equilibrated solution were measured to determine the extent of sorption and the percentage regeneration.

Samples of the washed, exhausted resin in State 2 were immersed in 2M ammonium bicarbonate solution for 15 hours at 20°C, then repeatedly rinsed with distilled water until the rinse water had an electrical conductivity of distilled water, which was within 1.04–1.09 µS/cm. The samples were then heated in 1 litre of distilled water for an hour with continuous stirring at 80±1°C, followed by washing several times in distilled water, partially drying on filter paper and storage as a wet solid. The regenerated samples were used again for equilibrium studies with a range of NiCl₂/CaCl₂ solutions for 15 hours at 20°C. The residual nickel/calcium concentrations of the sorbate in the equilibrated solution were then measured to determine the extent of sorption and the percentage regeneration.

In addition, samples exhausted by exposure to NiCl₂ solutions were regenerated using AB solutions followed by heating, then equilibrated with a range of NaCl solutions for 15 hours at 20°C. The residual sodium concentrations of the sorbate in the equilibrated solutions were then measured to determine the extent of sorption and the percentage regeneration.
Resin samples exhausted by exposure to either 0.01M NiCl$_2$ or 0.01M CaCl$_2$ solution were then regenerated with AB solution, followed by heating to 80±1°C, then tested for residual nickel and calcium content using XRF. The resin samples, exhausted (by 0.01M and NiCl$_2$ and 0.01M CaCl$_2$ solutions) and regenerated with AB and heating to 80°C were finely ground separately to determine the residual nickel and calcium content. Standards and samples were analysed using a Shimadzu EDX-800HS. Calibration graphs were plotted for both Ni$^{2+}$ and Ca$^{2+}$ content in the resin, and the residual concentrations of Ni$^{2+}$ and Ca$^{2+}$ obtained from those graphs.

All of the regeneration/analysis procedures outlined above were performed at least twice to ensure the accuracy of the results.

### 3.2.3.3 Resin Morphology

Morphologies were studied by SEM for the newly-synthesized resin and for resins regenerated by AB solution and heating after having been exhausted by nickel, calcium or sodium exposure. The SEM images obtained for regenerated resins were compared with the new resin.

Pore volumes of the above mentioned resins were monitored by a BET surface area analyzer, and the newly-synthesized resin was compared with nickel-exhausted resin after regeneration with AB solution and heating, sodium-exhausted resin after regeneration with AB solution and heating, and nickel-exhausted resin after regeneration with hydrochloric acid (HCl).
3.3  Results and Discussion

3.3.1  Sorption Isotherms

Typical equilibrium sorption isotherms of the polyampholytic resin (XPAA-EPEI-XG) measured in a range of NiCl₂ and CaCl₂ solutions are given in Fig. 3.2 for the adsorption of Ni²⁺ and Ca²⁺ ions.

![Sorption Isotherm Graph](image)

**Figure 3.2** Equilibrium sorption isotherm of NiCl₂ and CaCl₂ on XPAA-EPEI-XG resins at 20°C at a sorbent loading of 1.0 g (wet resin)/25 ml of equilibration solution. Each solution was equilibrated with the resin over 15 hours, with continuous stirring. Typical error for the sorption measurements was about ±0.01 mmol Ni or Ca/g (dry) resin sorbent.

The Langmuir and Freundlich isotherms were used to study the behaviour of the mixed-bead resin (see Section 2.3.2 in Chapter 2). The sorption isotherms of the synthesized polyampholytic resin show the classical behaviour of “Sirotherm” resins, and the sorption values were fitted well by both Langmuir and Freundlich isotherms.
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The maximum sorption capacities of the sorbent for NiCl$_2$ and CaCl$_2$ were relatively similar, which suggests similar exchange sites were involved in the sorption process. However, Ni$^{2+}$ had a slightly higher sorption binding constant, that is, it was found to be more strongly bound to the resins than Ca$^{2+}$ and this may be because of the diverse specificity of both cationic and anionic groups present in the polyampholytic resins. Both Ni$^{2+}$ and Ca$^{2+}$ had significantly stronger binding ability than monovalent ions such as Na$^+$ at low ion concentrations.

The values for the isotherms were calculated from a least-squares fit to the sorption data; a summary of the results is given in Table 3.1.

Table 3.1 Langmuir and Freundlich isotherm parameters for sorption of NiCl$_2$ and CaCl$_2$ on mixed-bead resins.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Units</th>
<th>Sorbate NiCl$_2$</th>
<th>Sorbate CaCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$</td>
<td>meq/g dry sorbent</td>
<td>0.34</td>
<td>0.31</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$K$</td>
<td>l/ meq</td>
<td>$7.94 \times 10^{-2}$</td>
<td>$7.90 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>Correlation coefficient</td>
<td></td>
<td>0.976</td>
<td>0.996</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$p$</td>
<td></td>
<td>419.28</td>
<td>551.95</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td></td>
<td>1.90</td>
<td>1.87</td>
</tr>
<tr>
<td></td>
<td>Correlation coefficient</td>
<td></td>
<td>0.996</td>
<td>0.987</td>
</tr>
</tbody>
</table>

3.3.2 Resin Regeneration

The accessible sites present in the polyampholytic resins (i.e. WA and WB groups) can be readily regenerated by distilled-water washing, by heating or by chemical/thermal regeneration techniques [120]. In an earlier study [120], ammonium bicarbonate played a major role in a chemical/thermal regeneration process which completely regenerated the WA/AB polyampholytic resins.
Reversible regeneration can be achieved by rinsing the resin, exhausted by exposure to excess Ni\textsuperscript{2+} and Ca\textsuperscript{2+} ions, with distilled water; where there was about 70\% and 57\% regeneration for Ni\textsuperscript{2+} and Ca\textsuperscript{2+}, respectively (Table 3.2). This degree of partial regeneration was probably due to simple exchange of the physisorbed divalent cations, electrostatically bound onto the polyampholytic resin groups, with hydronium ions. Increasing the temperature (from 20\(^\circ\)C to 80\(^\circ\)C) facilitated changes in pKa for both WA and WB groups [120], which are associated with the resin’s regeneration ability. It was found that heating to 80\(^\circ\)C with water washing increased the regeneration abilities to about 76\% and 70\%, for resins exhausted by Ni\textsuperscript{2+} and Ca\textsuperscript{2+}, respectively (Table 3.2).

<table>
<thead>
<tr>
<th>Regeneration technique</th>
<th>Percentage of Recovery</th>
<th>Ni\textsuperscript{2+}</th>
<th>Ca\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing at RT</td>
<td>70</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>Washing at 80(^\circ)C</td>
<td>76</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{4}HCO\textsubscript{3} + 80(^\circ)C</td>
<td>$\geq$ 96</td>
<td>$\geq$ 96</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3.3 Enhanced Capacity of Polyampholytic Resin

It was also discovered that resins exhausted by exposure to excess Ni\textsuperscript{2+}/Ca\textsuperscript{2+} ions showed higher IEX capacities following regeneration, using a combination of concentrated ammonium bicarbonate (AB) solution washing, followed by heating to 80\(^\circ\)C. The initial IEX capacity of the resins exposed to a 0.01M solution of Ni\textsuperscript{2+} and a 0.01M solution of Ca\textsuperscript{2+} was about 0.11 mmol/g for both ions. After regeneration with AB solution followed by heat, the IEX capacities for Ni\textsuperscript{2+} and Ca\textsuperscript{2+} ions (for the same concentrations as above) were 0.43 and 0.45 mmol/g, respectively. This indicates that the resins had gained increased capacities of about 4–5\(\times\) their initial capacities (Fig. 3.3
and Fig. 3.4). The increased capacity remained the same for these regenerated resins, which indicates that the combined process of saturation with divalent cations together with the AB/heat regeneration facilitated a permanently enhanced IEX capacity.

**Figure 3.3** Equilibrium sorption isotherm of NiCl₂ on new (initial) and regenerated XPAA-EPEI-XG resins at 20°C at a sorbent loading of 1.0 g (wet resin)/25 ml of equilibration solution. Each solution was equilibrated with the resin over 15 hours, with continuous stirring. Here the resin was regenerated with 2M ammonium bicarbonate solution, then heated to 80 ±1°C. Typical error for the sorption measurements was about ±0.01 mmol Ni/g(dry) resin sorbent.
Figure 3.4 Equilibrium sorption isotherm of CaCl$_2$ on new (initial) and regenerated XPAA-EPEI-XG resins at 20°C at a sorbent loading of 1.0 g (wet resin)/25 ml of equilibration solution. Each solution was equilibrated with the resin over 15 hours, with continuous stirring. Here the resin was regenerated with 2M ammonium bicarbonate solution, then heated to 80 ±1°C. Typical error for the sorption measurements was about ±0.01 mmol Ca/g(dry) sorbent.

By comparison, the other regeneration techniques used for this polyampholytic resin (Section 3.3.2), such as distilled water washing and heating with distilled water, did not enhance the sorption capacity. Sorption levels of sodium ions were also studied for the resin following exhaustion by NiCl$_2$ and then regeneration by the AB/heating process; the resins were also found to have an increased IEX capacity of about 2.5× higher than the initial resin (Fig. 3.5). That the increased capacity for the monovalent cation was significantly lower than for the divalent ions may reflect the better pore penetration of the less-hydrated sodium ion. By comparison, the resin regenerated following exhaustion by NaCl, then by the AB/heating process, did not show an increased capacity [120]. This suggests that the divalent cations used in this study
(Ni$^{2+}$/Ca$^{2+}$) were the cause of the increased capacity when used in combination with the AB/heating regeneration process.

![Equilibrium sorption isotherm of NaCl on new (initial) and regenerated XPAA-EPEI-XG resins after exhausted by Ni$^{2+}$ at 20°C at a sorbent loading of 1.0 g (wet resin)/10 ml of equilibration solution. Each solution was equilibrated with the resin over 15 hours, with continuous stirring. Here the resin was regenerated with 2M ammonium bicarbonate solution, then heated to 80 ±1°C. Typical error for the sorption measurements was about ±0.01 mmol Na/g (dry) resin sorbent.](image)

**Figure 3.5** Equilibrium sorption isotherm of NaCl on new (initial) and regenerated XPAA-EPEI-XG resins after exhausted by Ni$^{2+}$ at 20°C at a sorbent loading of 1.0 g (wet resin)/10 ml of equilibration solution. Each solution was equilibrated with the resin over 15 hours, with continuous stirring. Here the resin was regenerated with 2M ammonium bicarbonate solution, then heated to 80 ±1°C. Typical error for the sorption measurements was about ±0.01 mmol Na/g (dry) resin sorbent.

It is reasonable to speculate that the internal pore structure of the resin beads was expanded by the AB/heating regeneration process, which then increased access to adsorption sites in the beads. This mechanism seems reasonable because of the unique process by which ammonium and bicarbonate ions from the regeneration solution penetrate into the porous network, then, on heating, decompose within the pores to produce ammonia and carbon dioxide gases together with substantial local expansion.
That divalent cations also have to be present to effect this change is interesting, since the use of AB/heating alone did not cause this increase in capacity.

Further support for this model was obtained from BET surface-area analysis on samples before and after this regeneration process, as summarized in Table 3.3. Resins regenerated by the AB/heating process following exposure to Ni and Ca ions had significantly higher BET surface areas, about 3 times higher than the initial resin. The observed changes in BET surface area for different states of the resin support the view that the increased IEX capacities were due to a change in internal resin pore structure, allowing increased access to IEX sites. The resins regenerated with hydrochloric acid (HCl), and the resins exhausted with sodium chloride then regenerated with the AB/heating process did not show any significant increase in surface area. Thus, again, it appears that divalent cations help to expand the pores during the regeneration process. Of course, since this mixed-bead resin is composed of both the WA/WB groups, it is clear that it cannot be regenerated completely by washing in HCl alone.

**Table 3.3** BET surface area of the resin with different regeneration methods.

<table>
<thead>
<tr>
<th>Regenerated by</th>
<th>Form of Resin</th>
<th>BET Surface Area in m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Original resin</td>
<td>0.68 ± 0.09</td>
</tr>
<tr>
<td>NH₄HCO₃+Heat</td>
<td>Regenerated resin (Ni sorbed)</td>
<td>2.15 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>Regenerated resin (Na sorbed)</td>
<td>0.85 ± 0.10</td>
</tr>
<tr>
<td>HCl</td>
<td>Regenerated resin (Ni sorbed)</td>
<td>0.75 ± 0.04</td>
</tr>
</tbody>
</table>

SEM images of the different states of the resin also support the view that the resin had a more-expanded pore structure, at least on the surface of the resin beads, following the divalent ion-AB/heating process (Fig. 3.6).
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Figure 3.6 SEM image of typical WA/WB XPAA-EPEI-XG mixed-bead resins obtained after synthesis (unused resin) and regeneration with ammonium bicarbonate followed by heat: (a) unused resin; (b) exposed to sodium (NaCl); (c) exposed to nickel (NiCl₂); (d) exposed to calcium (CaCl₂). These images show the morphology and pore structure of the resins after regeneration following exposure to different salt solutions.

