SINGLE AND MULTICOMPONENT ION EXCHANGE OF SILVER, ZINC AND COPPER ON ZEOLITE 4A

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ABSTRACT

SINGLE AND MULTICOMPONENT ION EXCHANGE
OF SILVER, ZINC AND COPPER ON ZEOLITE 4A

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Ion exchange of heavy metals with zeolites is important in terms of different application areas. Industrial wastewater treatment and antibacterial applications are two essential areas that have taken great attention. While silver, zinc and copper are well known for their toxicity, they are also used as antibacterial agents in zeolites.

The objective of this study is to investigate the single and multicomponent ion exchange behavior of zeolite 4A for silver, zinc, copper and sodium ions. For this purpose Ag^{+}-Na^{+}, Zn^{2+}-Na^{+}, Cu^{2+}-Na^{+} binary systems and Ag^{+}-Zn^{2+}-Na^{+}, Ag^{+}-Cu^{2+}-Na^{+}, Cu^{2+}-Zn^{2+}-Na^{+} ternary systems were investigated in batch systems at 25°C and 0.1 N.

Binary ion exchange isotherms indicate that zeolite 4A has high selectivity for silver, zinc and copper with respect to sodium. All exchange isotherms lie above the diagonal over the whole range. Using the equilibrium data, the thermodynamic analysis of the binary systems were carried out. The thermodynamic equilibrium constants and the standard free energies of exchange were calculated as 340.9 and -14.5 kJ/mol for silver-sodium system, 40.5 and -4.6 kJ/mol for zinc-sodium system, and 161.2 and -6.3 kJ/mol for copper-sodium system, respectively. From these values, selectivity sequence of zeolite 4A was determined as $Ag^{+} > Cu^{2+} > Zn^{2+}$. This selectivity sequence was also verified by the results of ternary ion exchange experiments.

The experimental data were compared with the Langmuir and Freundlich isotherms. While Freundlich model gives a better correlation for Ag^{+}-Na^{+} and Zn^{2+}-Na^{+} exchange, Langmuir model represents a better fit to the experimental data of Cu^{2+}-Na^{+} exchange.

Keywords: Ion exchange, Zeolite 4A, Silver, Copper, Zinc

ÖZ

GÜMÜŞ, ÇİNKO VE BAKIRIN ZEOLİT 4A ÜZERİNE
TEK VE ÇOK BİLEŞENLİ İYON DEĞİŞİMİ

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Ağır metallerin zeolitlerle olan iyon değişimi farklı uygulama alanları açısından önemlidir. Endüstriyel atıksu arıtımı ve antibakteriyel uygulamalar büyük dikkat çeken iki önemli alandır. Gümüş, çinko ve bakır zehirli olarak bilinmelerine karşın zeolitler içersinde antibakteriyel madde olarak kullanılmaktadırlar.

Bu çalışmanın amacı zeolit 4A'nın gümüş, çinko, bakır ve sodyum iyonları için tek ve çok bileşenli iyon değişim davranışının incelenmesidir. Bu amaç doğrultusunda Ag^{+}-Na^{+}, Zn^{2+}-Na^{+}, Cu^{2+}-Na^{+} ikili sistemleri ve Ag^{+}-Zn^{2+}-Na^{+}, Ag^{+}-Cu^{2+}-Na^{+}, Cu^{2+}-Zn^{2+}-Na^{+} üçlü sistemleri kesikli sistem yöntemiyle 25°C ve 0.1 N'de incelenmiştir.

Ikili iyon değişim izotermleri zeolit 4A'nın Na^+'a göre Ag^+, Zn^{2+} ve Cu^{2+} için yüksek seçiciliği olduğunu göstermektedir. Bütün değişim izotermleri tüm aralık boyunca diyagonalin üzerinde yer almaktadır. Denge verileri kullanılarak ikili sistemlerin termodinamik analizi yapılmıştır. Termodinamik denge sabiti ve standart serbest enerjisi gümüş-sodyum sistemi için 340.9 ve -14.5 kJ/mol, çinko-sodyum sistemi için 40.5 ve -4.6 kJ/mol, bakır-sodyum sistemi için 161.2 ve -6.3 kJ/mol olarak hesaplanmıştır. Bu değerlerden zeolit 4A'nın seçicilik sırası $Ag^+ > Cu^{2+} > Zn^{2+}$ olarak belirlenmiştir. Bu seçicilik sırası üçlü iyon değişim deneylerinin sonuçları tarafından da doğrulanmıştır.

Deneysel veriler Langmuir and Freundlich izotermleri ile karşılaştırılmıştır. Freundlich modeli Ag^+-Na^+ and Zn^{2+}-Na^+ değişimi için daha iyi korelasyon verirken, Langmuir modeli Cu^{2+}-Na^+ değişiminin deneysel verilere daha iyi uyum göstermektedir.

Anahtar kelimeler: İyon değişimi, Zeolit 4A, Gümüş, Çinko, Bakır

To my mother and father…

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I would like to express my love to my mother and father for their continuous love, encouragement, support and patience through my life.

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A_s : Equivalent fraction of cation A in solution

A_z : Equivalent fraction of cation A in zeolite

$a_{A,s}$: Activity of cation A in solution

$a_{A,z}$: Activity of cation A in zeolite

C_e : Equilibrium aqueous metal ions concentration (mg/L)

f_A : Activity coefficient of cation A in zeolite

G : Free energy

I : Ionic strength

K : Energy of adsorption (L/mg)

K_a : Thermodynamic equilibrium constant

K_c : Kielland quotient

K_f : Adsorption capacity

K_m : Mass action quotient

m_A : Concentration of cation A in solution (mol/dm^3)

M_A : Concentration of cation A in zeolite (mol/kg)

q_e : Amount of metal ions adsorbed per unit mass of adsorbate at equilibrium (mg/g)

R : Universal gas constant (8.314J/molK)

T : Absolute temperature (K)

TN : Total Normality

Q : Ion exchange capacity

Z_A : Charge of cation A

Greek Letters

α_B^A : Separation factor

γ_A : Activity coefficient of cation A in solution

Γ : Solution non-ideality correction factor

$\gamma_{\pm AX}$: Mean molar activity coefficient of salt AX in solution

$\gamma_{\pm AX}^{(BX)}$: Mean molar activity coefficients of salt BX in the presence of salt AX

Δ : Change of property

CHAPTER 1

INTRODUCTION

1.1 General Information

Heavy metals are well known for their toxicity and their disposal into environment is a crucial industrial waste problem. Since they are not biodegradable, they tend to accumulate in living organisms [Petrus and Warchol, 2003] Silver, copper and zinc are three toxic heavy metals that should be removed from waste waters.

Due to having perfect malleability, ductility, electrical and thermal conductivity, silver is a very advantageous raw material in several industries [Akgül et al, 2006]. Silver is made use of mainly as silver halide in the photographic films. Silver is utilized in the industrial areas including the production of electrical contacts and switching gear, batteries, catalysts and mirrors [Begum, 2002]. The discharged effluents contain crucial amount of silver. The removal of this heavy metal from wastewaters is important due to its toxicity to living organisms [Akgül et al., 2006].

Copper is one of the main heavy metals which causes hemolysis, liver, and kidney damage, irritation of the upper respiratory tract, gastrointestinal disturbance. Wastes of industrial processes such as dyeing, paper, petroleum, copper/brass-plating, and copper-ammonium rayon are the principal ways through which copper enters the water bodies. Copper concentrations approach to 100–200 mg/dm^3 in the copper-cleaning, copper plating, and metal-processing industries which is high when the water quality standards are taken into consideration [Wang et al., 2007].

Zinc is widely used to galvanize other metals in order to prevent corrosion. Great amounts of zinc are also used to produce die-castings for the automotive, electrical

and hardware industries. Poisoning events have been reported after an exposure to zinc in water or beverages with a concentration of 1000-2500 mg/L [Stefanovič et al., 2007].

Heavy metals can be removed from aqueous solutions by several processes such as, chemical precipitation, adsorption, extraction, reverse osmosis, ultrafiltration and ion exchange [Keane, 1998]. Most of these methods have some disadvantages such as high capital and operational costs and problem of disposal of residual metal sludge [Hui et al, 2005]. Because of the simplicity of the application, heavy metal removal from aqueous solution by ion exchange is certainly an attractive option. [Keane, 1998]. The removal of heavy metal cations, transition metal ions and several trace elements from wastewaters may be done by using zeolites [Bekkum et al., 2001].

Zeolite is a crystalline aluminosilicate with a three dimensional framework structure having uniformly sized pores in molecular dimensions [Cejka et al, 2007]. Silica units in the zeolite framework are neutral. Incorporation of Al^{3+} into the silica framework makes the framework negatively charged. There are cations such as Na^{+}, K^{+} and Ca^{2+} within the pores of the channels in order to balance the negative charge of the framework. These cations provide ion exchange ability to zeolites [Auerbach, 2003].

Due to their ability to prevent the growth of microbes, antibacterial and antifungal materials have attracted great interest in recent years. Applications of these materials include household, industrial and public facility products, such as paints, toys, appliances, kitchen, school and hospital utensils. Organic antibacterial agents have been widely made use of. Nevertheless, the drawbacks of organic agents have been revealed such as low melting and boiling points, their tendency to volatilize or decompose. When compared with organic antibacterial agents, inorganic ones may have some advantages such as long lasting action period, chemical stability, thermal resistance, safe to use, effective against a broad spectrum of bacteria and easy to

manufacture and process when compared to. For this reason, the preparation of inorganic antibacterial material has gain importance in recent years [Li et al., 2002]. Zeolites have been utilized as the host inorganic compound so as to prepare such materials [Inoue et al., 2002].

Heavy metals such as silver, zinc, copper, mercury, tin, lead, bismuth, cadmium, chromium and thallium have antibacterial properties. When the ion-exchangeable cations in zeolite structure are exchanged with these metals, zeolite gains antibacterial activity [Niira et al, 1990]. There are numerous studies concerned with the use of natural and synthetic zeolites such as A, X, Y, Z and clinoptilolite supporting metal ions (Ag, Cu, Zn, Hg, Sn, Pb, Bi, Cd, Cr, Ti) as bactericides for water disinfection [Rivera-Garza et al., 2000].

Preferred examples of metal ions having a bactericidal property are ions of Ag, Cu, Zn. The metals can be used alone or as a mixture to provide antibacterial effect [Hagiwara et al, 1990]. Commercial concerns have asserted that when silver-zinc zeolite coatings are applied to stainless steel surfaces such as air ducts, countertops, or food preparation areas, they can decrease the bacterial load and reduce the contamination risk by pathogenic or food spoilage microorganisms [Galeano et al., 2003]. Although Ag-zeolite shows high antibacterial activity and low toxicity, the high reactivity of silver was found to be a problem. For example, the reduction of silver ions to elemental silver brings about to the loss antibacterial ability. Furthermore, silver is not very effective on fungus. Therefore it is necessary to find an alternative to silver. Due to having a lower cost, better antifungal ability and higher chemical stability than silver, copper may be an ideal substitute [Li et al., 2002].

1.2 Objectives of the Study

Ion exchange of heavy metals with zeolites is important. While their removal from aqueous solutions is essential in terms of wastewater treatment, their incorporation into zeolite structures is crucial in terms of antibacterial applications.

In this study commercial zeolite 4A is investigated for its exchange of Ag^{+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions. To be more specific the objectives of the study are as follows

- to determine the binary ion exchange behavior of zeolite 4A for Ag^{+}, Cu^{2+} and Zn^{2+} ions in batch mode at 25^{0}C and 0.1 total normality

- to examine the thermodynamics of the binary exchange and determine the selectivity sequence from these results

- to investigate the multicomponent ion exchange behavior of zeolite 4A for the Ag^{+}-Cu^{2+}-Na^{+}, Ag^{+}- Zn^{2+}-Na^{+} and Zn^{2+}- Cu^{2+}-Na^{+} ternary systems.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 THE ZEOLITES

2.1.1 Definitions and Basic Concepts

The history of zeolites began in 1756 with the discovery of the first zeolite mineral, stilbite by a Sweedish mineralogist Cronstedt. He recognized zeolites as a new class of minerals containing hydrated aluminosilicates of the alkali and earth alkali elements. Since the crystals showed intumescence when heated in a blowpipe flame, Cronstedt named the mineral as ‘zeolite’ which is the combination of two Greek words, ‘zeo’ and ‘lithos’ meaning ‘to boil’ and ‘a stone’ [Bekkum et al., 1991].