XRF data obtained for the solid resins exhausted by 0.01M NiCl₂ and 0.01M CaCl₂ solutions, then regenerated by the AB/heating process, showed the traces of both nickel and calcium of less than 4% of the fully adsorbed amounts (Fig.3.7). It is hard to
see how this low level of retained divalent cations could have so significantly changed the pore structure and enhanced sorption capacity. However, this factor could not be entirely ruled out, since the AB decomposition rate and hence gas evolution rate in the pores could be accelerated by the presence of residual Ni$^{2+}$ and Ca$^{2+}$ ions, which are known to react with AB in solution.

![Figure 3.7 XRF analysis data: (a) for Ni$^{2+}$ standards and for the resin sample exhausted by Ni$^{2+}$ followed by AB regeneration and heat; (b) calibration graph for Ni$^{2+}$; (c) for Ca$^{2+}$ standards and for the resin samples exhausted by Ca$^{2+}$ followed by AB regeneration and heat; (d) calibration graph for Ca$^{2+}$.]

It is easy to demonstrate the effects of added Ni$^{2+}$ in the presence of polymeric materials on the decomposition of AB in a heated solution (Fig 3.8), in which increased
bubbling was observed in the presence of added Ni\(^{2+}\). Enhanced evolution of ammonia and carbon dioxide gases from the decomposition of AB in the IEX pores seems to be the most likely explanation for the increased IEX capacity and expansion of pores in the resin.

![Image](image.jpg)

**Figure 3.8** Decomposition of AB at 80\(^{\circ}\)C: (a) AB solution with a polymeric nucleation material (Teflon) showing low gas production; (b) AB solution in the presence of Ni\(^{2+}\) and a polymeric material showing high gas production, causing the continuous flotation of the hydrophobic (Teflon) nucleation material.

Addition of CaCl\(_2\) was also found to accelerate AB decomposition in solution, with the evolution of gases and a visible precipitate of calcium carbonate. It therefore seems that both Ni\(^{2+}\) and Ca\(^{2+}\) ions caused the significant increase in pore size and IEX capacity in the presence of thermally decomposing AB. Thermal decomposition of AB in materials such as cellulose has been used industrially to open fibrous networks [133].
3.4 Conclusion

A novel method was developed for increasing the IEX capacity of a polyampholytic resin having both WA and WB groups in the same bead. Divalent cations appear to play a prime role in enhancing the exchange capacity by helping to expand the inner pore structure of these resins when using an ammonium bicarbonate solution/heating regeneration process. Ni$^{2+}$ and Ca$^{2+}$ ions were found to be more strongly bonded to these resins compared to Na$^+$ ions; this appears to be related to the changes in the internal structure of the resin during the regeneration process. These mixed-bead resins can be completely regenerated with this chemical/thermal regeneration process and could be more widely used commercially, without the need for acid and base washing and with enhanced capacity.
Chapter 4. Polyampholytic Resins: Ion-exchange Behaviour in a Continuous Process for Desalination and Regeneration using Ammonium Bicarbonate

4.1 Introduction

Polyampholytic resins containing both cationic and anionic groups can be used as ion exchange (IEX) resins for the removal of salts from neutral solutions. However, complete regeneration in situ can be difficult to achieve. This has been overcome in the past, using the Sirotherm process [66-68], by heating the resin and, more recently, using a combined process of washing with concentrated ammonium bicarbonate (AB) solution followed by heating, which produces complete regeneration of the resin [120, 121]. Unfortunately, repeated heating of polyampholytic resins can cause their degradation [134, 135]. Regeneration of polyampholytic resins with ammonium bicarbonate could overcome this problem.

The continuous-column process is a common method for water desalination using mixed-bed resins; regeneration with acid and bases is part of this [40]. However, there is an extra step: the cationic and anionic resins used have to be separated before the regeneration process. Rinsing of the mixed bed is also necessary after the acid/base regeneration process, which results in extra cost for commercial desalination.

Ammonium bicarbonate can displace salt ions bound to a resin by mass action. However, the selectivity of a cationic or anionic resin for a specific ion varies. For example, a weak-acid resin has a higher affinity for ions than a strong acid resin, while a strong base resin has a lower affinity for ions than a weak base resin [40, 44, 62].
The close physical proximity of the WA and WB groups in a polyampholytic IEX resin changes their behaviour compared with single anionic or cationic beads [120]. Therefore, the affinity of ions for cationic and anionic active sites differs, and depends on the structure of the mixed-bead resins. The relative affinities for counter-ions could be varied by altering the amount of cross linking [136] in the mixed-bead resins. As polyampholytic resins are not commonly used, clear evidence of polyampholytic selectivity for co-ions has not yet been reported. Further, the polymer matrix and the degree of cross-linking depend on the structure of the polymer; as a result, the same ion adsorption selectivity cannot be expected with polyampholytic resins.

Regeneration of polyampholytic resin in a batch process with ammonium bicarbonate followed by heating at 80°C, leads to the removal of ammonia (NH₃) and carbon dioxide (CO₂) from the IEX system (Chapter 2). These escaping gases could affect the continuous-column process by creating gaps in the close-packed resin bed. This could lead to channelling of eluent through the column and also into eluate, resulting in incomplete desalination. The thermal regeneration of the IEX resin is also limited by degradation of the resin. There is a need to examine the possibility of resin regeneration using AB without heating the resin, followed by desalination of saline. In the present study, a process is designed in which polyampholytic resins are used continuously for desalination and regeneration in a column without the need for resin heating.

4.2 Materials and Methods

4.2.1 Materials

The synthesized composite resin (XPAA-EPEI-XG) (mentioned in Section 2.2.2 in Chapter 2) was used as the IEX resin for this study.
Ammonium bicarbonate (99%) was obtained from May & Baker, Dagenham, England and 99% sodium chloride from Sigma-Aldrich, Australia. These salts were used as purchased.

4.2.2 Analysis

4.2.2.1 Determination of the Concentrations of Sodium, Ammonium, Chloride and Bicarbonate Ions

The concentrations of Na\(^+\), NH\(_4\)\(^+\) and Cl\(^-\) ions in solution were measured through their ionic activity using HQ440d-Hach ion selective electrodes (ISE). The concentration of HCO\(_3\)\(^-\) ions in the solution was measured, also by ionic activity, using an Orion Star A214-Thermo Scientific ISE. Typical errors for the measured concentrations of NH\(_4\)\(^+\), Na\(^+\), Cl\(^-\) and HCO\(_3\)\(^-\) ions, using the ISE process, were less than 0.1% of the instrument reading.

4.2.2.2 Determination of Physical and Chemical Properties of the Resin

The resin used in this study was synthesized as a new batch (i.e. not the batch used in Chapter 2 and 3), so the moisture content (Section 2.2.3.1 in Chapter 2), and the carboxylic and amine content (Section 2.2.3.3 in Chapter 2) of this resin were also measured.

4.2.3 Column Studies

4.2.3.1 IEX Studies with Sodium Chloride with a New Resin

IEX studies using the mixed-bead resin were carried out in a column using 0.1M NaCl solutions (at pH 5.6) at 20°C in a continuous-flow system at a rate of 10 ml/hr (Fig 4.1). About 9 g of the synthesized wet resin was used in each column study. Here the resin samples were packed tightly in a small-diameter column together with Milli-Q water up
to bed heights of about 30.4 cm and bed volume of 11.8 ml, taking care to exclude any air bubbles. A continuous flow of NaCl solution was passed at a fixed rate into the top of the column and 10 ml aliquot samples of the eluate were collected every hour. The eluate samples were tested for their electrical conductivity until the conductivity value was close to that of the 0.1M NaCl feed solution.

![Figure 4.1 Schematic diagram of the IEX process with mixed-bead resin in a fixed column with a continuous flow.](image)

**4.2.3.2 Resin Regeneration**

The exhausted resin in State 2 (Fig. 4.2) was taken out from the column and regenerated with 2M NH₄HCO₃ (AB) solutions for 15 hours at 20°C as a batch process, following the previously published procedure [120, 121], i.e. without heating. After this time, the
resin was converted into State 3 (Fig. 4.2). This regenerated resin was washed several times at room temperature (20°C) until the rinse water had a conductivity of Milli-Q water, which was within 1.04–1.09 µS/cm.

**Figure 4.2** Schematic diagram of the functional groups on the WA/WB polyampholytic resin used in this study in various process states.

### 4.2.3.3 Ion-exchange Studies with Sodium Chloride

The washed regenerated resin was partially dried on filter paper (moisture content about 50 w/w%), followed by 10 minutes of air drying in a filtered-air, laminar-flow cabinet, before being used again for the column tests. This partially dried resin was again packed in the column with Milli-Q water, and the desalting process again carried as above with a 0.1M NaCl feed solution. Each 10 ml of eluate was collected during continuous flow.
and tested for $\text{Na}^+$, $\text{NH}_4^+$, $\text{Cl}^-$ and $\text{HCO}_3^-$. This process was continued until the eluate concentration was that of the initial 0.1M NaCl.

The exhausted resin was regenerated and re-used several times during these IEX studies. All the regeneration/measurement procedures specified above were performed at least twice to ensure the accuracy of the results.

4.3 Results and Discussion

4.3.1 Physical and Chemical Properties of the Resin

The wet solid resin product (XPAA-EPEI-XG) had particle diameters in the range 0.3–1.2 mm and a moisture content of about 50%. The carboxylic acid content and the amine content in the resin are given in Table 4.1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>50%</td>
</tr>
<tr>
<td>Particle diameter (mm):</td>
<td></td>
</tr>
<tr>
<td>wet</td>
<td>0.30–1.2</td>
</tr>
<tr>
<td>dry</td>
<td>0.25–1.1</td>
</tr>
<tr>
<td>Carboxylic content (meq/g) dry</td>
<td>1.5–1.8</td>
</tr>
<tr>
<td>Amine content (meq/g) dry</td>
<td>2.2–2.4</td>
</tr>
</tbody>
</table>

4.3.2 Ion-exchange Behaviour

The IEX behaviour of the polyampholytic resin (XPAA-EPEI-XG) with continuous flow in a fixed column was studied, and the eluted amounts of both Na$^+$ and Cl$^-$ ions in the first IEX cycle is given in Fig. 4.3. It was found from previous studies that the eluent concentrations of Na$^+$ and Cl$^-$ ions were equal when equilibrated with NaCl solutions.
for the newly synthesized polyampholytic resins [120]. The maximum NaCl sorption density for the polyampholytic resin was found to be about 0.33 mmol/g (dry wt) when the resin was first exposed to 0.1M NaCl in these column studies.

![Figure 4.3](image)

**Figure 4.3** Eluted NaCl as a function of the volume of 0.1M NaCl passing through the mixed-bead resin at 20°C in the first IEX study.

### 4.3.3 Resin Regeneration

The exhausted resins were then regenerated using 2M AB solution in a batch process at room temperature. That is, the resin was regenerated without heating, which is known to cause degradation of these resins. Regeneration of the resin was performed initially as a batch process with AB, followed by washing with Milli-Q water to make sure the resin contained only the adsorbed AB. This was important, as it allowed a clear interpretation of the subsequent IEX process with NaCl.

After the resins were regenerated with AB solution, they were used again for the IEX studies. The IEX behaviour of the resin was found to have changed markedly in
that the inlet feedwater of 0.1 M NaCl was converted into an outlet solution with a similar concentration of NH₄Cl, as can be seen in Table 4.2 and Fig. 4.4. Clearly, Na⁺ ions were strongly adsorbed and HCO₃⁻ ions were strongly retained by the AB-regenerated resin.

**Table 4.2** Concentrations of NH₄⁺, Na⁺, Cl⁻ and HCO₃⁻ in each 10 ml of eluant sample during the desalination of a 0.1 M NaCl solution using regenerated resin.