According to Smith ‘ a zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration’ [Rabo, 1976].

Zeolites may be represented by the generalized chemical formula [Tsitsishvili et al., 1992].

$$\underset{\text{extraframework cations}}{M_{x/n}} \bullet \underset{\text{framework}}{[Al_xSi_yO_{2(x+y)}]} \bullet \underset{\text{water}}{{}_pH_2O} \qquad (2.1)$$

SiO_4 and AlO_4 tetrahedra linked through oxygen atoms construct the three dimensional polyanionic networks of zeolites. Depending on the structure type, zeolites contain regular channels or interlinked voids of which diameters are in the

micropore range. In the pores there are water molecules and the cations in order to balance the negative charge of the framework. The cations which are mobile and can be exchanged easily are alkali metal and alkaline earth metal cations [Elvers and Hawkins, 1996].

Zeolite like molecular sieves have expanded the field of zeolites to a great extent during the last two decades. In these new materials, the aluminum and the silicon of the classical zeolites are partially or completely exchanged by other elements. The most essential groups of these molecular sieves are:

1) Modifications of silica
2) Metallosilicates with three and tetravalent heteroatoms in place of aluminum as framework components, eg., boro- and gallosilicates, ferrisilicates, and titanosilicates
3) Alumino- and gallophosphates and compounds derived from them.

These compounds generally have similar framework structures with zeolites [Elvers and Hawkins, 1996].

2.1.2 Zeolite Framework Structures

Publications which include new tetrahedral frameworks are periodically reviewed by the structure commission of the International Zeolite Association (IZA). The commission assigns a three-letter code to each distinct new framework which are formally known as framework types. There are 135 different framework types with assigned three-letter codes [Auerbach et al., 2003].

2.1.2.1 The Basic Building Unit: The Tetrahedron

Tetrahedron (TO_4) is the primary building block of zeolite framework. The centre of a tetrahedron is occupied by a silicon or aluminum atom with four atoms of oxygen at the corners. Each oxygen atom is shared between two tetrahedral and hence forming a continuous framework [Tsitsishvili et al., 1992].
Different representations of a tetrahedron are shown in Figure 2.1.

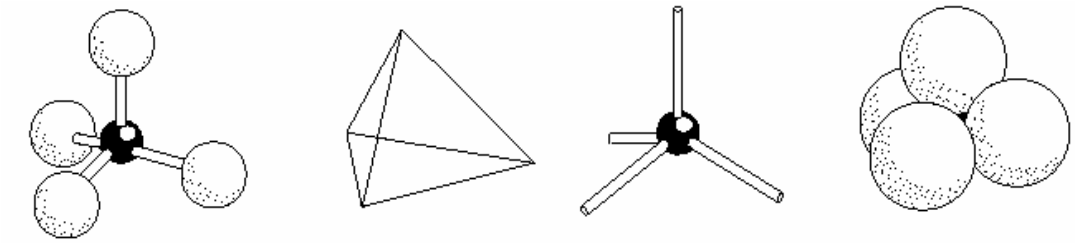


Figure 2.1. Different representations of tetrahedron a) ball-and-stick model, b)solid tetrahedron, c) skeletal tetrahedron, d) space filling and packed spheres [Kirk-Othmer Encyclopedia of Chemical Technology]

Due to carrying +4 charge, completely siliceous structure is uncharged. Incorporation of Al^{3+} into the silica framework makes the framework negatively charged. [Auerbach et al., 2003].
Tetrahedral silica and alumina units are represented in Figure 2.2.

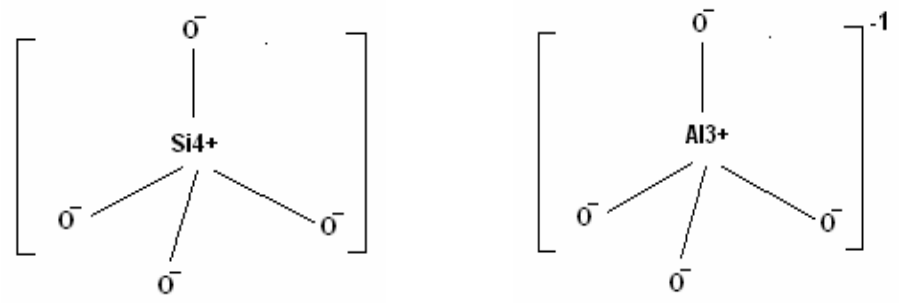


Figure 2.2. Tetrahedral silica and alumina units [Kamışoğlu, 2007]

In order to keep the overall framework neutral, there are extraframework cations together with water molecules within the structural channels. The extraframework cations are group I and group II elements, in particular Na, K, Li and Ca, Mg, Ba, Sr [Tsitsishvili et al., 1992].

The O-T-O angle is generally close to the ideal value of 109^o 28′ for a geometrically perfect tetrahedron. The T-O bond length is dependent on the particular metal cation. The bond length of SiO_4 tetrahedra is d(Si-O) ≈ 1.59-1.64 A^o and that of AlO_4 terahedra is usually d(Al-O) ≈ $1.73A^o$ [Auerbach et al., 2003].

2.1.2.2 Composite Building Units

By combining groups of BBUs, more complex composite building units (CBUs) can be formed. Rings are the simplest examples of CBUs. A ring containing n tetrahedra is named an n ring. The most common rings include 4, 5, 6, 8, 10, 12 tetrahedra [Auerbach et al., 2003].
Some examples of n rings are shown in Figure 2.3

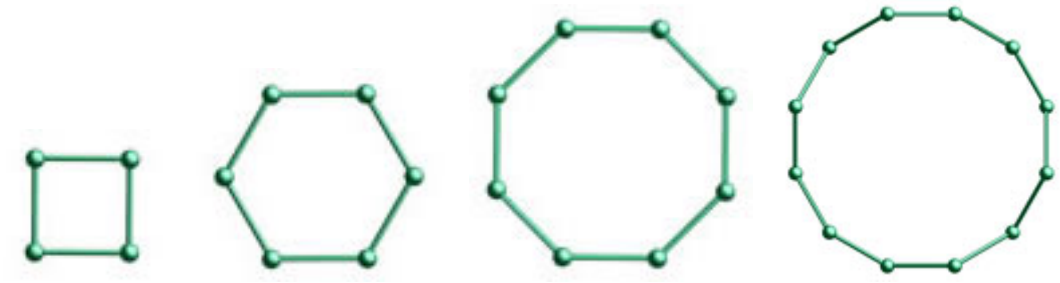


Figure 2.3. Some examples of n rings

The more complex units are obtained by constructing larger CBUs from n rings [Auerbach et al., 2003]. A cage is a polyhedral pore whose windows are too narrow to allow the penetration of species larger than water [McCusker et al., 2001]. Some examples of cages are shown in Figure 2.4.

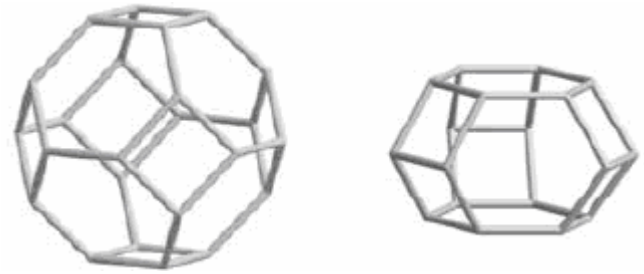


Figure 2.4. Some examples of cages a) sodalite cage, b) Cancrinite cage [McCusker et al., 2001]

Cages of different size and geometry can be obtained by linking rings of different sizes. As can be seen in Figure 2.4, sodalite cage and cancrinite cage are formed by connecting 4- and 6-rings in various arrangements [Auerbach et al., 2003].

2.1.2.3 Cavities

A cavity is a polyhedral unit that is different from a cage in terms of the contained windows which permit the penetration of molecules in and out of the cavity. It should not be infinitely extended [Auerbach et al., 2003].
The polyhedron in Zeolite A is a cavity and shown in Figure 2.5.

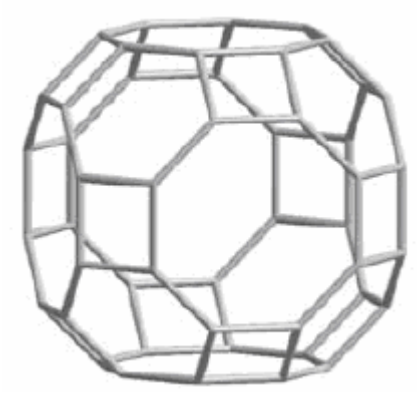


Figure 2.5. α- cavity of Zeolite A [McCusker et al., 2001]

2.1.3 Chemical and Physical Properties of Zeolites

Most of the chemical and physical properties of zeolites are determined by the aluminum content of their frameworks. This is usually expressed a Si/Al or SiO_2/ Al_2O_3 ratio in literature. Zeolites with SiO_2/ Al_2O_3 ratio less than 4 are named as low silica zeolites, with SiO_2/Al_2O_3 ratio between 4 and 20 are called as intermediate silica zeolites and with SiO_2/Al_2O_3 ratio between 20 and 200 are referred as high silica zeolites [Elvers and Hawkins, 1996].

Synthetic zeolites which contain alkali metal and alkaline earth metal cations are generally colorless crystalline powders. Colors occur as long as the zeolites consist of transition metal as impurities or if they have been altered by ion exchange with these elements [Elvers and Hawkins, 1996].

Densities of zeolites change with the openness of the framework structure and the nature of the cations, in general lying in the range 1.9-2.3 g/cm^3 [Elvers and Hawkins, 1996].

Hydrated zeolites release water when they are heated. Many zeolites can be made entirely free of adsorbed water by calcination at 400-500^oC. The zeolites retain their crystal structures upon heating. Enormous free volumes and interior surfaces can be made available for the adsorption of guest species by heating [Elvers and Hawkins, 1996].

The surface selectivity of zeolites as is also determined by the SiO_2/Al_2O_3 ratio. The surface of low silica zeolites is highly hydrophilic and that of high silica zeolites is hydrophobic [Bekkum et al., 1991].

As the Si/Al ratio increases, the cation concentration and the ion exchange capacity (which is proportional to aluminum content) decreases. The low silica zeolites which are represented by zeolite A and X are aluminum saturated, have highest cation concentration and give optimum adsorption properties in terms of capacity, pore size and three dimensional channel systems. They represent highly heterogeneous surfaces with a strongly hydrophilic surface selectivity [Bekkum et al., 1991].

Zeolites show ionic conductivity as a result of the mobile cations in their cavities and channels. The ionic conductivity depends on the nature and concentration of the cations, diameter of the channels. Zeolites can be used as solid-state electrolytes, membranes in ion-selective electrode and components of cathode materials in

batteries in the future as a result of their conductivity properties [Elvers and Hawkins, 1996].

Strong acids leads to the decomposition of low silica zeolites by dissolving the aluminum atoms out of the framework with breakdown of the crystal structure. The zeolites become less sensitive to the dealumination by acids with an increase in SiO_2/Al_2O_3 ratio. High silica zeolites can retain their structure stable even in strong mineral acids [Elvers and Hawkins, 1996].

2.1.4 Applications of Zeolites

Zeolites are widely used in primarily three applications: adsorbents, catalysts and ion exchange [Auerbach et al., 2003].

Adsorption processes are extensively used in industry for the aim of drying and purification of effluents in order to improve the quality of raw materials and final products. Silica gel, aluminum oxide and zeolites are principally used as sorbents. Zeolites have important advantages when compared with other adsorbents. First, zeolites have the ability to adsorb water in much higher quantities than other adsorbents. Secondly, when the temperature increases, the adsorption capacity related with water vapor decreases but not as sharp as with silica gel or aluminum oxide. Thirdly zeolites have low hydraulic resistance. Lastly, zeolites have marked selectivity for certain compounds, especially water vapor. Zeolites are different from other driers in that they posses molecular sieving properties (They can adsorb the molecules of substances whose the critical diameters are less than the size of the input openings of the zeolite, on the other hand larger molecules are not adsorbed.) [Tsitsishvili et al., 1992].