<table>
<thead>
<tr>
<th>Volume of 0.1 M NaCl/ml</th>
<th>Eluted NH₄⁺/M</th>
<th>Eluted Na⁺/M</th>
<th>Eluted Cl⁻/M</th>
<th>Eluted HCO₃⁻/M</th>
<th>Eluted NH₄⁺/M</th>
<th>Eluted Na⁺/M</th>
<th>Eluted Cl⁻/M</th>
<th>Eluted HCO₃⁻/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0003</td>
<td>0.0000</td>
<td>0.0009</td>
<td>0.0003</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0010</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.0195</td>
<td>0.0017</td>
<td>0.0305</td>
<td>0.0008</td>
<td>0.0118</td>
<td>0.0019</td>
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<td>30</td>
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<td>0.0043</td>
<td>0.0648</td>
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<td>0.1256</td>
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<td>0.0989</td>
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<td>0.0696</td>
<td>0.0007</td>
<td>0.0744</td>
<td>0.0062</td>
<td>0.0721</td>
<td>0.0005</td>
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<tr>
<td>50</td>
<td>0.1122</td>
<td>0.0053</td>
<td>0.0885</td>
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<td>0.0850</td>
<td>0.0066</td>
<td>0.0896</td>
<td>0.0005</td>
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<tr>
<td>60</td>
<td>0.0867</td>
<td>0.0057</td>
<td>0.0935</td>
<td>0.0006</td>
<td>0.1656</td>
<td>0.0061</td>
<td>0.0870</td>
<td>0.0005</td>
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<td>70</td>
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<td>0.0056</td>
<td>0.0930</td>
<td>0.0005</td>
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<td>0.0856</td>
<td>0.0065</td>
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<td>0.0005</td>
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<td>0.1606</td>
<td>0.0066</td>
<td>0.0963</td>
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<td>100</td>
<td>0.1261</td>
<td>0.0057</td>
<td>0.0935</td>
<td>0.0006</td>
<td>0.1794</td>
<td>0.0059</td>
<td>0.0958</td>
<td>0.0005</td>
</tr>
<tr>
<td>110</td>
<td>0.1489</td>
<td>0.0060</td>
<td>0.0958</td>
<td>0.0005</td>
<td>0.0778</td>
<td>0.0109</td>
<td>0.0952</td>
<td>0.0004</td>
</tr>
<tr>
<td>120</td>
<td>0.0961</td>
<td>0.0067</td>
<td>0.0989</td>
<td>0.0004</td>
<td>0.1617</td>
<td>0.0089</td>
<td>0.0961</td>
<td>0.0004</td>
</tr>
<tr>
<td>130</td>
<td>0.0867</td>
<td>0.0061</td>
<td>0.0986</td>
<td>0.0004</td>
<td>0.0933</td>
<td>0.0069</td>
<td>0.0958</td>
<td>0.0004</td>
</tr>
<tr>
<td>140</td>
<td>0.0789</td>
<td>0.0060</td>
<td>0.0992</td>
<td>0.0005</td>
<td>0.0794</td>
<td>0.0066</td>
<td>0.0977</td>
<td>0.0005</td>
</tr>
<tr>
<td>150</td>
<td>0.1133</td>
<td>0.0064</td>
<td>0.0986</td>
<td>0.0005</td>
<td>0.0678</td>
<td>0.0060</td>
<td>0.0989</td>
<td>0.0005</td>
</tr>
<tr>
<td>160</td>
<td>0.1028</td>
<td>0.0073</td>
<td>0.0989</td>
<td>0.0005</td>
<td>0.0967</td>
<td>0.0150</td>
<td>0.0994</td>
<td>0.0004</td>
</tr>
<tr>
<td>170</td>
<td>0.1233</td>
<td>0.0081</td>
<td>0.0992</td>
<td>0.0004</td>
<td>0.0889</td>
<td>0.0100</td>
<td>0.0994</td>
<td>0.0005</td>
</tr>
<tr>
<td>180</td>
<td>0.1017</td>
<td>0.0088</td>
<td>0.0997</td>
<td>0.0004</td>
<td>0.0850</td>
<td>0.0110</td>
<td>0.0997</td>
<td>0.0005</td>
</tr>
<tr>
<td>190</td>
<td>0.0789</td>
<td>0.0103</td>
<td>0.0004</td>
<td>0.1100</td>
<td>0.0107</td>
<td>0.0004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.0806</td>
<td>0.0109</td>
<td>0.0004</td>
<td>0.0928</td>
<td>0.0143</td>
<td>0.0004</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to Table 4.2, the initial concentrations of NH₄⁺ were low in the product water. The passage of NaCl led to an increase in the concentration of NH₄⁺ in the eluate. Finally, the NH₄⁺ became less concentrated in the eluate and the Na⁺ more concentrated, reaching a maximum concentration as mentioned, in the product water. At this point, the resin had become completely depleted and requires regeneration.
Figure 4.4 Eluted amounts of NH\text{\textsubscript{4}}\textsuperscript{+}, Na\textsuperscript{+}, Cl\textsuperscript{-} and HCO\textsubscript{3}\textsuperscript{-} as a function of the volume of 0.1M NaCl passing through the mixed-bead resin at 20°C after the first regeneration.

It is also clear from these results that the total number of sites available for Na\textsuperscript{+} adsorption from 0.1M NaCl feed solution was substantially increased after regeneration with AB solution. This was demonstrated by the volume of 0.1M NaCl that could be passed through the column before the eluate reached the same concentration as the inlet solution. This volume was about 170 ml for the regenerated resin, compared to about 40ml for the new resin. The presence of AB adsorbed onto the resin sites appears to have increased the adsorption of Na\textsuperscript{+} at cationic sites in the polymer matrix and strong holding of HCO\textsubscript{3}\textsuperscript{-} to the resin. Two explanations are possible for this IEX behaviour. One depends upon the selectivity of ions towards polyampholytic resins, while the second concerns the affinity of active sites of the resin for counter-ions during the IEX process. This will be discussed further in Section 4.3.4 and 4.3.5. The results also show that the levels of sorption/desorption of Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, Cl\textsuperscript{-} and HCO\textsubscript{3}\textsuperscript{-} in the regenerated
resins after the second and third regenerations were consistent (Fig. 4.5, Fig. 4.6 and Table 4.2).

**Figure 4.5** Eluted amounts of NH₄⁺, Na⁺, Cl⁻ and HCO₃⁻ as a function of the volume of 0.1M NaCl passing through the mixed-bead resin at 20°C after the second regeneration.

**Figure 4.6** Eluted amounts of NH₄⁺, Na⁺, Cl⁻ and HCO₃⁻ as a function of the volume of 0.1M NaCl passing through the mixed-bead resin at 20°C after the third regeneration.
The results of these continuous-flow adsorption studies following AB regeneration indicate that the resin is efficient at converting a 0.1M NaCl feedwater solution to NH₄Cl solution following regeneration of the resin by 2M NH₄HCO₃ without heating. The sorption density of Na⁺ ions increased considerably following the regeneration process but the density of Cl⁻ ions seemed to remain the same (Table 4.3). The HCO₃⁻ ions also seem to be retained by the resin following AB regeneration without heating.

Table 4.3 Sorption densities of Na⁺ and Cl⁻ on mixed-bead resins exposed to 0.1M NaCl solution.

<table>
<thead>
<tr>
<th>State of the Resin</th>
<th>Sorption Density (meq/g) dry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na⁺</td>
</tr>
<tr>
<td>Initial</td>
<td>0.33</td>
</tr>
<tr>
<td>After Regeneration with AB at room temperature</td>
<td>3.4</td>
</tr>
</tbody>
</table>

4.3.4 Preferential Adsorption of Ions by the Mixed-bead Resin

Generally, for SA-cationic resins, Na⁺ ions have higher selectivity over NH₄⁺ ions and for SB-anionic resins, Cl⁻ has higher selectivity over HCO₃⁻ ions [62]. However, for WA cationic resins this selectivity of ions is not the same and WA resins cannot be expected to have a similar selectivity as mentioned for SA resins (see Section 1.2.4 in Chapter 1). For the regenerated or AB saturated polyampholytic resin used in this study, this selectivity was found to be high for both Na⁺ and HCO₃⁻ ions. Therefore, it appears to be that this mixed bead resin has a different selectivity for both Na⁺ and HCO₃⁻ compared to SA and SB resins. Ions with greater ability to polarize, ions that react strongly with the IEX sites of the resin and ions that can form complexes with other counter-ions also play major roles in this case. Furthermore, it shows that when a mixed-
bead resin consists of both cationic and anionic groups in close proximity, it behaves in a manner different from single-bead anionic resins. The presence of tertiary amine groups adjacent to the carboxylic groups possibly helps to keep the HCO$_3^-$ groups attracted to the binding sites by forming additional hydrogen bonds internally (Fig. 4.7). Therefore, in mixed bead resins, there is a greater binding of HCO$_3^-$ ions, which show higher selectivity to the anionic sites than Cl$^-$ ions.

**Figure 4.7** Schematic diagram of the formation of a hydrogen bond between the HCO$_3^-$ and carboxylic group present in the resin.

### 4.3.5 Effect of Counter-ions on the IEX Process

Retention of HCO$_3^-$ in the resin with a polyampholytic nature could possibly attract counter-ions in the solution during the IEX process. Rapid adsorption of Na$^+$ has been observed in the presence of ammonium bicarbonate in this study. This may due to the formation of complexes or chelation [44] of ions in the resin. Other studies show that the presence of cationic resin together with anionic resin facilitates the adsorption of anions into the resin [109]. This could be a reason for the retention of HCO$_3^-$ in the resin during the desalination of NaCl, but other possible facts also need to be considered.
Complete removal of NH$_4^+$ and HCO$_3^-$ from the polyampholytic resins provided consistent adsorption levels of Na$^+$ and Cl$^-$ for the initial and AB-regenerated resins in previous studies (Chapter 2). This confirms that the presence of AB in the resin contributes to the enhanced adsorption of Na$^+$. The adsorption of counter-ions can be controlled by varying the amount of cross-linking in the resin. The synthesized polyampholytic resin has a better absorptivity of AB, which led to more adsorption of Na$^+$ into the resin after the regeneration.

### 4.3.6 A Complete Desalination Process using Polyampholytic Resins

The remarkable properties shown by the AB-regenerated polyampholytic resin suggests that continuous flow through a stationary-phase column could be used to convert relatively high-concentration NaCl solutions (e.g. 0.1M) to NH$_4$Cl solutions. This opens up the possibility of passing the product solution through a typical, single anionic-resin bed, pre-saturated with HCO$_3^-$ ions, which would, in turn, produce a product solution consisting of AB. As discussed earlier, this solution could then be readily and completely decomposed at modest temperatures, using a recently developed novel process with a bubble column evaporator [137] or using the modelled multiple column distillation [32] (see further details in section 5.3.3 in Chapter 5), into ammonia and carbon dioxide, leaving desalinated water. The gases can then be collected in cold water to re-form the AB solution. This gives a complete desalination process, without the need for resin heating or substantial depletion of acids and bases, as shown schematically in Fig. 4.8. Furthermore, the anionic bicarbonate resin could be conveniently regenerated using industrial waste CO$_2$, resulting in the complete purification of saline water, together with regeneration of exhausted resins. There would be minimal chemical waste in such a process.
Figure 4.8 Proposed desalination process using mixed-bead resin, together with ammonium bicarbonate recovery.
4.4 Conclusion

A complete desalination process has been developed to remove salt from saline water using a polyampholytic resin having both weakly acid (WA) and weakly base (WB) groups in the same bead. Ammonium bicarbonate solutions can be used as the regenerant throughout this process without the need for heating of the resins. This promises a more efficient process for continuous desalination which could be widely used commercially. Polyampholytic resins exhibit a distinct selectivity for counter-ions compared to single bead WA and AB resins in which HCO$_3^-$ shows greater binding constant with this resin. Currently, polyampholytic resins are not made in commercial quantities but this study suggests that there may be substantial value in producing these resins on a much larger scale. They could also be used to adsorb many other cations (e.g. heavy metal ions) and anions for separation and purification purposes.
Chapter 5. Regeneration of Strong-acid/Strong-base Mixed-bed Resins using Ammonium Bicarbonate for a Sustainable Desalination Process


5.1 Introduction

Mixed-bed systems comprising both strong-acid (SA) (cation) and strong-base (SB) (anion) ion-exchange (IEX) resins can be used for the removal of salt to produce drinking-quality water from saline feedwater. These synthetic SA and SB IEX resins can also be used in waste treatment [138-140], and heavy-metals [141, 142] and metal-acid [143] recovery processes. An extended and updated list of ion adsorption studies performed with SA and SB IEX resins is given in Table 5.1.
Table 5.1 Adsorption studies performed with strong-acid and strong-base ion-exchange resins.

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Functional Group</th>
<th>Grade</th>
<th>Ions Studied</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite</td>
<td>Sulfonic acid</td>
<td>IR 120</td>
<td>Cu²⁺, Zn²⁺, Ni²⁺, Cd²⁺, Pb²⁺, Mg²⁺, Na⁺</td>
<td>[139, 142, 144-146]</td>
</tr>
<tr>
<td>Amberlite</td>
<td>Sulfonic acid</td>
<td>IRN 77</td>
<td>Co²⁺, Ni²⁺, Cr³⁺</td>
<td>[147, 148]</td>
</tr>
<tr>
<td>Amberlite</td>
<td>Sulfonic acid</td>
<td>IRN 97H</td>
<td>Cr³⁺</td>
<td>[149]</td>
</tr>
<tr>
<td>Amberjet</td>
<td>Sulfonate</td>
<td>1200H</td>
<td>Cr³⁺</td>
<td>[149]</td>
</tr>
<tr>
<td>Amberjet</td>
<td>Sulfonic acid</td>
<td>1500H</td>
<td>Cr³⁺</td>
<td>[149]</td>
</tr>
<tr>
<td>Dowex</td>
<td>Sulfonic acid</td>
<td>50W</td>
<td>Cu²⁺, Zn²⁺, Ni²⁺, Cd²⁺, Pb²⁺</td>
<td>[150]</td>
</tr>
<tr>
<td>Lewatit</td>
<td>Quaternary amine</td>
<td>MP 500</td>
<td>CrO₄²⁻, HCrO₄⁻</td>
<td>[141]</td>
</tr>
<tr>
<td>Lewatit</td>
<td>Quaternary amine</td>
<td>K 6362</td>
<td>SO₄²⁻</td>
<td>[151]</td>
</tr>
<tr>
<td>Purolite</td>
<td>Quaternary amine</td>
<td>A520E</td>
<td>NO₃⁻, ClO₄⁻</td>
<td>[140, 152]</td>
</tr>
<tr>
<td>Amberlite</td>
<td>Quaternary amine</td>
<td>IRA 402</td>
<td>UO₂³⁺</td>
<td>[153]</td>
</tr>
<tr>
<td>Amberlite</td>
<td>Quaternary amine</td>
<td>IRA 400</td>
<td>CrO₄²⁻, SO₄²⁻, HCrO₄⁻, NO₃⁻, Cl⁻</td>
<td>[154-156]</td>
</tr>
</tbody>
</table>

Most IEX processes involve a number of resin beds in order to capture ions. Mixed-beds composed of IEX resins are suitable as they can adsorb ions in a single-step process. Regeneration of the exhausted resins in mixed-beds has to be carried out after separation of the two resins [119], mostly using acid and base washing [40]. In this process, the mixed-bed is subjected to bed expansion and fluidisation, followed by a settling of the resin, in which cation resins settle on the bottom. This is mainly because of the higher density in nature of SA resins compared to SB resins, as well as the mass of adsorbed ions increases the density of the resin. SA resins have a higher IEX capacity compared to SB resins. Thus SA resins become denser than SB resins after being
exposed to cations. A better separation of the resin layers and less resin mixing at the interface is desirable in order to achieve efficient regeneration [157]. If not, cross contamination is possible, as the regenerants interact with the wrong beads. This can result in poor-quality product water, a shorter production cycle and, in some instances, leakage of ions into the valuable process streams.

However, it is demonstrated in the present work that complete regeneration of mixed-bead resins can be achieved in situ by washing with concentrated ammonium bicarbonate (AB) solution. This process was found to be more effective than regeneration with AB using a resin heat-decomposition process, as described in Chapter 4. That is, instead of acid and base washing, AB can be used for the regeneration of such mixed-beds. This helps to save time, reduces the cost of the process and is easier to carry out. It also reduces the need to neutralize the concentrated acid and base waste solutions generated during the IEX rinsing cycle after regeneration.

Periodic inspections are also necessary for mixed-bed systems regenerated with acids and bases, as they are subjected to many washing processes [157]. With continuous use, some resin beads escape from the system, so that proper care and periodic maintenance is required. Lowering the operating cost, increasing throughput and improving product quality are the major commercial considerations in water purification using IEX resins.

Strong-acid/strong-base resins are the most commonly used IEX resins because they can be used over the entire pH range, in contrast to weak-acid (WA) and weak-base (WB) resins. SA/SB resins also experience less swelling and typically have a high thermal stability; by comparison, some WB resins are degraded when regenerated with
caustic solutions. The use of a single regenerant to regenerate these mixed beds is likely to be significantly more efficient than the existing acid/base method.

In this study, a novel regeneration process was developed, and tested for its viability and efficiency; the process uses ammonium bicarbonate regeneration in a mixed-bed system of commercially available SA and SB IEX resins.

5.2 Materials and Methods

5.2.1 Materials

A strong-acid resin (Amberlite IR 120, H\textsuperscript{+} form) and a strong-base resin (Amberlite IRA 402, Cl\textsuperscript{−} form), were used for the mixed-bed system studied in this work, purchased as analytical grade products from Sigma-Aldrich, Australia. Ammonium bicarbonate (99\%) was obtained from May & Baker, England and 99\% sodium chloride from Sigma-Aldrich, Australia.

Structures of the Amberlite IR 120 and Amberlite IRA 402 used in this study are shown in Fig. 5.1.

![Figure 5.1 Basic polymer structures of Amberlite IR 120 and IRA 402.](image-url)
Table 5.2 Basic properties of Amberlite IR 120 and IRA 402 used in this study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Amberlite IR 120</th>
<th>Amberlite IRA 402</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional group</td>
<td>Sulfonic acid</td>
<td>Quaternary amine</td>
</tr>
<tr>
<td>Matrix</td>
<td>Styrene-divinylbenzene (gel)</td>
<td>Styrene-divinylbenzene (gel)</td>
</tr>
<tr>
<td>Particle size (µm)</td>
<td>620−830</td>
<td>600−750</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>53−58</td>
<td>49−60</td>
</tr>
<tr>
<td>Capacity (meq/ml (wet bed volume))</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Cross-linkage (%)</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Operating pH</td>
<td>0−14</td>
<td>0−14</td>
</tr>
</tbody>
</table>

5.2.2 Analysis

5.2.2.1 Determination of the Concentrations of Sodium, Ammonium, Chloride and Bicarbonate Ions

The concentrations of Na\(^+\), NH\(_4\)^+ and Cl\(^-\) ions in the solutions were determined through their ionic activities using ion-selective electrodes (ISE) supplied by Hach (HQ440d-Hach). Typical errors for the measured concentrations of NH\(_4\)^+, Na\(^+\) and Cl\(^-\) ions, using the ISE process, were less than 0.1% of the instrument reading.

5.2.3 Column Studies

5.2.3.1 Resin Regeneration

Amberlite IR 120, received in its H\(^+\) form, was converted to the Na\(^+\) form by exposing it to brine solution, followed by washing with Milli-Q water to remove the excessive NaCl present at the resin. Samples of the strong-acid resin (Amberlite IR 120, Na\(^+\) form) and the strong-base resin (Amberlite IRA 402, Cl\(^-\) form) of wet weight roughly 4.2 g
and 5.4 g, respectively, were used to maintain roughly equal IEX capacity in the columns. The resin beads were mixed and packed into a thin column with Milli-Q water, without trapping any air bubbles, up to bed heights of about 14.5 cm and bed volume of 9.6 ml.

Regeneration studies for the mixed-bed resins were performed with 0.1M NH₄HCO₃ (AB) solutions (at pH 8.5) at room temperature (22°C), in a continuous-flow system at a rate of about 10 ml/hr (Fig. 5.2). The AB solution was passed through the column from the top, and each 10 ml of eluate was collected and tested for the level of Na⁺, NH₄⁺ and Cl⁻ until, the values of Na⁺ and Cl⁻ were reduced to levels less than 0.5 ppm and 0.2 ppm, respectively, and the value of NH₄⁺ was similar to that of the 0.1M NH₄HCO₃ feed solution.

**Figure 5.2** Apparatus for the study of the regeneration process in a mixed-bed system (SA/SB), in a fixed column with a continuous flow.
5.2.3.2 Desalination

The mixed-bed system regenerated by AB to State 2 (Fig. 5.3) was then exposed from the top to 0.1M NaCl solutions at 22°C and pH 5.6, in a continuous-flow system at a rate of 10 ml/hr. The eluate was collected in 10 ml samples and tested for the level of Na⁺, NH₄⁺ and Cl⁻ until it reached the values of Na⁺ and Cl⁻ for drinking quality water, as per the guidelines of the World Health Organization (WHO) [17].

Figure 5.3 Schematic diagram of the process states of the functional groups in the mixed-bed ion-exchange resin.

All of the above procedures were performed at least twice to ensure the accuracy of the results.
5.3 Results and Discussion

5.3.1 Mixed-bed Resin Behaviour with Salts

5.3.1.1 Ion-exchange Behaviour with NH₄HCO₃

The IEX behaviour of the mixed-bed SA/SB IEX resins was studied with continuous flow in a fixed column. The eluted amounts of Na⁺, Cl⁻ and NH₄⁺ in the first IEX cycle demonstrate the regeneration behaviour of these mixed-bed systems, as given in Fig. 5.4 and Table 5.3.

![Figure 5.4](image)

**Figure 5.4** Concentrations of Na⁺, Cl⁻, and NH₄⁺ in the eluate as a function of the volume of 0.1M AB feed solution to a NaCl saturated mixed-bed resin at 22°C.
Table 5.3 Amounts of Na\(^+\), Cl\(^-\) and NH\(_4^+\) in each 10 ml of eluant sample during the regeneration of exhausted mixed-bed resins and cumulative millimoles (Cum.mmol) eluted.

<table>
<thead>
<tr>
<th>Volume of 0.1M AB/ml</th>
<th>Na(^+) Eluted</th>
<th>Cl(^-) Eluted</th>
<th>NH(_4^+) Eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>M</td>
<td>Cum. mmol</td>
</tr>
<tr>
<td>10</td>
<td>164</td>
<td>0.0071</td>
<td>0.071</td>
</tr>
<tr>
<td>20</td>
<td>880</td>
<td>0.0383</td>
<td>0.454</td>
</tr>
<tr>
<td>30</td>
<td>1210</td>
<td>0.0526</td>
<td>0.980</td>
</tr>
<tr>
<td>40</td>
<td>1400</td>
<td>0.0609</td>
<td>1.589</td>
</tr>
<tr>
<td>50</td>
<td>1480</td>
<td>0.0643</td>
<td>2.232</td>
</tr>
<tr>
<td>60</td>
<td>1530</td>
<td>0.0665</td>
<td>2.897</td>
</tr>
<tr>
<td>70</td>
<td>1590</td>
<td>0.0691</td>
<td>3.589</td>
</tr>
<tr>
<td>80</td>
<td>1680</td>
<td>0.0730</td>
<td>4.319</td>
</tr>
<tr>
<td>90</td>
<td>1830</td>
<td>0.0796</td>
<td>5.115</td>
</tr>
<tr>
<td>100</td>
<td>1730</td>
<td>0.0752</td>
<td>5.867</td>
</tr>
<tr>
<td>110</td>
<td>1430</td>
<td>0.0622</td>
<td>6.489</td>
</tr>
<tr>
<td>120</td>
<td>813</td>
<td>0.0353</td>
<td>6.842</td>
</tr>
<tr>
<td>130</td>
<td>311</td>
<td>0.0135</td>
<td>6.977</td>
</tr>
<tr>
<td>140</td>
<td>112</td>
<td>0.0049</td>
<td>7.026</td>
</tr>
<tr>
<td>150</td>
<td>44.7</td>
<td>0.0019</td>
<td>7.046</td>
</tr>
<tr>
<td>160</td>
<td>14.7</td>
<td>0.0006</td>
<td>7.052</td>
</tr>
<tr>
<td>170</td>
<td>6.23</td>
<td>0.0003</td>
<td>7.055</td>
</tr>
<tr>
<td>180</td>
<td>2.08</td>
<td>0.0001</td>
<td>7.056</td>
</tr>
<tr>
<td>190</td>
<td>0.976</td>
<td>0.0000</td>
<td>7.056</td>
</tr>
<tr>
<td>200</td>
<td>0.512</td>
<td>0.0000</td>
<td>7.056</td>
</tr>
</tbody>
</table>

The cumulative amounts of Na\(^+\) and Cl\(^-\) desorbed from the resins showed that 100 ml of 0.1M AB was consumed during regeneration of the resin (Fig. 5.5). In commercial practice, the volume of AB used for the regeneration could be reduced by increasing its concentration, if necessary. Although, concentrated AB solutions, even at room temperature, can form decomposition bubbles, especially when exposed to foreign substances and even IEX materials [121]. This can create pore expansions if the AB is present inside the porous matrix of the material. Bubbling of concentrated AB solution can produce channels inside the mixed-bed resin; it is therefore important to maintain
the concentration of AB below 0.5M, at atmospheric pressure. However, larger beds operated at significantly higher pressures would suppress these bubbling effects.

![Cumulative desorption of Na⁺, Cl⁻, and NH₄⁺ in the eluate as a function of the volume of 0.1M AB feed solution to a NaCl saturated mixed-bed resin at 22°C.](image)

**Figure 5.5** Cumulative desorption of Na⁺, Cl⁻, and NH₄⁺ in the eluate as a function of the volume of 0.1M AB feed solution to a NaCl saturated mixed-bed resin at 22°C.

These results clearly demonstrate that AB has the ability to efficiently regenerate these mixed-bed resins following exhaustion by Na⁺ and Cl⁻. This suggests that the resins could be regenerated by AB without difficulty, even with modest concentrations of AB, such as 0.1M. Therefore, AB is potentially a good alternative regenerant for the recovery of exhausted resins during desalination processes.

### 5.3.1.2 Ion-exchange Behaviour with NaCl

When the AB regenerated resin was used for desalinating a 0.1M NaCl solution, it typically recovered about 60 ml of drinking-water product, containing AB, from about 9.6 g of resin (Fig. 5.6, Fig. 5.7 and Table 5.4). Typically, the eluent contained about 0.1M of AB and had a pH value of about 8.5 during the IEX process with NaCl solution,
which indicates that the ammonium and bicarbonate ions were fairly equally displaced from the resin. In these experiments, only the ammonium ion concentration was measured in the eluate, using the ISE system. This basic process can be applied to desalination in a continuous process to produce water containing AB, which can then be purified with the low-cost, low-energy bubble column evaporator (BCE) method [137] or by multiple distillation columns (MDC) [32] or by direct heating of the product solution. The decomposition gases produced could then be used to regenerate concentrated AB solutions for further re-use.