Zeolites are utilized in adsorption technology both in gas and liquid phases. Processes can be classified based on the method of regenerating the loaded adsorbent and the method of making the contact between the fluid and the adsorbent.
Dehydrated zeolites of type A and X are extensively made use of in industry as drying agents. Their use is preferred if small quntities of water have to be removed from gases or liquids. Zeolite A and X are also well established in purification processes. They are used in the removal of carbon dioxide from gas streams and also removal of H_2S and organic sulfur compounds mainly from natural gas [Elvers and Hawkins, 1996].

Zeolitic adsorbents of the 5A type (Ca form of zeolite A) are utilized in some significant industrial processes for the separation of mixtures of substances. They are used as alternatives to carbon molecular sieves and activated carbons in order to the recover hydrogen from reformer, refinery and coke oven gases in diverse PSA processes [Elvers and Hawkins, 1996].

Zeolite cracking catalysts started to be used in the world in the 1960's and they rapidly replaced the amorphous aluminosilicate catalysts. Zeolite catalysts are extensively used in oil refineries for cracking, hydrocracking and isomerization [Tsitsishvili et al., 1992].

A unique property of using zeolites as catalyst is that the reactions may be shape selective. Shape selectivity in catalysis is similar to the molecular sieve effect in adsorption. That is, it can take place as long as the pores of the catalysts posses similar dimensions to those of the molecules participating in the reaction. When compared with the amorphous alumina silica and high alumina catalysts, the zeolite catalysts have higher activity and give higher gasoline yields and less coke formation [Elvers and Hawkins, 1996].

Ion exchange is a fundamental property of most zeolites. There are various applications where the ion exchange properties of zeolites are used. Some of these are water softening in detergents, wastewater treatment (involving municipal, industrial, agricultural and radioactive) and animal food supplementation [Bekkum et al., 2001].

The most essential use of synthetic zeolites based on their ion exchange properties is detergents builders. This is the largest usage area of zeolites [Elvers and Hawkins, 1996]. Zeolite builders exchange Ca^{2+} and Mg^{2+} ions present in hard waters with Na^{+} ions present in the zeolites [Karge and Weitkamp, 1989]. Sodium tri-polyphosphate was chosen as the water softener for detergent formulations until people started to become aware of its environmental effect in 1970's. Increases in the levels of phosphates in natural waters were causing to eutrophication. Zeolites having selectivity for calcium and magnesium over sodium are apparent candidates to replace phosphates. While most zeolite types, including both natural and synthetic ones, have been tested for their abilities in water softening, zeolite A has been mainly made use of due to its high calcium selectivity [Bekkum et al., 2001].

Zeolites are usually used for the removal of ammonia and ammonium ions from municipal and agricultural wastewater. Clinoptilolite, chabazite, mordenite and phillipsite have been used widely for this aim. Clinoptilolite, especially, exhibits good selectivity for NH_4^{+} [Bekkum et al., 2001].

Zeolites can be used to remove heavy metal cations, transition metal ions and various trace elements from wastewaters [Bekkum et al., 2001]. Natural zeolites as cheap materials are widely used to remove toxic metal cations such as Fe, Mn, Cu, Co, Zn, Pb, Cd, Ni and Hg, from industrial wastes to protect the environment [Cejka et al., 2007]. Clinoptilolite has take great attention due to its attractive selectivity for certain heavy metals such as Pb, Cd, Zn, Ni, Fe, Mn [Ouki and Kavannagh, 1997].

Zeolites are usually used for the removal of certain radio-nuclei from low and medium level nuclear-waste. $^{90}Sr^{2+}$ and $^{137}Cs^{+}$ are the main radioactive components of nuclear waste. Clinoptilolite and chabazite are frequently utilized for radioactive waste treatment due to their abundance and good ion exchange selectivities for the common radionuclides. Phillipsite has also found applications. Laumontite in its calcium form shows a high selectivity to $^{90}Sr^{2+}$. The synthetic zeolites 4A and 13X have been exhibited to be beneficial in the removal of $^{90}Sr^{2+}$ from simulated low-level waste. A synthetic mordenite removed $^{137}Cs^{+}$ from simulated and real wastes in an effective way [Bekkum et al., 2001].

Ion exchange is usually the preferred way for the insertion of metals, metal oxides, sulphides and other chalcogenides into suitable matrices for the creation of sensors, optics and electronics as part of the nanotechnology search - for which zeolites are perfect media [Cejka et al., 2007].

2.1.5 Zeolite A

Zeolite A is one of the most significant industrial zeolite, produced in hundreds of thousands of tons every year. It has various applications such as as water softening in detergents, additive in polyvinylchroride thermoplastics, industrial gas drying, separation in linear and branched hydrocarbons [Auerbach et al., 2003].

The aluminosilicate framework of zeolite A is composed of alternating SiO_4 and AlO_4 tetrahedra. The tetrahedra are linked over the oxygen atoms in the corners which results in a larger building unit named as β-cages (or sodalite cage). Eight β-cages are combined together over the 4-rings and form a larger cavity called an α-cage. The diameter of this large cavity is 11.4 A^o and the diameter of the largest window (8-ring) is 4.1A^o [Leiggener and Calzaferri , 2005].
Figure 2.6 shows the framework structure of zeolite A.

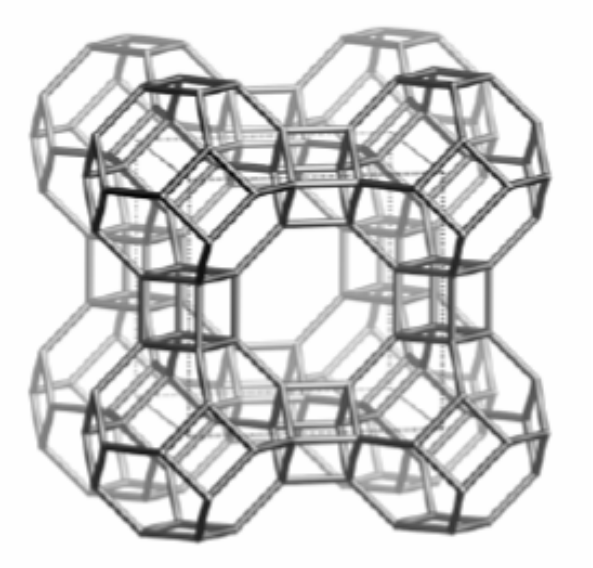


Figure 2. 6. Framework of Zeolite A [Database of Zeolite Structures]

The chemical formula of the NaA zeolite is as the following [Elvers and Hawkins, 1996]

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]27H_2O \qquad (2.2)$$

The entrance from α-cage to β-cage can only take place through a six-membered ring which is named as hexagonal window. The extraframework cations, which are needed to balance the anionic charge of the framework, are distributed in various crystallographic locations and may have an important effect on its relevant properties. According to earlier X-ray studies of zeolite NaA, 8 Na^+ ions are located near the centers of the six-membered rings of the β-cage, 3 Na^+ ions are found in eight membered rings of the α-cage and the last Na^+ ion is placed near a four-membered ring in α -cage [Wang et al., 2004].

The ultimate exchange capacity of a zeolite is dependent on the chemical composition. Zeolites with a low Si/Al ratio have a higher exchange capacity [Breck, 1974].

As it is seen from the formula the Si/Al ratio is 1 in NaA which results in a high exchange capacity.
The exchange capacity of Zeolite A, Zeolite X, and Zeolite Y are 7, 6.4 and 5 meq/g respectively in anhydrous base [Breck, 1974]. Zeolite A with having the lowest Si/Al ratio has the highest cation exchange capacity.

2.2 ION EXCHANGE

2.2.1 Introduction

Ion exchange phenomenon has been thought of the oldest physical process known to humanity which dates back to descriptions in the Bible and writings of Aristotle. Ion exchange was the first property of zeolites for scientific studies when, in 1958, Eichorn revealed that natural zeolites chabazite and natrolite could reversibly exchange cations. At the turn of nineteenth century Gans synthesized aluminosilicates having the ability of water softening. Gans named them 'Permutits' and they were used to soften domestic and industrial water for many years [Cejka et al., 2007].

2.2.2 Ion Exchange in Zeolites

One of the most essential properties of zeolites is the ability to undergo reversible cation exchange [Gould, 1971]. Extensive studies of the ion exchange processes in mineral and synthetic zeolites have been conducted [Breck, 1974].

Cation exchange behavior of zeolites depends on:
1) the nature of the cation species, the size of the cation, both anhydrous and hydrated, and cation charge
2) the temperature

3) the concentration of the cation species in solution
4) the anion species associated with the cation in solution
5) the solvent (most exchange has been occured in aqueous solutions, although some work has been done in organic solvents)
6) the structural characteristics of the particular zeolite [Breck, 1974].

Zeolites are treated with aqueous solutions containing the cations to be exchanged in the most generally used ion exchange processes. The zeolites, usually in the form of hydrogen and ammonium are heated with crystalline salts in solid state ion exchange reactions. Furthermore, ion exchange takes place on impregnating zeolites with solutions of metal salts [Elvers and Hawkins, 1996].

Cation exchange in zeolites is accompanied by alteration of adsorption behavior, selectivity, catalytic activity and other essential physical properties. Due to the fact that many of these properties depend on controlled cation exchange with particular cation species, detailed information on the cation exchange equilibria is important [Breck, 1974].

2.2.3 Ion Exchange Equilibrium

When an ion exchanger containing cation B is placed in an electrolyte solution containing cation A, ions B will migrate from the exchanger to the solution and ions A from the solution to the ion exchanger. Ion exchange equilibrium is reached after a certain time. At equilibrium both the ion exchanger and the solution contain both ions A and B [Helfferich, 1962].

A binary ion exchange reaction in zeolites may be represented by the following equation:

$$z_A B^{z_B^+}_{(z)} + z_B A^{z_A^+}_{(s)} \Leftrightarrow z_A B^{z_B^+}_{(s)} + z_B A^{z_A^+}_{(z)} \qquad (2.3)$$

where A and B are competing cations, Z_A and Z_B are the respective charges of the exchanging cations, the subscripts z and s refer to the zeolite and solution phases [Dyer et al., 1981].

Ion exchange equilibrium may be characterized by the ion exchange isotherm. It is an equilibrium plot of the concentration of an exchanging ion in solution against the concentration of that same ion in the exchanger at constant temperature and constant solution normality. The isotherm is usually constructed by plotting the equivalent fraction of the entering ion in solution (A_s) versus the equivalent fraction of the same ion in the zeolite (A_z) [Dyer et al., 1981].

The equivalent fraction of the entering cation $A^{z_A^+}$ in solution is defined by:

$$A_s = \frac{z_A m_A}{z_A m_A + z_B m_B} \qquad (2.4)$$

where m_A and m_B are the concentrations (mol/L) of $A^{z_A^+}$ and $B^{z_B^+}$ in solution [Dyer et al., 1981].

The equivalent fraction of the entering cation $A^{z_A^+}$ in zeolite is defined by:

$$A_z = \frac{z_A M_A}{z_A M_A + z_B M_B} = \frac{z_A M_A}{Q} \tag{2.5}$$

where M_A and M_B are the concentration (mol/kg) of $A^{z_A^+}$ and $B^{z_B^+}$ in zeolite and Q is the ion exchange capacity [Dyer et al., 1981].

$A_s + B_s = 1$ and $A_z + B_z = 1$ for binary exchange due to the charge neutrality.

The selectivity of the ion exchanger for one of the two ions is often expressed by the separation factor which is defined as [Helfferich, 1962]

$$\alpha_B^A = \frac{A_z B_s}{B_z A_s} \tag{2.6}$$

The separation factor is not constant. It depends on the total concentration of the solution, the temperature and the equivalent fraction of the ion.

In a system in which the ion exchanger shows no preference for ion A or B, the equivalent fraction of the ions in the exchanger are same with the equivalent fraction of the ions in the solution. In this case, the ion exchange isotherm is linear and is the diagonal. In general actual ion exchangers prefer one counter ion in preference to the other ion. If the ion A is preferred, the factor α_B^A is greater unity and the isotherm lies above the diagonal. If ion B is preferred α_B^A is smaller than unity and the isotherm lies below the diagonal [Helfferich, 1962].