Figure 5.6 Concentration of Na\(^+\) and Cl\(^-\) in the eluate as a function of the volume of 0.1M NaCl feed solution to an AB saturated mixed-bed resin at 22°C.
Figure 5.7 Cumulative desorption of Na\(^+\) and Cl\(^-\) in the eluate as a function of the volume of 0.1M NaCl feed solution to an AB saturated mixed-bed resin at 22°C.

Table 5.4 Amounts of Na\(^+\), Cl\(^-\) and NH\(_4\)\(^+\) in each 10 ml of eluant sample during the desalination process with AB regenerated mixed-bed resins and cumulative millimoles (Cum.mmol) eluted.

<table>
<thead>
<tr>
<th>Volume of 0.1 M NaCl/ml</th>
<th>Na(^+) Eluted</th>
<th>Cl(^-) Eluted</th>
<th>NH(_4)(^+) Eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>M</td>
<td>Cum. mmol</td>
</tr>
<tr>
<td>10</td>
<td>0.631</td>
<td>0.0000</td>
<td>0.000</td>
</tr>
<tr>
<td>20</td>
<td>0.775</td>
<td>0.0000</td>
<td>0.001</td>
</tr>
<tr>
<td>30</td>
<td>0.689</td>
<td>0.0000</td>
<td>0.001</td>
</tr>
<tr>
<td>40</td>
<td>1.57</td>
<td>0.0001</td>
<td>0.002</td>
</tr>
<tr>
<td>50</td>
<td>12.8</td>
<td>0.0006</td>
<td>0.007</td>
</tr>
<tr>
<td>60</td>
<td>20.5 *</td>
<td>0.0009</td>
<td>0.016</td>
</tr>
<tr>
<td>70</td>
<td>165</td>
<td>0.0072</td>
<td>0.088</td>
</tr>
<tr>
<td>80</td>
<td>410</td>
<td>0.0178</td>
<td>0.266</td>
</tr>
</tbody>
</table>

* The maximum allowable level of sodium (Na\(^+\)) in the sample for drinking purpose according to water quality guidelines.
5.3.2 Selectivity of Ions to the Mixed-bed SA/SB Resins

IEX selectivity coefficients for various cations are quite diverse; Na\(^+\) typically has higher selectivity than NH\(_4\)\(^+\) ion [62]. However, during the IEX process, the Law of Mass Action plays a dominant role, especially for SA and SB resins. Na\(^+\) is readily replaced by NH\(_4\)\(^+\), and the process is completely reversible, as confirmed by the results obtained in this study. The IEX selectivity coefficients for anions are different, with Cl\(^-\) typically having stronger binding than HCO\(_3\)\(^-\) [62]. However, again the Law of Mass Action supports regeneration of the SA/SB mixed-bed resins, even though the relative ion-selectivity coefficients facilitate the desalting process.

5.3.3 A Complete Desalination Process without the use of Acid and Base Washing

The properties shown by the AB regenerated SA/SB mixed-bed resins suggest that the continuous-flow column processes could be used to desalinate NaCl solutions at relatively high concentrations (e.g. 0.1M or higher), producing a product solution of AB. As discussed earlier, this solution can be readily and completely decomposed at modest temperatures using a recently developed novel process [32, 137]. The gases produced, ammonia and carbon dioxide, can then be recollected in cold water to re-form a concentrated AB solution. These combined processes suggest that a complete and continuous desalination process is possible, without the need for resin heating or substantial depletion of acids and bases, as shown schematically in Fig. 5.8. This process combines the complete purification of saline water to drinking water with the regeneration of exhausted resins through a recycling process, with minimal chemical waste.
Figure 5.8 Schematic diagram for a complete desalination process using a strong-acid/strong-base (in the ratio of 2:3) mixed-bed system, in a resin filter as a pilot study. BCE and MDC are defined as bubble column evaporator and multiple distillation columns, respectively.

This process is described schematically in Fig. 5.8, where an initial mixed-bed resin, assumed to be exhausted by the adsorption of ammonium bicarbonate, is used to extract NaCl from the feedwater. The product water containing low levels of NaCl but significant levels of NH₄HCO₃ is further treated in a hot air BCE or MDC or by simple heating to produce drinking water and NH₃ and CO₂ gases. These gases are then collected in cold water to re-form the concentrated AB solution, which is then used to displace NaCl from the depleted resin to return the resin to its initial state. The displaced NaCl concentrate is discarded.

Studies have shown the energy requirements for various desalination methods (see Table 1.2 in Chapter 1). The multiple distillation columns used in Forward Osmosis with AB solutions also demonstrate the economic viability of that technique. MDC require an electrical power less than 0.25 kWh/m³ to produce the specified water.
quality, containing ammonia below 1 ppm, in the final product water [32]. Further, this method can be used for draw concentrations less than 1M, which clearly makes it suitable for use in the proposed IEX process.

The proposed resin-regeneration and desalination processes described in this work could be introduced as a cyclic adsorption process (as described in Fig. 5.8), and the regenerant then used to make new draw solution. Most importantly, the proposed process does not require special treatment of the resulting concentrated waste water, such as neutralization, precipitation or separation, which is crucial in acid-base IEX resin regeneration. Therefore, the proposed method should be economically viable and able to provide efficient regeneration and desalination in a wide-range of water treatment applications.

5.4 Conclusion

A complete, simple desalination process was developed to remove salt from saline water using commercially available strong-acid and strong-base resins combined together in a single column. Ammonium bicarbonate solution was used as a regenerant throughout this process without the need for heating the resins, which offers a more effective process for continuous desalination to produce drinking quality water. The proposed complete desalination process could be widely used commercially because it does not require the costly consumption of acid and base solutions for resin regeneration.
Chapter 6. A Model for Ion-exchange Behaviour of Polyampholytic Resins using Polystyrene Latex


6.1 Introduction

Synthetic polyampholytic resins have been used in ion-exchange (IEX) studies but have been largely neglected over the last few decades because mixed beds of anion and cation-exchanging beads are easier to regenerate. The ion adsorption behaviour of such resins composed of weak acid (WA) and weak base (WB) functionalities have been determined in batch equilibrium studies [53, 67, 68, 76, 77, 81]. However, there is little known of their dynamic properties, that is in fixed-bed, continuous-flow systems [53, 54, 78, 79], probably because of the difficulty in achieving their complete regeneration. Our recent studies have shown that ammonium bicarbonate (AB) can be used to completely regenerate WA and WB polyampholytic resins [120, 121]. Therefore, it is useful to develop an ionization model to describe the adsorption/desorption behaviour of such resins using a polystyrene latex colloid synthesized with the same WA/WB groups, in close proximity on the surface of each latex particle.

Polyampholytic latices with small particle sizes, similar to polyampholytic IEX resins, have been synthesized recently consisting of carboxylic and tertiary amine groups [158]. Studies have shown that polyampholytic polystyrene latex can also be used for metal-ion adsorption, and it has the ability to adsorb various divalent cations
In addition, these latices have the ability to exchange ions with both cations and anions [159]. This behaviour has also been found with protein molecules and biomolecules which have both cationic and anionic sites that have been shown to bind with multivalent ions [160-162]. A large number of factors influence the ion-adsorption properties of these kinds of polyampholytic ion-exchangers, including temperature [53, 120, 158] duration of equilibration [163], ionic strength of the electrolyte solutions [81, 82], pH [158, 163, 164], the ratio of acid to basic groups and the affinities of counter-ions [64, 66, 80-83].

The pH of the IEX system plays a controlling role during the ion-adsorption process with WA/WB latex [158], as the ionization of the active sites on the latex surface is pH dependent. Therefore, IEX studies need to be performed considering the pH of the electrolyte solutions. This will also help us to understand the IEX behaviour of counter-ions with other exchanging ions/groups.

Surface ion adsorption models can be used to describe the surface-charge behaviour of polyampholytic latex particles, determined from zeta-potential measurements taken in an appropriate range of solutions. In this case, when the latex particles are immersed in an aqueous ionic solution (i.e. with high-dielectric constant) there is a selective adsorption or desorption of ions to/from the surface by chemical interaction. This creates a surface charge and a diffuse layer of oppositely charged ions in solution, retained close to the charged surface. The ions which are free to move within the electric field generated by the charged surface are loosely associated with the charged surface and move in the fluid according to electric attraction and thermal motion. This creates the “diffuse electrical double-layer” around a charged surface. The nominal thickness of this double-layer in the electrolyte solution is called the Debye length ($\kappa^{-1}$) and this distance changes with the concentration of the electrolyte solution.
Table 6.1 Debye lengths of NaCl solutions at different concentrations at 25°C.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>0.1</th>
<th>0.01</th>
<th>0.001</th>
<th>0.0001</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye Length (nm)</td>
<td>0.96</td>
<td>3.04</td>
<td>9.62</td>
<td>30.4</td>
</tr>
</tbody>
</table>

Surfaces become charged due to the adsorption or desorption of ions, and the surface charge density can be calculated from the amount of electrical charge \(q\), present on a surface of given area. The surface charge density on a particle also determines its surface potential, for a given electrolyte solution. The experimentally measured zeta potential values, obtained using electrokinetic methods, are generally of slightly lower magnitude than the true surface potentials, but in some systems there is excellent agreement between zeta and the surface potentials, so it is often assumed that these two potentials are the same [165].

Measured zeta potentials can be simply converted to surface-charge densities if the radius of curvature (i.e. radius \(a\)) of the (latex) particles is large compared with the Debye length \((\kappa^{-1})\) of the solution. That is, for large values of the parameter \(\kappa a\) (>50), a surface flat-plate model can be used [166], whereas for lower \(\kappa a\) values, more complicated models have to be used to take particle curvature into account [167, 168].

Polyampholytic latices are zwitterionic, and mostly exhibit a pH of net zero charge (pzc) or an isoelectric point (IEP). Surface studies and ionization models can be used to calculate the IEP of such latices and the behaviour of adsorption sites present on the particles [169-171] in different solution conditions. The affinities of ions for surfaces and the ionization constants of charged groups both strongly correlate with the pH [158].

The ionization behaviour of carboxylic and amine groups on amino-acid molecules [125, 126] in aqueous solution can be used to explain the ionization
behaviour of polyampholytic resins at different pH and temperatures [120], but such simple molecules are unlikely to represent the IEX behaviour of solid resins. Therefore, surface studies of synthesized polyampholytic latices were selected here as a model system for the study of the ionization behaviour of the amine and carboxylic groups in these resins.

The ion-adsorption or ion-exchange process can be very complicated, and depends on both the adsorbing ion and on the chemical and physical properties of the substrate. Hydrolysis of metal ions influences the affinity of these ions for adsorption to a surface [172, 173]. Surface complexation mechanisms can prime the metal ion for adsorption to surfaces by forming chemical bonds with the functional groups present in the adsorbent surface [174, 175]. Different adsorbent materials, such as synthetic polymers, metal oxides, activated carbon, natural materials and biological substrates, have been studied to explain the adsorption behaviour of cations and anions and the affinity of ions for surfaces [158, 175]. Some of the studies have been performed on a qualitative basis and the ionization behaviour of active groups has also been quantitatively studied [173] in an attempt to explain this adsorption behaviour. Metal-carboxyl ligand stability constants for metal ion adsorption onto biological substrates have also been determined [176-178].

In the present study, ionization and binding constants were determined to help explain the adsorption of ions onto combined WA/WB resins. Polyampholytic latex colloids with WA and WB surface groups were synthesized and used as a model for these resins. Ion-exchange and adsorption behaviour with sodium chloride and AB solutions were studied. Measurements of zeta potentials of the latex in a wide range of solutions were used to characterise the surface charge properties of this latex surface
and hence create a charging model to describe the IEX process for surfaces having both WA and WB groups, similar to the polyampholytic resins.

6.2 Materials and Methods

6.2.1 Materials

Styrene (99%), methacrylic acid (99%), diethylaminoethyl methacrylate (99%) and ammonium persulfate (98%) were used during this synthesis. All the chemicals were purchased from Sigma-Aldrich, Australia, as reagent grade.

Ammonium bicarbonate (99%) from May & Baker, Dagenham, England and sodium chloride (98%) from Sigma-Aldrich, Australia, were used as purchased. Sodium ion, chloride ion and ammonium ion standard solutions, of 100 ppm and 1000 ppm, were obtained from Hach Pacific, Australia.

6.2.2 Synthesis of Polyampholytic Polystyrene Latex Colloids

The polyampholytic latex samples were synthesized following the previously published procedure [158, 179]. Here, 60 g of styrene monomer, 6 g of methacrylic acid and 12.9 g of diethylaminoethyl methacrylate were mixed in a baffled flask and the reaction mixture adjusted to pH 1.5 using nitric acid (HNO₃). The total volume of the reaction mixture was maintained at 600 ml. This mixture was sparged with nitrogen gas (AR) overnight to remove any dissolved O₂ from the system, prior to addition of the initiator, 0.3 g of ammonium persulfate. The reaction mixture was then heated at 70°C in the presence of N₂ gas purging, and the mixture stirred continuously at 60 rpm for 24 hours (Fig. 6.1). The resulting suspension was cooled and filtered through glass wool to remove any coagulum present in the reaction mixture. The final product was stored in a glass bottle at room temperature.
Figure 6.1 Schematic diagram (a) and photograph (b) of the reaction apparatus used for the preparation of latex solutions.