The simple relation between the separation factor and the ion exchange isotherm is shown in the Figure 2.7

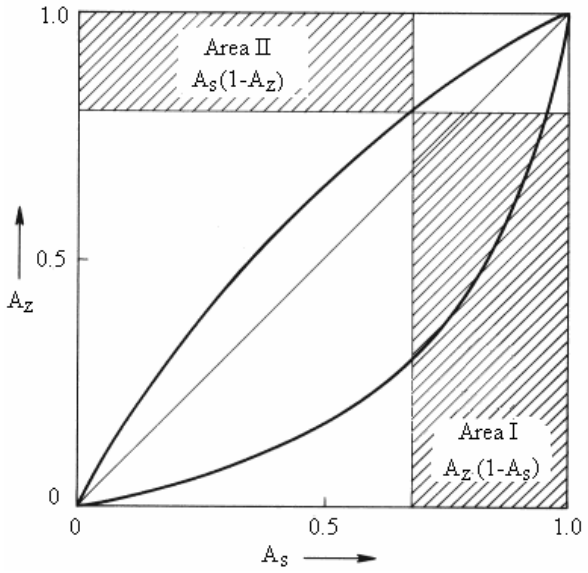


Figure 2.7. Ion Exchange Isotherm and Separation Factor [Helfferich, 1962]

$$\alpha_B^A = \frac{A_z B_s}{B_z A_s} = \frac{A_z(1-A_s)}{(1-A_z)A_s} = \frac{\text{Area I}}{\text{Area II}} \qquad (2.7)$$

Equation and figure shows that the separation factor is given by the ratio of the two rectangular areas which lie below and above the ion exchange isotherm [Helfferich, 1962].

The ion exchange isotherm for the exchange of cations in zeolites can be classified into five types (Figure 2.8) [Breck, 1974].

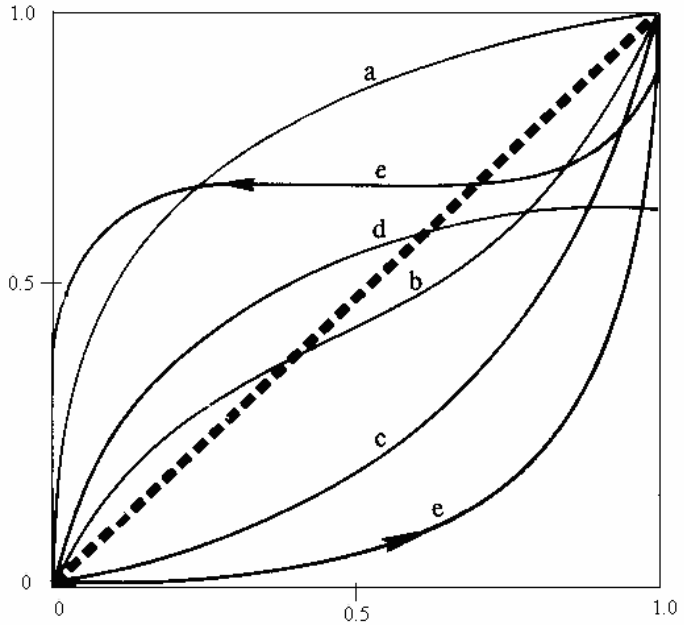


Figure 2.8. Types of ion exchange for reaction $A_s + B_z \leftrightarrow A_z + B_s$ [Breck, 1974]

In curve a, the zeolite exhibits selectivtity for the entering cation over the entire range of zeolite composition ($\alpha_B^A > 1$).

In curve b, the entering cation displays a selectivity which is reversal with increasing equivalent fraction in zeolite.

In curve c, the zeolite exhibits a preference for the ion in the zeolite over the entire range of zeolite composition ($\alpha_B^A < 1$).

In curve d, complete exchange is not accomplished by the entering ion A although the entering cation is initially preferred. Az_{max} is lower than unity.

In curve e, there seems an unusual case where exchange results in two zeolite phases producing a hysteresis loop.

For an ion exchange isotherm a mass action quotient (K_m) can be defined as follows [Dyer et al., 1981].

$$K_m = \frac{\mathrm{A}_z^{z_B} m_B^{z_A}}{B_z^{z_A} m_A^{z_B}} \tag{2.8}$$

2.2.4 Thermodynamics of Ion Exchange

While separation factor and mass action quotient correspond to one specific point on the isotherm, the equilibrium constant is an integral quantity representing the whole isotherm surface.

The relation between the equilibrium constant, the activities of the ions in the exchanger and the solution is dependent on the definition of the activities [Helfferich, 1962].

The thermodynamic equilibrium constant is defined as

$$K_a = \frac{\mathrm{a}_{\mathrm{A},z}^{z_B} \mathrm{a}_{\mathrm{B,s}}^{z_A}}{\mathrm{a}_{\mathrm{A,s}}^{z_B} \mathrm{a}_{\mathrm{B},z}^{z_A}} = \frac{(\mathrm{A}_z f_A)^{z_B} (m_B \gamma_B)^{z_A}}{(\mathrm{B}_z f_B)^{z_A} (m_A \gamma_A)^{z_B}} \tag{2.9}$$

where a, γ and f denote activity, activity coefficient in the solution and the activity coefficient in the exchanger respectively [Dyer et al., 1981].

The thermodynamic equilibrium constant K_a is related to the mass action quotient and the activities through the following relation [Dyer et al., 1981].

$$K_a = K_m \Gamma \frac{f_A^{z_B}}{f_B^{z_A}} \tag{2.10}$$

where

$$\Gamma = (\gamma_B^{z_A} / \gamma_A^{z_B}) \tag{2.11}$$

γ_A and γ_B are the single ion acitivity coeffients of the ions $A^{z_A^+}$ and $B^{z_B^+}$ in the solution, respectively.

f_A and f_B are the activity coefficients for ions $A^{z_A^+}$ and $B^{z_B^+}$ in solid phase.

It is not possible to evaluate γ_A and γ_B separately by experiment, because positive ions are always found in solution an association with an equivalent number of negative ions. The ratio Γ can be evaluated in terms of the mean molar stoichiometric activity coefficients in mixed salt solutions via the following equation

$$\Gamma = \frac{\gamma_B^{z_A}}{\gamma_A^{z_B}} = \frac{\left[\gamma_{\pm BX}^{(AX)}\right]^{z_A(z_B+z_x)/z_x}}{\left[\gamma_{\pm AX}^{(BX)}\right]^{z_B(z_A+z_x)/z_x}} \tag{2.12}$$

where $\gamma_{\pm BX}^{(AX)}$ and $\gamma_{\pm AX}^{(BX)}$ are the mean molar activity coefficients of salt AX in the presence of salt BX and the converse [Dyer et al., 1981].

$\gamma_{\pm BX}^{(AX)}$ and $\gamma_{\pm AX}^{(BX)}$ can be evaluated from $\gamma_{\pm BX}$ and $\gamma_{\pm AX}$ using the method of Glueckauf [Glueckauf, 1949].

When the total concentration of the solution is less than 1 mol/L, the thermodynamic equilibrium constant is calculated from the following equation [Dyer et al., 1981].

$$\ln K_a = (z_B - z_A) + \int_0^1 \ln K_c dA_z \tag{2.13}$$

where K_c is the Kielland quotient and defined as

$$K_c = K_m \Gamma \tag{2.14}$$

Equation 2.14 enables the determination of K_a by graphical integration of a plot of $\ln K_c$ against A_z [Dyer et al., 1981].

The standard free energy per equivalent of exchange can be evaluated from [Dyer et al., 1981].

$$\Delta G^o = -(RT\ln K_a)/z_A z_B \tag{2.15}$$

2.3 ADSORPTION ISOTHERMS

The adsorption isotherm is the equilibrium relation between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature. Langmuir and Freundlich equations are used to describe the adsorption isotherm [McCabe et al., 1993]. These two isotherms were first derived and used for the

adsorption of gases by microporous adsorbent, and then extended for the adsorption of solutes from aqueous solutions [Hui et al., 2005].

Langmuir and Freundlich isotherm can be given as follows

Langmuir isotherm $$q_e = \frac{q_{max} K C_e}{1 + K C_e} \quad (2.16)$$

Freundlich isotherm $$q_e = K_f C_e^{1/n} \quad (2.17)$$

where C_e: equilibrium aqueous metal ions concentration (mg/L)

q_e : the amount of metal ions adsorbed per unit mass of adsorbate at equilibrium (mg/g)

q_{max}: maximum adsorption capacity (mg/g)

K: energy of adsorption (L/mg)

K_f : adsorption capacity

1/n : adsorption intensity

Linearized forms of these equations are utilized in order to find the unknown parameters.

Linearized form of Langmuir isotherm $$\frac{1}{q_e} = \frac{1}{K q_{max} C_e} + \frac{1}{q_{max}} \quad (2.18)$$

Linearized form of Freundlich isotherm $$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (2.19)$$

CHAPTER 3

LITERATURE SURVEY

Sherry and Walton (1967) investigated the ion exchange of zeolite Linde 4A for cations Ag^+, Ti^+, Ca^{2+}, and Sr^{2+} at a total concentration of 0.1N and at 5, 25 and 77°C. The ion exchange isotherm demonstrated that NaA zeolite exhibited marked selectivity towards silver ion. All the Na^+ ions were replaced by Ag^+ ions. Extremely high selectivity of the zeolite for Ag^+ indicated the extensive binding of Ag^+ by the negatively charged aluminosilicate network. In addition, in their study thermodynamic values for the exchanges were calculated. The free energy and enthalpy of the Ag^+-Na^+ exchange were reported as -16.44 ± 0.17 kJ/eq and -11.63 ± 1.88 kJ/eq respectively.

Barrer et al. (1968) studied the thermodynamics and thermochemistry of cation exchange Na^+-Li^+, Na^+-K^+, Na^+-Rb^+, Na^+-Cs^+, Na^+-Ag^+, Na^+-Ti^+, Na^+-Ca^{2+}, Na^+-Sr^{2+}, Na^+-Ba^{2+} in zeolite Y. It was observed that Li^+, K^+ and Ag^+ replaced all the Na^+ at 25°C whereas the remainder replaced approximately 70% of the Na^+. Thermodynamic affinity sequence from the exchange equilibria was determined for two groups, the former giving complete exchange and the latter giving partial exchange with Na^+. The sequence was determined for the former group as $Ag^+ > K^+ > Na^+ > Li^+$ and for the latter group as $Ti^+ > Cs^+ > Rb^+ > Ba^{2+} > Na^+ > Sr^{2+} > Ca^{2+}$.

Gal et al. (1970) examined the ion exchange equilibria of synthetic zeolite 4A with Ni^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+} ions. Their study provided basic information on Ni^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+} types of zeolite 4A which included their chemical composition, the thermal stability of the crystal lattices and the thermodynamic data on the ion exchange equilibria. The ion exchange experiments were conducted by using 0.1 N

solutions of the divalent metal chlorides at room temperature. According to the isotherm zinc replaced practically all sodium ions and the isotherm terminated at unit equivalent fraction. By comparing the results of the thermodynamic data, they concluded that the main factor governing the exchange equilibria was the size of the divalent cations. The standard free energy of exchange between Na and Zn ions was calculated as -3.64 kJ/eq. According to the DTA and X-ray examination of the samples, it was concluded that Co, Zn and Cd zeolites were stable even when they were completely dehydrated up to 750-800°C.

Maes and Cremers (1974) studied the ion exchange of bivalent transition metal ions Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} on synthetic NaX and NaY zeolites at 0.01 total normality and a pH of 5.5-6 at 5, 25 and 45°C. The selectivity of both X and Y zeolite for the transition metal ions as determined by them has the following order: $Cu^{2+}>Zn^{2+}>Co^{2+}>Ni^{2+}$. It was concluded that the exchange was governed mainly by ion hydration characteristics, ionic radius of the exchanging cation and the coordination ability of the transition metal ion.

Langella et al. (2000) examined North Sardinia clinoptilolite in order to evaluate the cation exchange properties of this zeolite. They obtained the exchange isotherms of NH_4^+-Na^+, Cu^{2+}-Na^+, Zn^{2+}-Na^+, Cd^{2+}-Na^+ and Pb^{2+}-Na^+ at 25°C and 0.1 total normality. From the value of the calculated thermodynamic quantities such as equilibrium constant and the standard free energy, the selectivity sequence was determined as $NH_4^+>Pb^{2+}>Na^+>Cd^{2+}>Cu^{2+}\approx Zn^{2+}$. It is proved that Sardinia clinoptilolite had a low selectivity for Cu^{2+} and Zn^{2+}.