The synthesized latex samples were then purified by repeated dispersion in water, followed by centrifuging [158, 180] in a Sigma 2-6 centrifuge at a relative centrifugal force (rcf) of $2.4 \times g$, using initially 4.5 ml of the samples with 35.5 ml of Milli-Q water,
followed by several more dispersions in water, until the conductivity of the supernatant remained constant at less than 25 µS/cm.

### 6.2.3 Analysis

#### 6.2.3.1 Surface Area of the Latex Particles

The specific surface area of the latex was determined by the Bruner-Emmett-Teller (BET) method using a Micrometrics TriStar 3000. The samples were initially freeze-dried, vacuum dried at 80°C in a vacuum compartment, then used for adsorption/desorption studies with nitrogen gas. The BET surface area was obtained. The particle size of the (assumed spherical) colloid particle was then estimated from the surface area.

#### 6.2.3.2 Morphology of the Latex Particles

The morphology of the latex particles was studied using transmission electron microscopy (TEM, JEOL 1400) and images were captured with a GATAN digital camera interfaced with GATAN digital micrograph software. The latex samples were diluted 100,000× in Milli-Q water, applied to a formvar-coated copper grid, and allowed to dry. The samples were then examined using the TEM, and images captured to measure the particle size of the latex.

#### 6.2.3.3 Particle Density of the Latex Dispersions

The particle density of the latex was determined by drying a known volume of purified latex solution in an oven at 104°C for 18 hours. The initial and the final weights of the latex samples were measured and the particle density calculated based on the particle size obtained from TEM studies.
6.2.3.4 Variation in Zeta Potentials of the Polyampholytic Latex with pH

Dynamic light scattering (DLS) analysis was used in this study, and zeta-potential measurements for the latex samples in different electrolyte solutions were obtained using a Malvern Zetasizer Nano-ZS particle analyser with zetasizer software 6.32. Samples of about 1 ml were loaded into polystyrene cells using syringes in a laminar flow cabinet (i.e. ensuring free from dust particles) and the measurements were recorded.

The purified latex was diluted 2,500× in Milli-Q water, then used for pH studies. pH studies with this polystyrene latex were carried out in the presence of 10 mM NaCl. The samples were prepared using 15 ml of latex, with the total volume of the mixture 20 ml. The pH of the colloid was adjusted using 0.1M, 0.01M and 0.001M NaOH and HCl solutions. The samples were prepared at pH 2.0, 4.0, 5.6, 8.0, 10.0 and 12.0, and the zeta potentials measured after 30 minutes equilibration at 22°C.

6.2.3.5 Measurement of the Zeta Potentials and Equilibrium Ion Adsorption on the Latex in Electrolyte Solutions

In this study, cation and anion adsorption onto the latex was studied by measuring the concentrations of Na⁺, NH₄⁺ and Cl⁻ ions in the equilibrated solutions through their ionic activities using ion-selective electrodes (ISE) supplied by Hach (HQ440d-Hach). The concentration of HCO₃⁻ ions in the solution was measured, also by ionic activity, using an Orion Star A214-Thermo Scientific ISE. Typical errors for the measured concentrations of NH₄⁺, Na⁺, Cl⁻ and HCO₃⁻ ions, using the ISE process, were less than 0.1% of the instrument reading.

Purified 5 ml latex samples were equilibrated with different salt solutions, resulting in a total volume of 10 ml. A series of NaCl solutions (0.1–0.6M) at pH
5.7−5.9 and NH₄HCO₃ solutions (0.1−0.5M) at pH 8 were equilibrated with the colloid samples for 30 minutes. The zeta potential for each sample was measured after diluting the samples 1,000× in Milli-Q water at 22°C. The equilibrated colloid dispersions were filtered through 0.1 µm filter, and the concentrations of Na⁺, NH₄⁺, Cl⁻ and HCO₃⁻ ions were measured in the filtrates to determine the amount of ions adsorbed to the latex.

Another set of latex samples, pre-treated with 0.5M NaCl solution followed by washing with Milli-Q water and centrifuging, was used for equilibrium studies in 1 mM NaCl and in a series of NH₄HCO₃ solutions (0.1M–0.5M) at pH 8.2–8.3. The zeta measurements were taken after diluting the samples 1,000× in Milli-Q water; the concentrations of Na⁺, NH₄⁺, Cl⁻ and HCO₃⁻ ions were measured in the dispersion filtrate, and the amount of adsorbed ions was determined using those values.

Another series of latex samples was pre-treated with 0.5M NH₄HCO₃, washed with Milli-Q water and centrifuged several times. The samples were then equilibrated with a series of NaCl solutions (0.1M–0.5M) at pH 6. Zeta measurements again were obtained after diluting 1,000× in Milli-Q water and the concentrations of Na⁺, NH₄⁺, Cl⁻ and HCO₃⁻ ions were measured in the dispersion filtrate, to determine the amount of adsorbed ions.

6.3 Results and Discussion

6.3.1 Particle Size and the Morphology of the Polyampholytic Latex

The TEM studies showed that the particle diameter of the polyampholytic latex was about 100 nm (Fig. 6.2); whereas, the particle size calculated using BET measurements was about 110 nm (Table 6.2), which represents a reasonable agreement. The TEM
images also showed the spherical shape of the latex particles. In later calculations, an average latex particle radius of 55 nm was assumed.

Figure 6.2 TEM images of the synthesized latex particles.

Table 6.2 Properties of the polyampholytic latex.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>100–110</td>
<td>nm</td>
</tr>
<tr>
<td>BET surface area</td>
<td>25.9 ± 0.1</td>
<td>m²/g</td>
</tr>
<tr>
<td>Particle density of raw product</td>
<td>4.66×10¹¹</td>
<td>particles/ml</td>
</tr>
</tbody>
</table>

6.3.2 Variation in the Zeta Potential of the Polyampholytic Latex with pH

Zeta potentials as a function of pH were studied, and it was found that the latex had an IEP of 6.9, as shown in Fig. 6.3. Similar curves have been obtained for this kind of ampholytic latex, as published in other studies [158, 181]. The theoretical zeta potential curve was obtained using the model explained in Section 6.3.3.
The zeta potentials of spherical latex particles in a range of electrolyte solutions and pH values were studied, at 22°C. The zeta potentials and the Debye lengths ($\kappa^{-1}$) of each electrolyte solution were used to calculate the corresponding surface-charge densities ($\sigma_0$) using Equation (6.1), assuming that the solution Debye length was significantly less than the radius of the particles. This is because Equation (6.1) was derived for flat surfaces. Since the particles used in this study were about 55 nm in radius, this equation is reasonable for Debye lengths of about 5 nm or less. The background electrolyte of 10 mM NaCl used in this study corresponds to a Debye length of 3.04 nm and a $\kappa a$ value of about 20.

The surface-charge density on a flat isolated surface immersed in 1:1 electrolyte solution [165] is given by the following equation, assuming that the measured zeta potential is equal to the surface potential ($\Psi_0$):

$$\sigma_0 (\text{C/m}^2) = \frac{3.57 \times 10^{-11}}{\kappa^{-1}(\text{m})} \times \sinh[\Psi_0 (\text{mv}) \times 0.01946]$$  \hspace{1cm} (6.1)
The Debye lengths can be readily calculated for any simple electrolyte from the simple relation:

\[
\frac{1}{\kappa} \text{(nm)} = \frac{1.0557 \times 10^{13}}{\sqrt{\Sigma_i C_i(B)Z_i^2}} \tag{6.2}
\]

where \( C_i(B) \), the bulk ion concentration at 25°C, is in number/m\(^3\) and \( z_i \) the valency of the ion.

For 1:1 electrolytes this becomes:

\[
\frac{1}{\kappa} \text{(nm)} = \frac{0.304}{\sqrt{M}} \tag{6.3}
\]

where \( M \) is the salt concentration in mol/l at 25°C.

However, calculation of surface-charge densities (\( \sigma \)) for situations where \( \kappa a < 10 \) requires the equation developed by White and Ohshima [168] which for any \( z:z \) electrolyte, is given by:

\[
\sigma = \frac{2\varepsilon_r\varepsilon_0 kT}{z|q|} \sinh \left( \frac{z|q|\zeta}{2kT} \right) \left[ 1 + \frac{1}{\kappa a} \cosh^2 \left( \frac{z|q|\zeta}{4kT} \right) + \frac{1}{(\kappa a)^2} \frac{8\ln \left[ \cosh \left( \frac{z|q|\zeta}{4kT} \right) \right]}{\sinh^2 \left( \frac{z|q|\zeta}{2kT} \right)} \right]^{1/2} \tag{6.4}
\]

For the case of a flat surface (\( \kappa a >> 1 \)), this becomes:

\[
\sigma = \frac{2\varepsilon_r\varepsilon_0 kT}{z|q|} \sinh \left( \frac{z|q|\zeta}{2kT} \right) \tag{6.5}
\]

The Debye length of any solution is given by:

\[
\kappa^{-1} = \left( \frac{\varepsilon_r\varepsilon_0 kT}{q^2 \Sigma_i C_i(B)Z_i^2} \right)^{1/2} \tag{6.6}
\]

which for \( z:z \) electrolytes becomes:

\[
\kappa^{-1} = \left( \frac{\varepsilon_r\varepsilon_0 kT}{2q^2 C(B)Z^2} \right)^{1/2} \tag{6.7}
\]

where \( z \) is the valency of the ion, \( q \) is the electric charge of an electron, \( \zeta \) is the zeta potential, \( k \) is the Boltzmann constant and \( T \) absolute temperature. \( \varepsilon_0 \) is the vacuum
dielectric constant (permittivity of free space) and $\varepsilon_r$ is the relative dielectric constant of the solution.

Table 6.3 shows the surface-charge densities obtained for the synthesized polyampholytic latex particles according to surface flat-plate model and the equations of White and Ohshima for smaller particles. The theoretical flat-plate model was calculated using the theoretical zeta potential values as mentioned in Fig. 6.3.

**Table 6.3** Surface charge densities calculated according to the surface flat-plate model and the White and Oshima model for latex particles with 55 nm radius in 10 mM NaCl at different pH (i.e. $\kappa a \sim 20$).

<table>
<thead>
<tr>
<th>pH</th>
<th>Theoretical Flat-plate Model (C/m$^2$)</th>
<th>Calculated Flat-plate Model (C/m$^2$)</th>
<th>Calculated White and Oshima Model (C/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>7.69×10$^{-3}$</td>
<td>8.39×10$^{-3}$</td>
<td>8.70×10$^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>7.38×10$^{-3}$</td>
<td>7.14×10$^{-3}$</td>
<td>7.51×10$^{-3}$</td>
</tr>
<tr>
<td>6</td>
<td>2.04×10$^{-3}$</td>
<td>3.40×10$^{-3}$</td>
<td>3.59×10$^{-3}$</td>
</tr>
<tr>
<td>8</td>
<td>−2.27×10$^{-3}$</td>
<td>−1.67×10$^{-3}$</td>
<td>−1.77×10$^{-3}$</td>
</tr>
<tr>
<td>10</td>
<td>−7.63×10$^{-3}$</td>
<td>−8.26×10$^{-3}$</td>
<td>−8.67×10$^{-3}$</td>
</tr>
<tr>
<td>12</td>
<td>−9.59×10$^{-3}$</td>
<td>−1.10×10$^{-2}$</td>
<td>−1.14×10$^{-2}$</td>
</tr>
</tbody>
</table>

### 6.3.3 Development of an Ion Adsorption Model for H$^+$ on Amphoteric Latex Surfaces

We can use the measured zeta potentials (surface potentials) of the particles in different pH and electrolyte solutions in the Boltzmann ion-distribution model in a theoretical analysis using the Law of Mass Action via numerical solutions, to describe an ion adsorption model (H$^+$) for surface amines and carboxyl groups.
A simple surface ionization model was developed based on the surface-ion binding constants for H\(^+\) ions, when immersed in aqueous NaCl solution. The ion adsorption processes and the corresponding equilibrium constants are given below.

\[
\text{SCOOH} \leftrightarrow H^+ + \text{SCOO}^- \\
K_{\text{SCOOH}} = \frac{[\text{SCOO}^-] \exp\left(-\frac{|q_e|\psi_0}{kT}\right)}{[\text{SCOOH}]} \tag{6.8}
\]

\[
\text{SNR}_2H^+ \leftrightarrow H^+ + \text{SNR}_2 \\
K_{\text{SNR}_2} = \frac{[\text{SNR}_2]^+}{[\text{SNR}_2H^+] \exp\left(\frac{|q_e|\psi_0}{kT}\right)} \tag{6.9}
\]

where S corresponds to the surface binding group and [SNR\(_2\)], [SNR\(_2\)H\(^+\)], [SCOOH] and [SCOO\(^-\)] are the surface site densities of each group. The total site densities [SCOOH] and [SNR\(_2\)] are input as variables in the calculation, with the two binding or dissociation constants. [H\(_B^+\)] is the concentration of hydrogen ions in the bulk solution.