Majdan et al. (2003) examined the adsorption of Mn^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+}on A-type zeolite. The selectivity sequence was reported as $Cu^{2+}>Co^{2+}>Mn^{2+}>Zn^{2+}>Cd^{2+}>Ni^{2+}$ for the concentration range 10^{-4}-10^{-3} M.

Inglezakis et al. (2003) investigated the single and multicomponent ion exchange behaviour of natural Greek clinoptilolite for Pb^{2+}, Cu^{2+}, Fe^{2+} and Cr^{3+} ions. The effect of acidity on the ion exchange process and the influence of clinoptilolite on solution were also studied. The selectivity sequence at a total concentration of 0.01N and acidity 2 was determined as $Pb^{2+}>Fe^{2+}>Cr^{3+}\geq Cu^{2+}$ in both single and multicomponent solutions. On the other hand, the selectivity sequence was reported as $Pb^{2+}> Cr^{3+} > Fe^{2+} \approx Cu^{2+}$ in single metal solutions where acidity was not adjusted. Cu^{2+} and Cr^{3+} were reported as the most sensitive cations with respect to acidity. They concluded that ion exchange of metals was favored at high acidity values due to the fact that H^{+} ions competed with the metal ions at low acidities.

Top and Ülkü (2004) studied Ag^{+}-Na^{+}, Zn^{2+}-Na^{+}, and Cu^{2+}-Na^{+} equilibria for clinoptilolite-rich mineral at 25°C and 0.1 N total solution normality. The standard free energies of exchanges for Ag^{+}–Na^{+}, Zn^{2+}–Na^{+}, and Cu^{2+}–Na^{+} binary systems were calculated as -6.0, 2.03, and 3.09 kJ/eq respectively. The selectivity sequence was determined as $Ag^{+}>Zn^{2+}>Cu^{2+}$ as a result of these thermodynamic values.

Hui et al. (2005) examined the removal performance and the selectivity series of mixed metal ions (Co^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+} and Ni^{2+}) in aqueous solution by adsorption process on pure and chamfered edge zeolite 4A prepared from coal fly ash and commercial grade zeolite 4A. Parameters such as initial metal ion concentration, adsorbent dose and contact time on the adsorption process were studied. The affinity order was determined as $Cu^{2+}> Cr^{3+}> Zn^{2+}> Co^{2+}> Ni^{2+}$ at the tested concentration of 300 mg/L for coal fly ash prepared and commercial zeolite 4A. Langmuir model showed a better fit to the experimental data than the Freundlich model for all cases. It was seen that metal ions can be removed more effectively with increasing the mass of zeolite 4A.

Ören and Kaya (2006) investigated the factors which affected adsorption characteristics of Zn^{2+} on two natural zeolites namely Gördes and Bigadiç found in western Turkey. Studies on the effect of grain size revealed that a decrease in grain size of Bigadiç zeolite caused an increase in adsorption capacity, whereas grain size had little effect on the adsorption capacity of Gördes zeolite. The results also showed that increasing the initial concentration of Zn^{2+} solution resulted in an increase in the adsorption capacity to a certain degree, and then it became steadier at higher concentration values. Comparison of the experimental data with the Langmuir and Freundlich models revealed that Freundlich isotherms were better fitted with the experimental data than Langmuir isotherms.

Tangkawanit et al. (2005) examined the ion exchange of Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} into an analcime at a total normality of 0.01 and a temperature range 298-333 K. The selectivity series of analcime for the entering cations as determined by them has the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$ according to the calculated values of free energy of exchange. They concluded that the selectivity of the zeolite was determined by the cation size and the cation hydration energy.

Akgül et al. (2006) studied the ability of natural zeolite, clinoptilolite, for the removal of silver ions from aqueous solutions. They invesitigated the effects of metal ion concentration, adsorption time and the acidic treatment on the adsorption process. Maximum adsorption capacity of the clinoptilolite for Ag^{+} ion was found as 33.23 mg Ag^{+}/g zeolite. In terms of adsorption isotherms, it was reported that both Langmuir and Freundlich gave good fit for the experimental data. They showed that an increase in initial concentration of Ag^{+} ions resulted in an increase in the amount of Ag^{+} ions adsorbed up to a certain value. Since short adsorption time was preferred for the minimum energy consumption, clinoptilolite was offered as an efficient adsorbent for the removal of Ag^{+} ions due to its short adsorption time. It was observed that when the zeolite samples carrying Ag^{+} ions were treated with an acid solution, the adsorption capacity of the zeolite sample decreased.

Wang et al. (2007) investigated the removal of copper ions from aqueous solutions using Na-mordenite. The effects of solution pH, adsorbent dose, ionic strength and temperature on copper adsorption capacity were studied. It was resulted that Langmuir, Freundlich, and Dubinin-Radushkevich models could be applied to the adsorption system studied. The results of the thermodynamic parameters showed that the sorption process was spontaneous and endothermic in nature. The sorption capacity increased with an increase in solution pH, a decrease in ionic strength and adsorbent dose. It was concluded that Na-mordenite can be used to separate copper ions from aqueous solutions.

Caputo and Pepe (2007) made a review on the thermodynamic aspects of ion exchange in Italien natural zeolites such as philipsite, chabazite and clinoptilolite for various cations , namely Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cs^{+}, Sr^{2+}, Ba^{2+}, Co^{2+}, NH_4^{+}, K^{+} and Ca^{2+}. They reported ion exchange isotherms and the most important thermodynamic quantities, such as the equilibrium constant and the standard Gibbs free energy. According to the thermodynamic quantities, the selectivity order was evaluated as the following for philipsite, chabazite and clinoptilolite respectively.

$Ba^{2+} > Cs^{+} \approx K^{+} > Pb^{2+} > NH_4^{+} > Ca^{2+} > Na^{+} > K^{+} > Sr^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+}$

$Cs^{+} > NH_4^{+} > K^{+} > Pb^{2+} > Na^{+} > Ba^{2+} > Cd^{2+} > Sr^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+}$

$Cs^{+} > NH_4^{+} > Pb^{2+} > Na^{+} > Sr^{2+} > Cd^{2+} > Zn^{2+} \approx Cu^{2+}$

Kocaoba et al. (2007) studied the removal of heavy metals such as Cd^{2+}, Cu^{2+} and Ni^{2+} from aqueous solutions by using natural clinoptilolite obtained from Biga-Çanakkale region of Turkey at different initial concentration, zeolite amount, agitation speed and pH. The selectivity series for the concerned cations was reported as $Cd^{2+}>Ni^{2+}>Cu^{2+}$. Langmuir and Freundlich equations were used in order to describe the sorption equilibrium and it was seen that the experimental data fit sufficiently well to the Langmuir model. They concluded that clinoptilolite was an effective and inexpensive adsorbent for the removal of Cd^{2+}, Cu^{2+} and Ni^{2+} from aqueous solutions.

CHAPTER 4

MATERIALS AND METHODS

4.1 Ion Exchanger

In this study synthetic zeolite 4A was used in order to investigate the ion exchange of Ag^{+}-Na^{+}, Zn^{2+}-Na^{+}, Cu^{2+}-Na^{+} binary systems and Ag^{+}- Zn^{2+}- Na^{+}, Ag^{+}- Cu^{2+}- Na^{+}, Cu^{2+}- Zn^{2+}- Na^{+} ternary systems.

The commercial zeolite 4A obtained from Sigma Aldrich Company and has the following chemical formula

$Na_{12}[(SiO_2)_{12}(AlO_2)_{12}]nH_2O$

The zeolite is in powder form. It has a pore diameter of $4A^{o}$.

4.1.1 Characterization of Ion Exchanger

The characterization of the commercial zeolite NaA was done by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA).

4.1.1.1 X-Ray Diffraction (XRD)

Phase identification of the commercial zeolite 4A was done by Rigaku Ultima IV X-ray diffractometer at METU Central Laboratory. Operating conditions of XRD are given in Table 4.1

Table 4.1. Operating Conditions of XRD

Filter	Ni
Radiation	Cu-Kα
Voltage	40 kV
Current	40 mA
Speed	10 ^{o}/min

4.1.1.2 Scanning Electron Microscopy (SEM)

Morphological properties of commercial zeolite 4A was investigated by Quanta 400 FE-SEM scanning electron microscopy at METU Central Laboratory. The sample was coated with gold before analysis.

4.1.1.3 Thermogravimetric Analysis (TGA)

Water content of commercial zeolite 4A was determined by Shimadzu DTG 60-H at METU Chemical Engineering Department. The conditions used in TGA analysis are given in Table 4.2

Table 4.2. Conditions Used in TGA Analysis

Temperature range	25 – 800^{0}C
Heating range	10^{0}C/min
Purge gas	N_2
Purge gas flow rate	50 mL/min

4.2 Chemicals

The chemicals used in this study were analytical grade reagents obtained from Merck. The aqueous solutions of Ag^{+}, Zn^{2+} and Cu^{2+} were prepared by dissolving $Ag(NO_3)$, $Zn(NO_3)_26H_2O$, $Cu(NO_3)_23H_2O$ in highly deonized water obtained from Millipore Ultrapure Water System.

4.3 Atomic Absorption Spectrophotometry (AAS)

Philips PU9200X AAS and Shimadzu AA-6300 atomic absorption spectrophotometry at METU Chemical Engineering Department were used to determine the concentration of Ag^{+}, Zn^{2+} and Cu^{2+} in solution. In all experiments an air-acetylene flame, flowing at 0.9-1.2 L/min was used. Hollow cathode lamps of Ag, Zn and Cu (Unicam) were used. Silver, zinc and copper were measured at the wavelengths of 328.1, 213.9 and 324.8 nm respectively.
Atomic absorption spectrophotometry was calibrated before each experiment with standards that were prepared from commercially provided 1000 mg/L stock solutions.

Stock solutions of 0.1N were prepared and the concentrations of the prepared solutions were verified by Atomic Absorption Spectrophotometry using standard solutions. Each solution was analyzed by making appropriate ratio of dilutions in order to adjust the concentration range suitable for the cation of interest.

4.4 Binary Experiments

Commercial Zeolite NaA was used for the investigation of Ag^{+}-Na^{+}, Zn^{2+}-Na^{+}, Cu^{2+}-Na^{+} binary systems.
For binary equilibrium experiments the solid to liquid ratio was varied so as to obtain the different points on the ion exchange isotherm at a constant temperature and

constant normality. Keeping the solution volume constant at 20 mL, the masses of commercial zeolite NaA were varied between 0.05-1 g. The weighed amounts of zeolites were added to the vessels containing 20 ml of solution and stirred for 8 hours at room temperature which was sufficient for reaching equilibrium. (It is known that Ag^+ ion is very sensitive to light. In order to prevent photo reduction of Ag^+ ion, the experiments containing this ion was carried out in ambergris colored vessels wrapped in aluminum foil). Then, the mixtures were separated by centrifuging at 3000 rpm (SED 30)**.** The solution part was analyzed for the cation of interest by Atomic Absorption Spectrophotometer. Following the cation analysis in AAS, binary ion exchange isotherms were plotted as equivalent fraction of the exchanging ion in solution versus the equivalent fraction of the same ion in the zeolite for the systems Ag^+-Na^+, Zn^{2+}-Na^+, Cu^{2+}-Na^+ .

4.5 Ternary Experiments

Commercial Zeolite NaA was used for the investigation of Ag^+-Zn^{2+}-Na^+, Ag^+-Cu^{2+}-Na^+ and Zn^{2+}-Cu^{2+}-Na^+ ternary systems.

Solutions of Ag^+, Zn^{2+}, Cu^{2+} at 0.1N total concentration were again prepared from $Ag(NO_3)$, $Zn(NO_3)_2 6H_2O$, $Cu(NO_3)_2 3H_2O$ salts respectively. 0.25 and 0.50 g of zeolite NaA was mixed with solutions containing different proportions of two competing cations (varying between 0.01-0.09N) at a constant concentration of 0.1N and stirred for 8 hours at room temperature. Then mixtures were separated by centrifuging at 3000 rpm and the solution parts were analyzed for the cation of interest by AAS in the same manner like in binary experiments. Following the cation analysis in AAS, ternary ion exchange isotherms representing equivalent fraction of each ion in solution and the equivalent fraction of that ion in the zeolite for the systems of Ag^+- Zn^{2+}-Na^+, Ag^+-Cu^{2+}-Na^+, Zn^{2+}- Cu^{2+}-Na^+ were plotted.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Characterization of Commercial Zeolite 4A

The characterization of the commercial zeolite 4A was done by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA).

5.1.1 X-ray diffraction (XRD) Analysis

Powder X-ray diffraction analysis was used for the phase identification of the commercial zeolite 4A. Figure 5.1 shows the powder XRD pattern of the commercial zeolite NaA.

Figure 5.2 shows the characteristic XRD pattern of zeolite A in literature. Comparison of the characteristic peaks in XRD pattern of the commercial zeolite 4A with that of zeolite A given in literature indicates that the sample used in this study has a single crystalline phase.

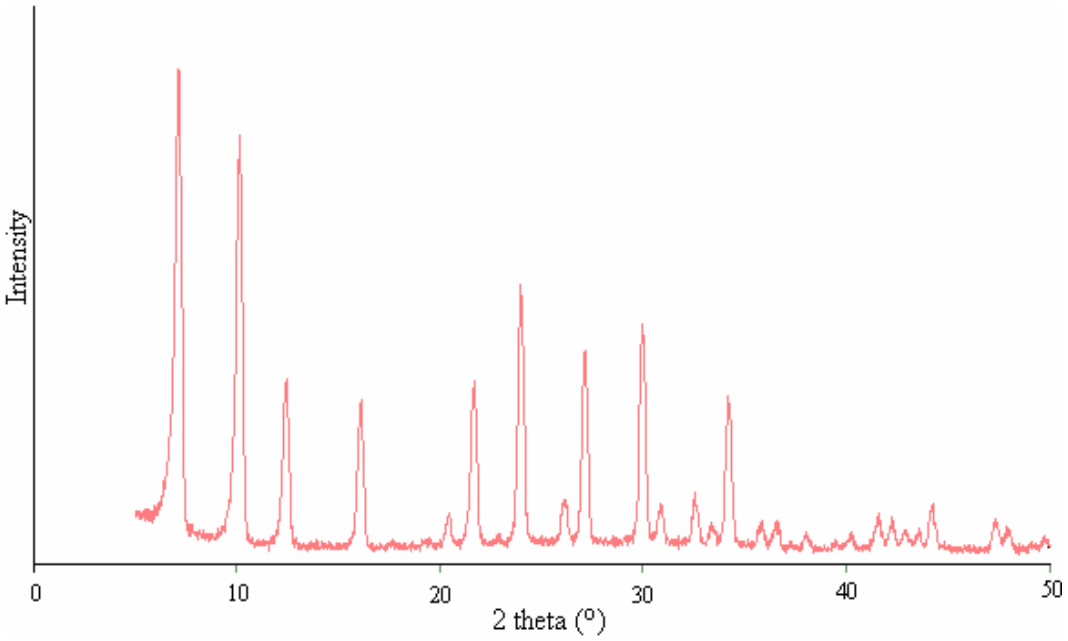


Figure 5.1. X-ray diffraction pattern of commercial zeolite NaA

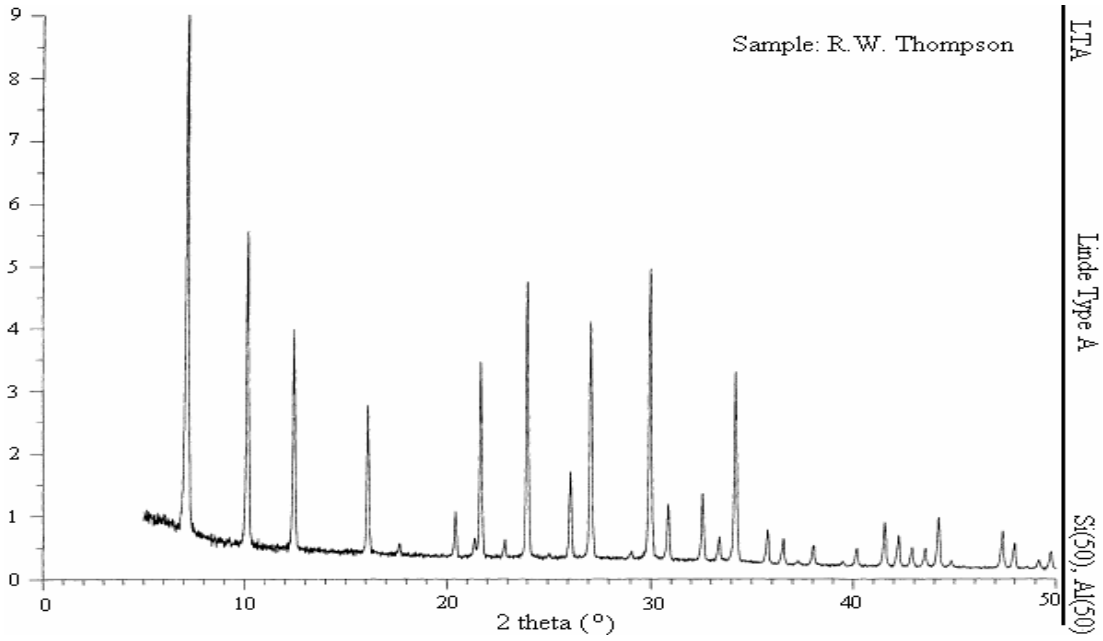
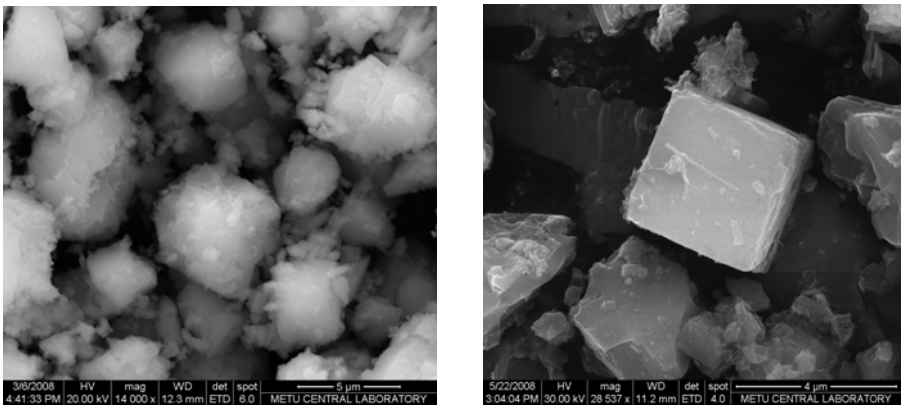


Figure 5.2. Characteristic XRD Pattern of Zeolite A [Robson, 2001]

5.1.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used in order to see the morphological properties of commercial zeolite 4A. Figure 5.3 shows the scanning electron micrographs of commercial zeolite 4A.

Characteristic cubic shape of zeolite A can be seen in Figure 5.2.b.



(a) (b)

Figure 5.3. Scanning electron micrographs of commercial zeolite 4A
a) 14000X magnification b) 28537X magnification

5.1.3 Thermogravimetric Analysis

Water content of commercial zeolite 4A was determined by thermogravimetric analysis. Figure 5.4 gives the TGA of commercial zeolite 4A.

The water content of commercial zeolite 4A used in this study was determined as 18.501 wt % from TGA analysis.

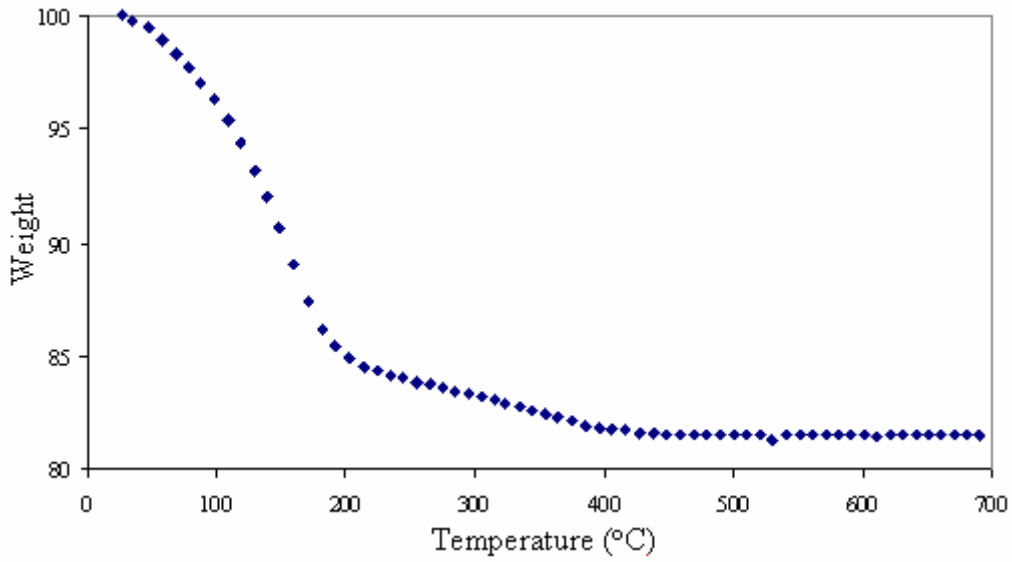


Figure 5.4. TGA Scan of commercial zeolite 4A

5.2 Ion Exchange Capacity

Having obtained the moisture content as 18.5 wt %, the ion exchange capacity of commercial zeolite 4A was determined as 5.737 meq/g wet resin. (The calculation of exchange capacity is given in Appendix A.)

5.3 Binary Systems Ion Exchange Isotherms

Binary ion exchange isotherms for the systems Ag^{+}-Na^{+}, Zn^{2+}-Na^{+} and Cu^{2+}-Na^{+} were obtained at 0.1 N and 25°C. The isotherms were drawn as equivalent fractions of exchanging cations in solution versus equivalent fraction of exchanging cations in zeolite phase. The isotherms for Ag^{+}-Na^{+}, Zn^{2+}-Na^{+} and Cu^{2+}-Na^{+} systems are shown in Figure 5.5, 5.6 and 5.7 respectively. Comparison of the isotherms is given in Figure 5.8.

The experimental isotherms for Ag^{+}-Na^{+}, Zn^{2+}-Na^{+} and Cu^{2+}-Na^{+} binary systems conform to type 'a' in Breck's classification [Breck, 1974]. As inferred from the isotherms, zeolite 4A is selective for all the ions examined. The isotherms are all above the diagonal over the whole range which means that the separation factor is always greater than 1 for each case.

Comparison of isotherms qualitatively shows that the selectivity of zeolite 4A for silver and copper with respect to sodium is greater than that of zinc. But it is difficult to differentiate between silver and copper. Thermodynamic analyses of the binary systems were carried out in order to determine the selectivity sequence among cations silver, copper and zinc.

Equilibrium isotherms are also plotted in different units (meq/g zeolite vs meq/L solution). These isotherms are shown in Figures 5.9, 5.10 and 5.11 for Ag^{+}-Na^{+}, Zn^{2+}-Na^{+} and Cu^{2+}-Na^{+} systems respectively. Their comparison is given in Figure 5.12. While maximum exchange level of Ag^{+}-Na^{+} and Cu^{2+}-Na^{+} systems are almost same, that of Zn^{2+}-Na^{+} system is lower than these two systems.