The surface-charge density of the amphoteric latex is defined below:

\[
\sigma_{\text{calc}} \left(\frac{C}{m^2}\right) = |q|[\text{SNR}_2H^+] - |q| [\text{SCOO}^-] \tag{6.10}
\]

In these ion adsorption equations, it is assumed that the pH is the same throughout the solution, that is, within the bulk solution and next to the surface, because pH is defined in terms of the activity of the hydrogen ion (see Equation 6.11) not its number density or concentration. In each case, in the ion adsorption equations given above the bulk hydrogen ion concentrations were used, which for the dilute solutions considered in this work, corresponds closely to the ion activities. The exponential Boltzmann distribution terms arise, in each case, from the effect of the surface electrostatic potentials on the chemical potential of each of the charged surface groups (i.e. SCOO\(^-\) and SNR\(_2\)H\(^+\)).

\[
pH = -\log_{10}(a_{H^+}) \tag{6.11}
\]
Since, at equilibrium, the ion activity $a_{H^+}$ should be the same throughout the solution, so should the pH value. Earlier models have assumed that the pH is different next to the charged surfaces. It is interesting, however, that removing this assumption still produces the same ion adsorption equations (see above), if we add the reasonable assumption that the chemical potentials of all charged surface groups are affected by the surface electrostatic potential. This different view changes the way we develop ion surface equilibria equations. In this work, we have assumed that the pH is the same throughout the solution. These arguments are illustrated below using the fundamental and important case of the ionization of $SCOOH$ groups immersed in aqueous solution.

We can describe equilibrium in terms of the chemical potentials ($\mu$) of solution species and surface species. Thus, at equilibrium:

$$\mu_{H^+} + \mu_{SCOO^-} = \mu_{SCOOH}$$  \hspace{1cm} (6.12)

and therefore,

$$\mu_{H^+}^0 + kT \ln a_{H^+} + \mu_{SCOO^-}^0 + kT \ln \theta - |q_e|\psi_0 = \mu_{SCOOH}^0 + kT \ln(1 - \theta)$$  \hspace{1cm} (6.13)

where $\theta$ is the fraction of ionized carboxyl groups on the surface and $\mu^0$ is the standard chemical potential.

For dilute solutions, $a_{H^+} = c_{H^+}^B$, where $c_{H^+}^B$ is the concentration of hydrogen ions in the bulk solution. Hence all the constant terms can be combined to give a simple surface equilibrium equation:

$$K_s = \frac{\theta}{(1-\theta)} c_{H^+}^B \exp \left( -\frac{|q_e|\psi_0}{kT} \right)$$  \hspace{1cm} (6.14)

This is the form of the equilibrium equation used in this work and in many earlier studies. However, here this equation was derived with the assumption that the activity
and chemical potential of the hydrogen ion were the same throughout the solution, i.e. in the bulk solution and at the surface.

The Boltzmann term in Equation (6.14) comes from the electrostatic energy of the ionized carboxylic groups, not from the increased hydrogen ion concentration next to a negatively charged surface (which is given by: \( c_i(x) = c_i(B) \exp\left[-\frac{z_i q e \psi_x}{kT}\right] \)). Further, the \( c_i(x) \) is the ion concentration at distance \( x \) from the charged surface. The form of Equation (6.14) has led to misleading interpretations of this equation.

The results obtained from analysis of the zeta potentials obviously depend on the surface adsorption model, whereas a solution equilibrium analysis gives direct adsorption values, which were used for comparison.

The surface site densities of the \( SCOO^- \), \( SCOOH \), \( SNR_2H^+ \) and \( SNR_2 \) groups were calculated using the flat-surface model with the Law of Mass Action. The best pH range for IEX applications using this polyampholytic latex was found to be about 6.8–8.0 (see Fig. 6.4, Fig. 6.5 and Fig. 6.6). The \( pK_{NR2} \) and \( pK_{COOH} \) values used in this model were 9 and 6, respectively. By comparison, amine and carboxylic groups in simple molecules in solution have values around 9.78 (e.g. glycine) and 4.75 (e.g. acetic acid) [120, 125, 126]. Glycine, which consists of both carboxylic and amine functionalities, shows diverse ionization constants (i.e. \( K_{COOH} \) and \( K_{NH2} \) at 25°C, are respectively \( 4.47 \times 10^{-3} \) and \( 1.66 \times 10^{-10} \)). The tertiary amine [131] and diethylaminoethyl methacrylate [182] also have different \( pK_a \) values, as shown in Table 6.4. Glycine was used to explain the IEX behaviour of polyampholytic resins in previous studies [120], which had a primary amine group. However, the synthesized latex should be more similar to the polyampholytic resin structure, with ionization constants of carboxyl and amine groups.
Figure 6.4 Calculated surface-charge site densities of $SCOO^-$ and $SCOOH$ groups as a function of pH at 22°C in 10 mM NaCl.

Figure 6.5 Calculated surface charge site densities of $SNR_2H^+$ and $SNR_2$ groups as a function of pH at 22°C in 10 mM NaCl.
Figure 6.6 Schematic diagram of sorption of Na\textsuperscript{+} and Cl\textsuperscript{−} onto the resin (inset), and the calculated surface charge densities of $SCOO^−$ and $SNR_{2}H^+$ groups as a function of pH at 22°C in 10 mM NaCl.

Table 6.4 Ionization constants of amines in aqueous solution at 25°C.

<table>
<thead>
<tr>
<th>Base</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethylamine</td>
<td>$1.91 \times 10^{-11}$</td>
</tr>
<tr>
<td>Diethylaminoethyl methacrylate</td>
<td>$3.63 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

6.3.4 IEX Behaviour of Polyampholytic Latex with Different Salts

In this study all of the zeta measurements were taken in diluted salt solutions of NaCl and NH\textsubscript{4}HCO\textsubscript{3}, with $\kappa \alpha < 5$. Therefore, the White and Oshima equation (6.4) was used to calculate the corresponding surface-charge densities of the latex particles.

Zeta-potential measurements obtained for the polyampholytic latex in a series of NaCl solutions were used for the calculation of the surface-charge densities of the
particles (Fig. 6.7). The adsorption isotherms for Na\(^+\) and Cl\(^-\) ions on latex particles were also measured, and the results are shown in Fig. 6.8. For NaCl and NH\(_4\)HCO\(_3\) solutions, the IEX behaviour of the polyampholytic resins [120] had similar adsorption isotherms. This adsorption agrees with the results obtained for the isotherms of Na\(^+\) and Cl\(^-\) adsorbed onto the polyampholytic latex. However, the adsorption capacity of NaCl was lower than the values obtained for the polyampholytic resins [120, 121].

The measured zeta potentials and the Debye lengths (\(\kappa^{-1}\)) of each electrolyte solution were used in the surface-charge density (\(\sigma_0\)) calculations. The Debye lengths used were always significantly less than the radius of the latex particles. According to the model, at pH 5.7–5.9, the surface-charge site density of the SNR\(_2\)H\(^+\) groups was greater than for the SCO\(_O\)\(^-\) groups, resulting in a greater adsorption of Cl\(^-\) ions than Na\(^+\) ions.

![Graph](image)

**Figure 6.7** Calculated surface-charge densities of latex particles as a function of the concentration of NaCl at 22°C.
Figure 6.8 Equilibrium adsorption isotherms for Na\(^+\) and Cl\(^-\) ions on the polyampholytic latex, as a function of solution concentration, at 22\(^\circ\)C.

NH\(_4\)HCO\(_3\) solutions were used in a similar study, and it was found that the latex had a negative zeta potential (Fig. 6.9) at pH 8: that is, the surface density of the \textit{S}COO\(^-\) groups was greater than the \textit{S}NR\(_2\)H\(^+\) groups. However, the equilibrium ion adsorption isotherms showed higher adsorption of HCO\(_3^-\) over NH\(_4^+\) ions (Fig. 6.10). Adsorption of anions, such as OH\(^-\) and HCO\(_3^-\), at the surface of the latex particles will produce negative zeta potentials, which confirms that HCO\(_3^-\) ions must have been adsorbed into the resin. These results suggest that the average affinity of HCO\(_3^-\) ions for the latex was relatively high; and this behaviour could be further investigated using suitable mixed electrolyte solutions.
Figure 6.9 Calculated surface-charge densities of latex particles as a function of concentration of \( \text{NH}_4\text{HCO}_3 \) at 22°C.

Figure 6.10 Equilibrium adsorption isotherms for \( \text{NH}_4^+ \) and \( \text{HCO}_3^- \) ions adsorbed onto the polyampholytic latex, at 22°C.
The sorption isotherms obtained for NaCl and NH₄HCO₃ show that maximum sorption density for the latex was around 0.11 mmol/m² (Figs. 6.8 and 6.10). Further, the adsorption and desorption of Na⁺ and NH₄⁺ ions were the same as for Cl⁻ and HCO₃⁻ ions. The sorption isotherms obtained for this latex with these ions were well fitted with both Langmuir and Freundlich isotherms, as shown in Table 6.5.

**Table 6.5** Langmuir and Freundlich isotherm parameters for sorption of NaCl and NH₄HCO₃ onto polyampholytic latex.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameter</th>
<th>Units</th>
<th>Sorbate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaCl</td>
</tr>
<tr>
<td>Langmuir</td>
<td>q&lt;sub&gt;max&lt;/sub&gt;</td>
<td>meq/m² of sorbent</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>l/ meq</td>
<td>3.34×10⁻³</td>
</tr>
<tr>
<td></td>
<td>Correlation coefficient</td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td>Freundlich</td>
<td>p</td>
<td></td>
<td>22131</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td></td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>Correlation coefficient</td>
<td></td>
<td>0.97</td>
</tr>
</tbody>
</table>

The results of equilibrium studies performed on the latex samples in a series of NH₄HCO₃ solutions in the presence of 1 mM NaCl at pH 8.2–8.3, pre-treated with 0.5M NaCl solution followed by several washings with Milli-Q water and centrifugation, show IEX behaviour as illustrated in Fig. 6.11. Negative zeta potential values were obtained with the equilibrated NH₄HCO₃ solutions in this study. Surface-charge densities of the latex particles are shown in Fig. 6.12. Adsorption of NH₄⁺ and HCO₃⁻ ions onto the polyampholytic latex equilibrated with NH₄HCO₃ solutions showed a similar adsorption level to the equilibration in NH₄HCO₃ and 1 mM NaCl. This
confirms that NH$_4^+$ and HCO$_3^-$ ions have greater affinity during the IEX process, when exchanging with Na$^+$ and Cl$^-$ ions by mass-action.

![Equilibrium adsorption isotherm](image1.png)

**Figure 6.11** Equilibrium adsorption isotherms for NH$_4^+$ and HCO$_3^-$ ions on polyampholytic latex, in the presence of 1 mM NaCl at 22°C, for the pre-treated latex with 0.5M NaCl solution.

![Surface-charge densities](image2.png)

**Figure 6.12** Surface-charge densities of latex particles as a function of concentration of NH$_4$HCO$_3$ with 1 mM NaCl at 22°C for latex pre-treated with 0.5M NaCl solution.
Further studies, using latex samples pre-treated with 0.5M NH₄HCO₃ and equilibrated with NaCl solutions showed the IEX by adsorption of Na⁺ and Cl⁻, and desorption of NH₄⁺ and HCO₃⁻ ions (Fig. 6.13). The surface-charge density of the latex was again calculated from the measured zeta potential values, as shown in Fig. 6.14. The positive zeta potential values obtained here show that more positive ions adsorbed onto the latex particles; the adsorption isotherms (Fig. 6.13) for this study clearly confirm that more Na⁺ ions were adsorbed onto the surface. All these studies show that this polyampholytic latex has the ability to exchange equally the monovalent counterions Na⁺, NH₄⁺, Cl⁻ and HCO₃⁻ according to the Law of Mass Action.

**Figure 6.13** Equilibrium adsorption isotherms for Na⁺ and Cl⁻ ions on polyampholytic latex, at 22°C for latex pre-treated with 0.5M NH₄HCO₃ solution.
Figure 6.14 Surface-charge densities of latex particles as a function of the concentration of NaCl at 22°C for latex pre-treated with 0.5M NH₄HCO₃ solution.

Polyampholytic latex can be used as a model to examine the monovalent ion adsorption behaviour of polyampholytic resins, when the two materials have the same IEX groups. This comparison could be extended to help explain the more complex adsorption behaviour of divalent, trivalent and multivalent ions.

6.4 Conclusion

A basic ion adsorption model was used here to accurately describe the surface-charge behaviour of amphoteric latex particles with varying pH. This model was developed using a modified approach which assumes that the bulk pH value remains constant throughout the solution, even close to the charged particle surfaces. These observations were supported by direct adsorption isotherm measurements using ion-selective electrodes. The IEX behaviour of ions to the weak acid and weak base (i.e. carboxylic
and tertiary amine) groups of the latex can be well described and used as a model to explain the ion-exchange properties of a recently developed regeneration method for polyampholytic resins, using ammonium bicarbonate.
Chapter 7. Summary and Conclusions

7.1 Summary

Ion-exchange (IEX) resins are widely used for different separation and purification applications in various industries. Regeneration is crucial for such resins once they become exhausted. Improvements of current technologies or development of alternative methods can provide more efficient regeneration processes for these resins. This project was mainly focussed on the chemical/thermal regeneration of IEX resins, with minimum chemical waste, providing benefits commercially as well as environmentally. This novel regeneration technique demonstrates the potential use of a single regenerant, with complete regeneration of the resin, which could easily be adopted for desalination, water treatment and many other separation and purification processes.