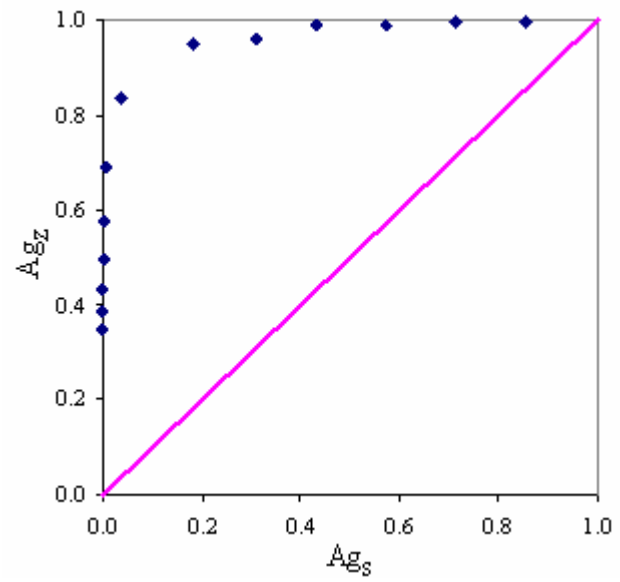


Figure 5.5. Ion exchange Isotherm of Zeolite 4A for Ag^+- Na^+ Binary System at 25°C and 0.1 N

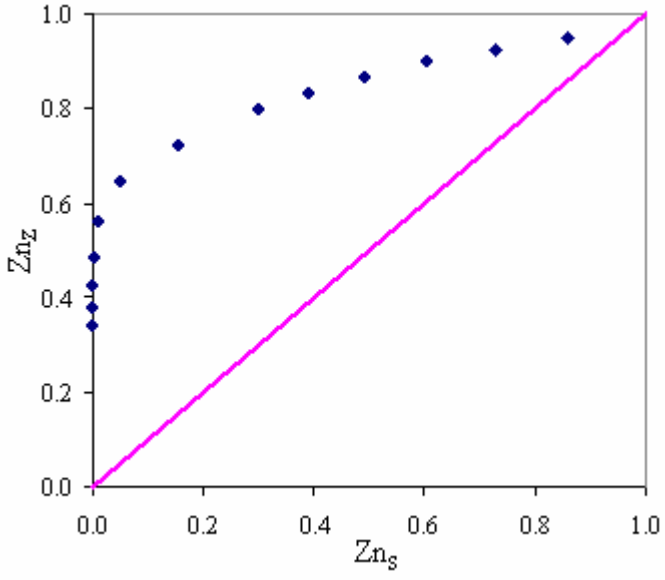


Figure 5.6. Ion exchange Isotherm of Zeolite 4A for Zn^{2+}- Na^+ Binary System at 25°C and 0.1 N

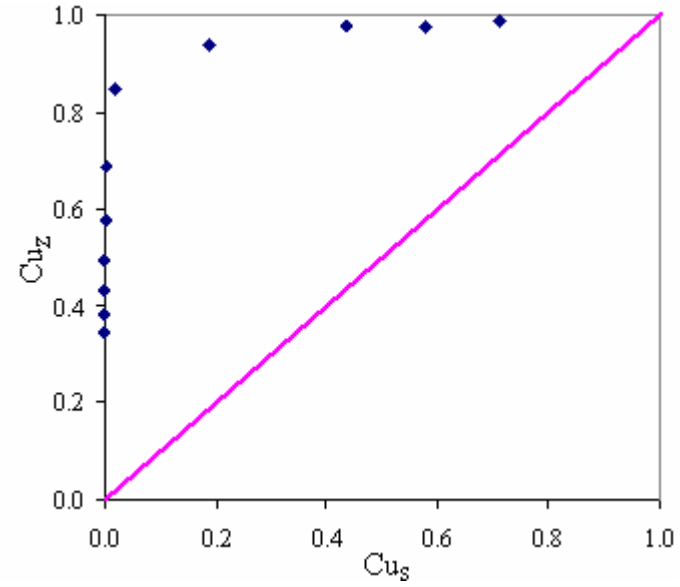


Figure 5.7. Ion exchange Isotherm of Zeolite 4A for Cu^{2+}- Na^{+} Binary System at 25°C and 0.1 N

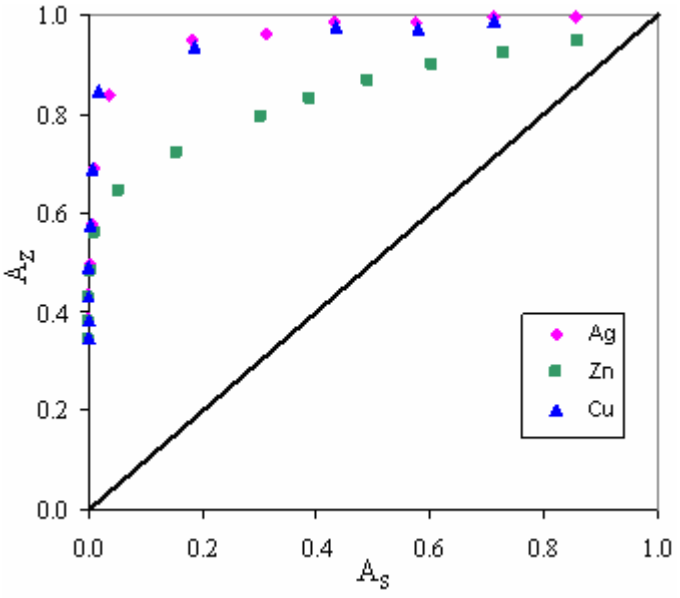


Figure 5.8. Comparison of Ag^{+}, Zn^{2+} and Cu^{2+} Ion Exchange Isotherms of Zeolite 4A at 25°C and 0.1 N

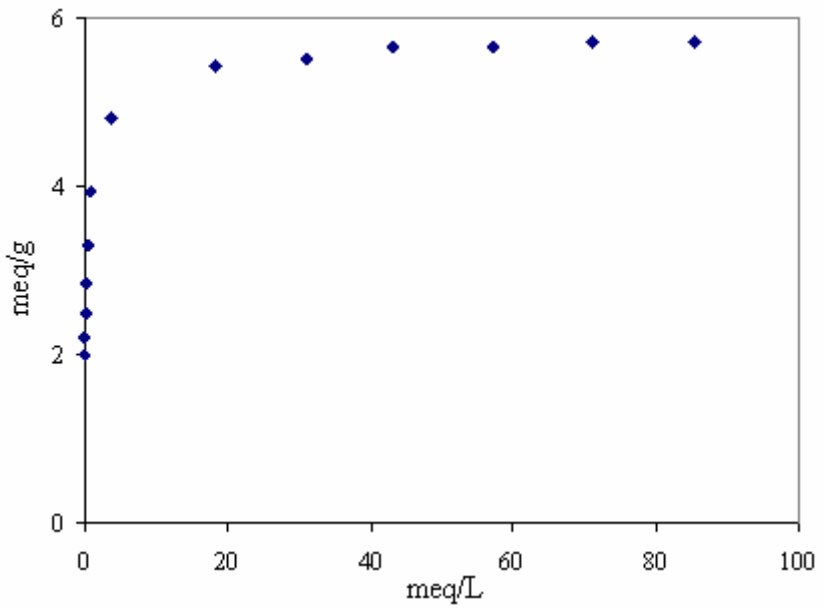


Figure 5.9. Ion exchange Isotherm of Zeolite 4A for Ag^{+}- Na^{+} Binary System at 25°C and 0.1 N (meq/g versus meq/L)

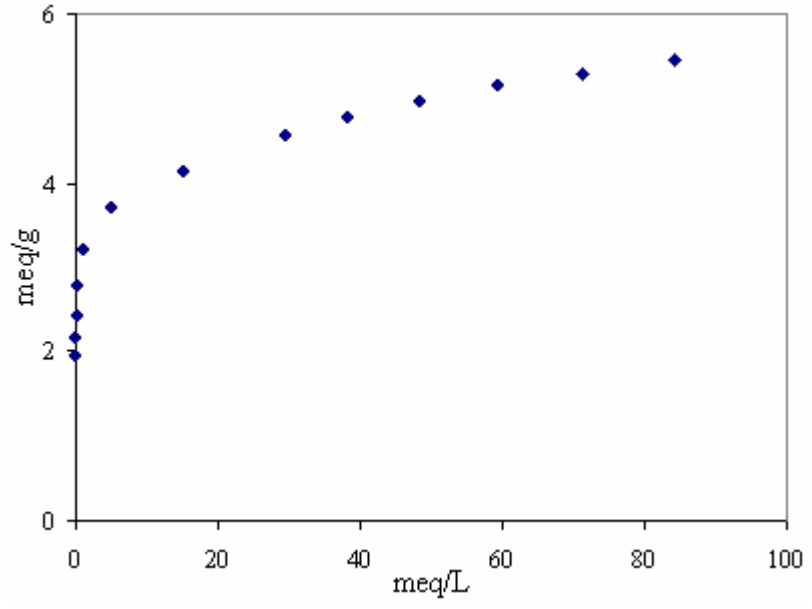


Figure 5.10. Ion exchange Isotherm of Zeolite 4A for Zn^{2+}- Na^{+} Binary System at 25°C and 0.1 N (meq/g versus meq/L)

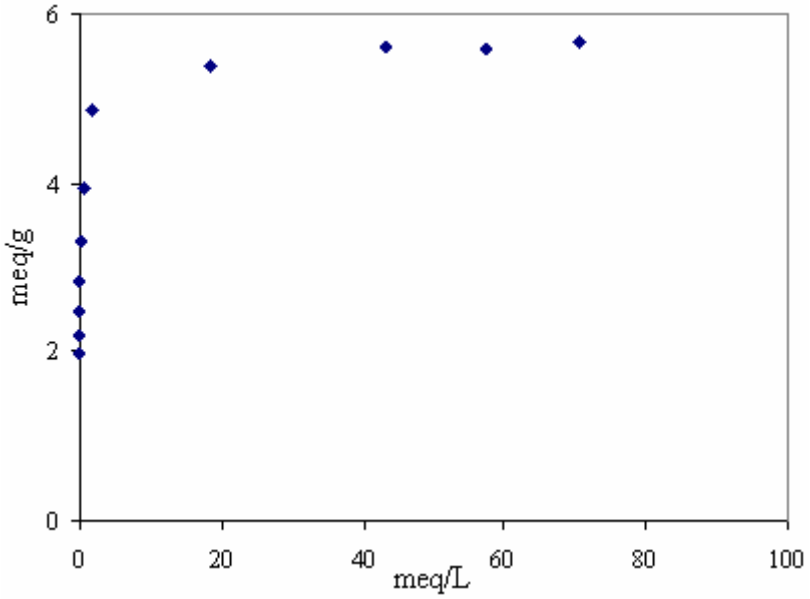


Figure 5.11. Ion exchange Isotherm of Zeolite 4A for Cu^{2+}- Na^{+} Binary System at 25°C and 0.1 N (meq/g versus meq/L)

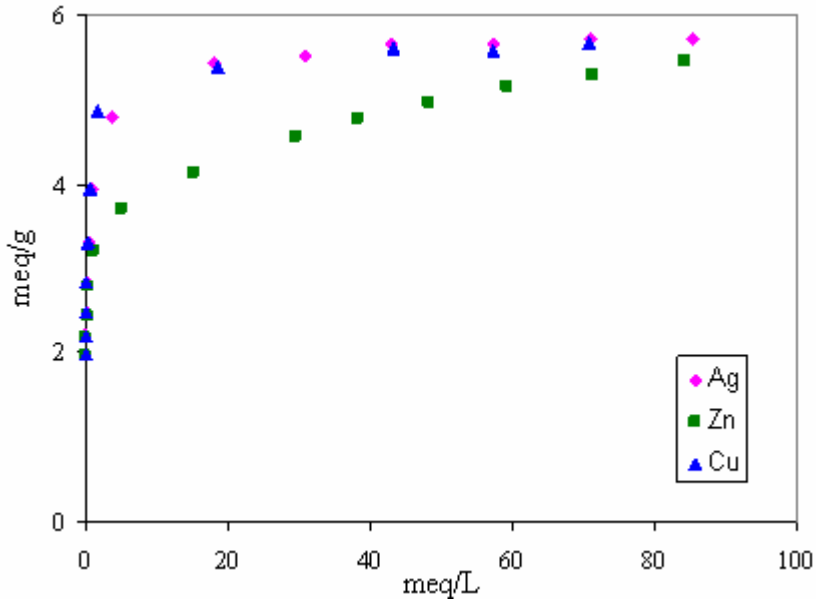


Figure 5.12. Comparison of Ag^{+}, Zn^{2+} and Cu^{2+} Ion Exchange Isotherms of Zeolite 4A at 25°C and 0.1 N (meq/g versus meq/L)

5.4 Thermodynamic Analysis of Binary Systems

Using the equilibrium data, the thermodynamic analysis of the binary systems were carried out as follows.