Chapter 2 presents a study on the synthesis and properties of a mixed-bead polyampholytic resin, comprising weakly acidic (carboxylic acid) and weakly basic (tertiary amine) groups, which was produced with properties similar to the thermally regenerable Sirotherm resins. In this study 1,1’-azobis(cyclohexanecarbonitrile) (ABCN) was used as the initiator instead of 2,2’- azobisisobutyronitile (AIBN) used by Chanda et. al [53, 54]. The particle size of the resin was maintained in the range 0.3–1.2 mm to achieve optimal adsorption levels and to ensure relevance to commercial use. This resin typically had a capacity of about 0.5 mmol NaCl per gram. A new chemical/thermal IEX regeneration process was developed for this resin and it was found from this study that treatment with ammonium bicarbonate (AB), followed by heat treatment (80°C) provides 100% regeneration for this polyampholytic resin. After exposure to saline solution, the resin can be regenerated and re-used while minimizing chemical waste to the environment. Two types of binding sites can be inferred from the
results: accessible and easily exchangeable, and accessible, less readily exchangeable sites, which are active during the IEX process. It was suggested that AB is the only possible recyclable regenerant which could be used with these resins. It was also shown that polyampholytic resins, with chemically attached anionic and cationic groups in close proximity, can be regenerated only partially when using sequential acid and base washing.

In Chapter 3, a novel method was developed for increasing the IEX capacity of a mixed-bed resin. The low IEX capacities of polyampholytic resins restrict their commercial applications. However, exposing the polyampholytic resins to some divalent cations appears to provide increased capacity by expanding the inner pore structure of the resin during the AB regeneration process. Nickel (Ni$^{2+}$) and calcium (Ca$^{2+}$) ions were found to be strongly bonded to the resins, compared to Na$^+$. Traces of both Ni$^{2+}$ and Ca$^{2+}$ of less than 4% remaining in the resin contributed to the changes in internal structure and this, apparently, occurred during the regeneration with concentrated ammonium bicarbonate solutions, followed by heating. It was found that the IEX capacity was increased by 4–5× and this was consistent with corresponding increases in observable pore size, as measured by scanning electron microscope, and surface area as measured by the Brunauer-Emmett-Teller method. These modified resins can also be completely regenerated with the developed chemical/thermal regeneration process. Further, as these resins are with enhanced capacity, they could be more widely used commercially. Also, the regenerant used here can be recycled and reused in the same process, eliminating chemical waste.

In chapter 4, the newly synthesized polyampholytic resin was used to demonstrate a complete desalination process which was developed to remove salt from saline water
in a continuous-flow system. Regular heating of polyampholytic resins causes their degradation, so the exhausted resins were regenerated using AB washing but without heating the resin. This method promises a more efficient process for continuous desalination, which could be incorporated in industrial processes where highly purified water is required. This mixed-bead resin had a higher selectivity for \( \text{Na}^+ \) and \( \text{HCO}_3^- \) ions over \( \text{NH}_4^+ \) and \( \text{Cl}^- \) ions, apparently due to the close proximity of the cationic and anionic groups in the resin. Two possible explanations have been given for the adsorption behaviour of ions onto this polyampholytic resin. The first is the preferential adsorption of ions by the mixed-bead resin, and the second is the effect of counter-ions on the IEX process. It was confirmed that the presence of AB in the resin contributes to the enhanced adsorption of \( \text{Na}^+ \) and also the synthesized polyampholytic resin had a better absorptivity of AB, which led to more adsorption of \( \text{Na}^+ \) into the resin after regeneration. From this study, the utility of producing these resins on a much larger scale has been shown and it could be justified on the basis that they could also be used to adsorb many other cations (e.g. heavy metal ions) and anions for separation and purification purposes.

Based on these earlier studies, in Chapter 5 a complete, simple, detailed desalination process was developed to remove salt from saline water using commercially available strong-acid (SA) and strong-base (SB) resins in a mixed-bed column. It was demonstrated that AB solutions could be used for regenerating the resin \textit{in situ} and that when this was used for the desalination of a 0.1M NaCl solution, it typically recovered about 60 ml of drinking-water product, as per the guideline of World Health Organisation [17] for \( \text{Na}^+ \) and \( \text{Cl}^- \) ions, containing AB, from about 9.6 g of resin. Further, it was proposed that a bubble column evaporator [137] or a multiple distillation system [32] could be used to eliminate AB from the product water and also recover the
NH$_3$ and CO$_2$ decomposition gases to re-form the regenerant solution. This cyclic process offers a more effective method for continuous desalination to produce drinking quality water. The proposed novel process is based on use of a single regenerant and has substantial potential benefits in terms of reducing the cost of chemical consumption and regeneration steps. Further, this process can be widely used with existing commercial SA and SB mixed-bed systems, giving an immense advantage, especially for desalination applications.

Further development in this process could be achieved using a pilot study, which should be able to identify the most important data for mixed-bed systems, before applying commercially. Data could be generated regarding bed volumes, input and output flow-rates of water, and the percentage recovery of water and regenerants can be obtained more accurately, as well as possible problems and the appropriate changes can be made. A second development could be via the synthesis of polyampholytic SA and SB resins, as the new regeneration method can provide complete regeneration, *in situ*, unlike the partial regeneration by acid or base. As the resins can be regenerated *in situ* and the regenerant can be recycled and re-used, this method could have useful applications in desalting water on ships and submarines where there is limited available space. This method might also find use in the separation of radioactive ions, for example, in product waste generated from nuclear power plants, since there is a reduced need for the production of waste acid and base washings, which may contain low level radioactive contamination. This technology could also, be used to purify mixed-electrolyte feed solutions.

The kinetic behaviour of the mixed-bead resin was studied, as a part of this project, using a prototype latex colloid, and this is reported in Chapter 6. The main purpose of this study was to determine the ionization behaviour of the carboxyl and
tertiary amine (SCOOH and SNR₂) groups in the latex surface, as a model for the polyampholytic resin structure. Polystyrene based polyampholytic (zwitterionic) latex was synthesized with an isoelectric point (IEP) of 6.9 and particle size of about 110 nm. The ion-exchange (IEX) ability of this latex with sodium chloride and ammonium bicarbonate (AB) was studied and it was found that Na⁺, NH₄⁺, Cl⁻ and HCO₃⁻ ions exchanged readily with the surface groups following the Law of Mass Action. The latex typically had an adsorption capacity of about 0.11 mmol/m² for both NaCl and NH₄HCO₃ electrolyte solutions. Surface adsorption constants, i.e. K_NR₂ and K_COOH, were assumed to be similar to solution values, that is: 1×10⁻⁹ M and 1×10⁻⁶ M, respectively. The precise ionization ability of the active groups is specific to the type of polymer used to form the latex particles. Calculated surface charge densities, obtained from zeta potential studies, show that the best pH range for IEX studies with this polyampholytic latex was 6.8–8.0. The average affinity of HCO₃⁻ ions was found to be higher than Cl⁻ during the IEX process, when using the latex colloid.

7.2 Concluding Remarks

The use of AB solutions for in situ resin regeneration offers a new process, especially for mixed-bead or mixed bed systems. This has expanded the scope of use of IEX resins for continuous desalination processes, with less cost and minimal chemical waste. Studies reported here have shown that this method can be applied to resins with weak-acid, weak-base, strong-acid and strong-base functional groups and it could possibly be used for all types of resins. The value of the use of AB regenerant solutions lies in their suitable ion exchange properties and ready thermal decomposition into gases, which can be easily separated from the product water and then collected and re-used as regenerant solution. This removes the need for the separation of beads and the use of
acid and base washing. This provides significant advantages of use for this method for many industrial processes, where mostly pure water is required. Further, this method is not limited to desalination but also can be used for many other applications related to separation and purification processes. In conclusion, this method could be more widely used in the future with various other improvements, such as the use of combined group polymer resins.
References


Appendix I Sample of Raw Electrical Conductivity Data for NH₄HCO₃ Solutions used in Chapter 2.

Table A.1 Electrical conductivity with concentration of NH₄HCO₃ at 25°C.

<table>
<thead>
<tr>
<th>Concentration of the NH₄HCO₃ solution (mol/l)</th>
<th>Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>115.3</td>
</tr>
<tr>
<td>0.005</td>
<td>553</td>
</tr>
<tr>
<td>0.01</td>
<td>1076</td>
</tr>
<tr>
<td>0.05</td>
<td>5000</td>
</tr>
<tr>
<td>0.1</td>
<td>9600</td>
</tr>
<tr>
<td>0.5</td>
<td>40300</td>
</tr>
<tr>
<td>1</td>
<td>70100</td>
</tr>
</tbody>
</table>
Appendix II Sample of Raw Conductivity Data of Eluted 0.1M NaCl used in IEX Study in Chapter 4.

Table A.2 Eluted NaCl with the volume of 0.1M NaCl passing through the mixed-bead resin at 20°C in the first IEX study.

<table>
<thead>
<tr>
<th>Volume of 0.1M NaCl (ml)</th>
<th>Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>18.7</td>
</tr>
<tr>
<td>20</td>
<td>1540</td>
</tr>
<tr>
<td>30</td>
<td>8740</td>
</tr>
<tr>
<td>40</td>
<td>10970</td>
</tr>
<tr>
<td>50</td>
<td>11520</td>
</tr>
</tbody>
</table>
Appendix III Infra-red (IR) Spectrum of the Polyampholytic Latex Studied in Chapter 6.

Figure A.1 IR spectrum of the polyampholytic latex colloid composed of polymerization with styrene, methacrylic acid and diethylaminoethyl methacrylate.

Sample type : Solid
Sample matrix : Dry KBr
Number of scans : 16
Resolution : 4 cm$^{-1}$
Instrument : Shimadzu, IR Prestige-21

Table A.3 Functional groups and the corresponding peak values obtained for the polyampholytic latex colloid from the IR spectrum.

<table>
<thead>
<tr>
<th>Group</th>
<th>Wave number (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>1574</td>
</tr>
<tr>
<td>C=O (strong)</td>
<td>1732</td>
</tr>
<tr>
<td>CH$_2$ or CH</td>
<td>2949</td>
</tr>
<tr>
<td>OH and NH (broad)</td>
<td>3448</td>
</tr>
</tbody>
</table>
Appendix IV Sample of Raw Zeta Potential Values Obtained for the Latex Samples Equilibrated with Different Salt Solutions in Chapter 6.

Table A.4 Zeta potential values for the latex sample equilibrated with NaCl.

<table>
<thead>
<tr>
<th>Concentration of NaCl (mol/l)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>29.5</td>
</tr>
<tr>
<td>0.2</td>
<td>31.1</td>
</tr>
<tr>
<td>0.3</td>
<td>31.4</td>
</tr>
<tr>
<td>0.4</td>
<td>32.0</td>
</tr>
<tr>
<td>0.5</td>
<td>32.3</td>
</tr>
<tr>
<td>0.6</td>
<td>32.2</td>
</tr>
</tbody>
</table>

Table A.5 Zeta potential values for the latex sample equilibrated with NH₄HCO₃.

<table>
<thead>
<tr>
<th>Concentration of NH₄HCO₃ (mol/l)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-17.6</td>
</tr>
<tr>
<td>0.2</td>
<td>-20.0</td>
</tr>
<tr>
<td>0.3</td>
<td>-28.5</td>
</tr>
<tr>
<td>0.4</td>
<td>-32.6</td>
</tr>
<tr>
<td>0.5</td>
<td>-37.5</td>
</tr>
</tbody>
</table>
**Table A.6** Zeta potential values for the latex sample equilibrated with NH₄HCO₃ and 1 mM NaCl at 22°C for the pre-treated latex with 0.5M NaCl solution.

<table>
<thead>
<tr>
<th>Concentration of NH₄HCO₃ (mol/l)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-19.4</td>
</tr>
<tr>
<td>0.2</td>
<td>-28.2</td>
</tr>
<tr>
<td>0.3</td>
<td>-36.5</td>
</tr>
<tr>
<td>0.4</td>
<td>-37.1</td>
</tr>
<tr>
<td>0.5</td>
<td>-39.2</td>
</tr>
</tbody>
</table>

**Table A.7** Zeta potential values for the latex sample equilibrated with NaCl at 22°C for the pre-treated latex with 0.5M NH₄HCO₃ solution.

<table>
<thead>
<tr>
<th>Concentration of NaCl (mol/l)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>17.5</td>
</tr>
<tr>
<td>0.2</td>
<td>18.2</td>
</tr>
<tr>
<td>0.3</td>
<td>19.7</td>
</tr>
<tr>
<td>0.4</td>
<td>20.3</td>
</tr>
<tr>
<td>0.5</td>
<td>20.5</td>
</tr>
</tbody>
</table>