For the calculation of the solution non-ideality correction factor Γ, the mean molar stoichiometric activity coefficients of the single salt solution was first evaluated by modified Debye-Hückel equation [Dyer et al., 1981]. To evaluate the constants 'a' and 'b' in Debye-Hückel equation, the given values of $\gamma_{\pm}$ were used. Two expressions were obtained, each of which containing both 'a' and b'. By writing 'b' in terms of 'a', a quadratic expression containing only 'a' was obtained. This equation was solved in terms of 'a' and then 'b' was determined. Having obtained the constants 'a' and 'b', values of $\gamma_{\pm}$ were calculated at the desired ionic strength.

Glueckauf's equations were used to calculate the mean molar stoichiometric activity coefficients of mixed salts. Then the solution non-ideality correction factor (Γ) was determined by using equation 2.12. It is seen from the Figures 5.13–5.15, Γ does not vary with solution composition for univalent-univalent exchange (Ag^{+}-Na^{+}), whereas it increases with increasing solution concentration for univalent-divalent exchange (Na^{+}-Zn^{2+} and Na^{+}-Cu^{2+}). Deviation from ideality was seen for the univalent-divalent exchange.

Logarithms of the corrected selectivity coefficients (K_c) versus the equivalent fraction of the exchanging cations in zeolite phase (Kielland plot) are given in Figures 5.16, 5.17 and 5.18. The corrected selectivity coefficient decreases with increasing equivalent fraction of exchanging cation in zeolite phase.

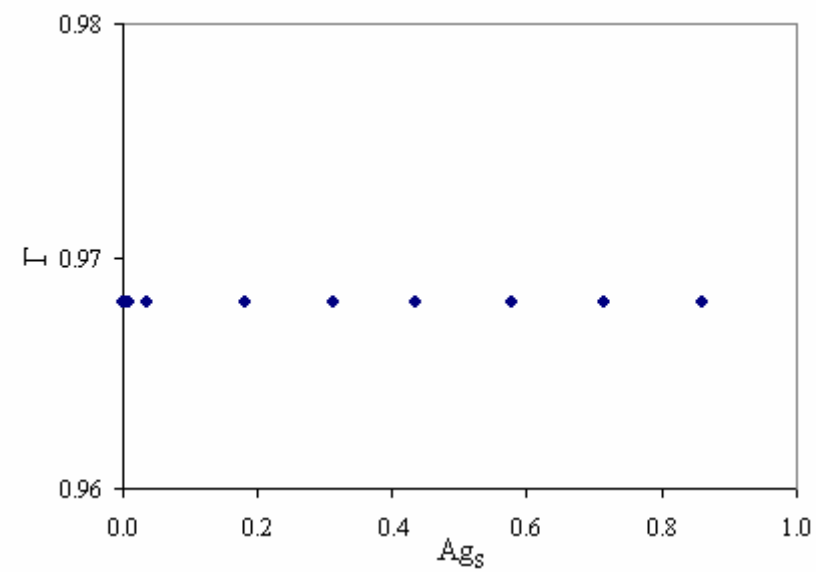


Figure 5.13. Change in Non-ideality Correction Factor with Equivalent Fraction of Silver in Solution for Ag^{+}- Na^{+} Exchange

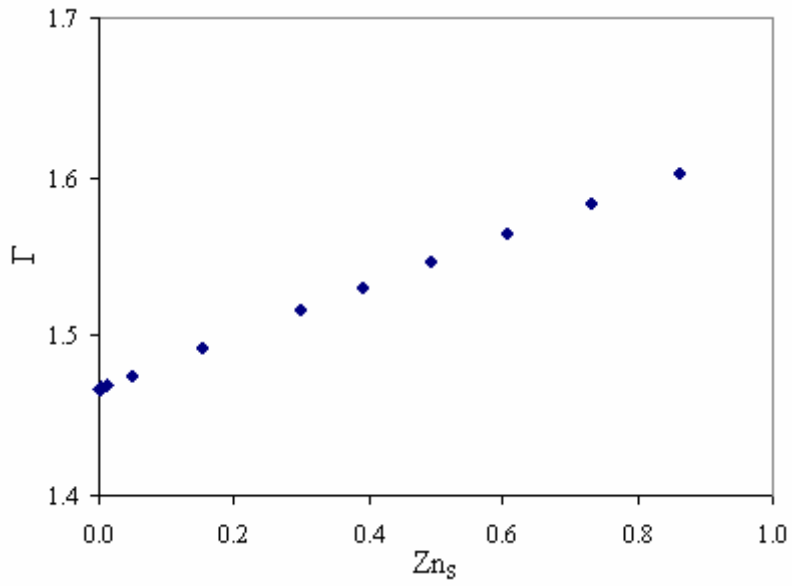


Figure 5.14. Change in Non-ideality Correction Factor with Equivalent Fraction of Zinc in Solution for Zn^{2+}- Na^{+} Exchange

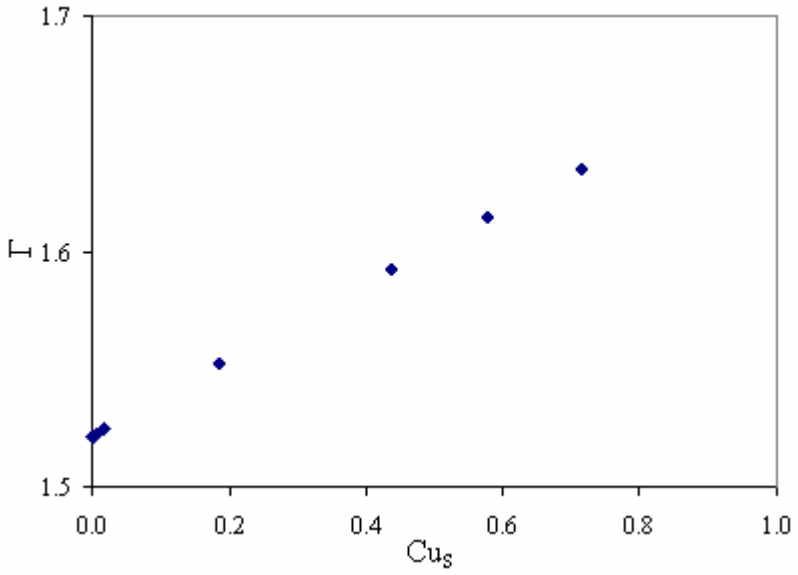


Figure 5.15. Change in Non-ideality Correction Factor with Equivalent Fraction of Copper in Solution for Cu^{2+}- Na^{+} Exchange

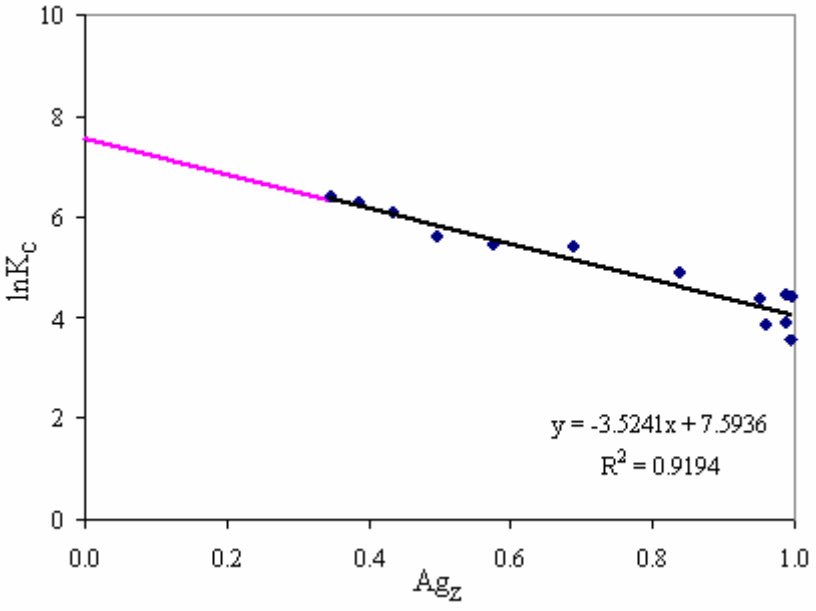


Figure 5.16. Kielland Plot for Ag^{+}-Na^{+} Binary System

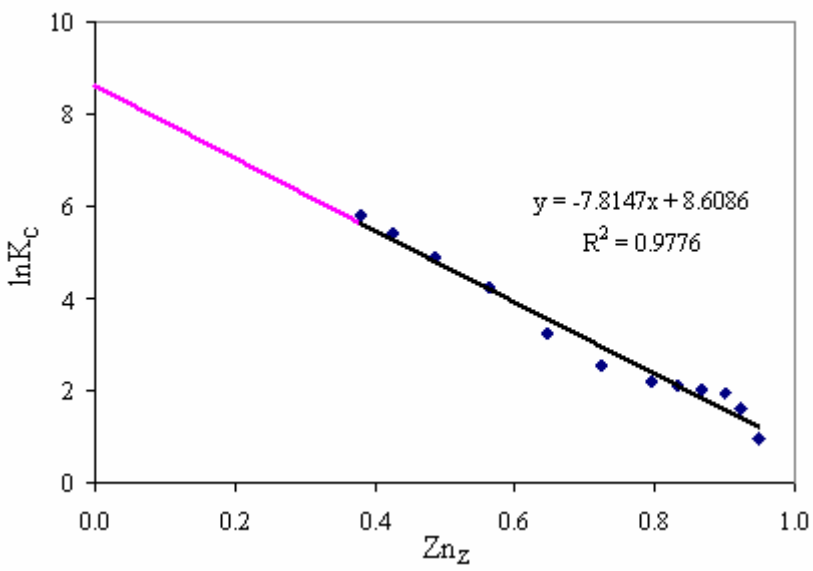


Figure 5.17. Kielland Plot for Zn^{2+}-Na^{+} Binary System

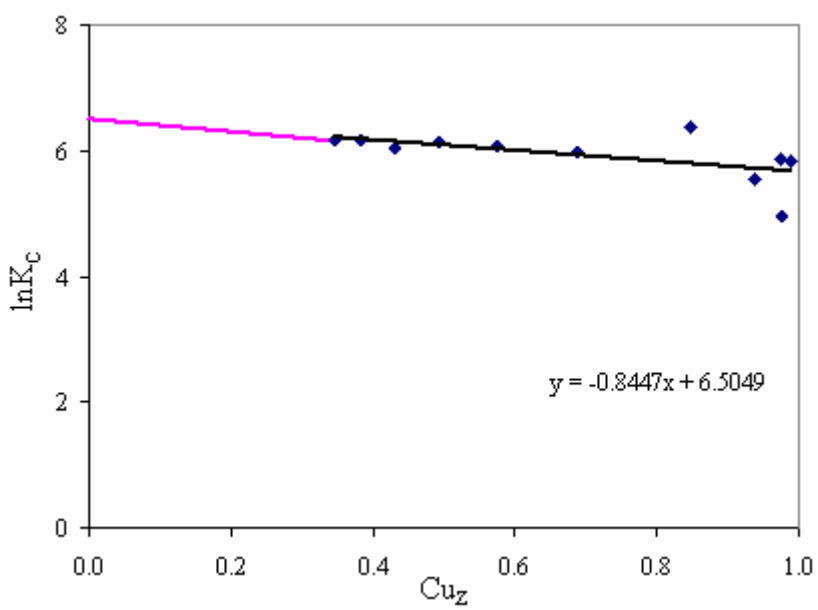


Figure 5.18. Kielland Plot for Cu^{2+}-Na^{+} Binary System

Thermodynamic equilibrium constant for each binary exchange was calculated by using equation 2.13. In order to determine the second term in the equation graphical integration of the Kielland plot (lnKc against Az) was utilized. Having obtained the value of K_a, standard free energy of exchange was calculated. Numerical values of thermodynamic equilibrium constant and standard free energies are given in Table 5.1.

Table 5.1 Calculated Values of K_a and ΔG

System	K_a	ΔG (kJ/mol)
Ag^+-Na^+	340.89	-14.46
Zn^{2+}-Na^+	40.50	-4.59
Cu^{2+}-Na^+	161.18	-6.30

Free energy decrease is largest for Ag^+-Na^+ exchange and lowest for Zn^{2+}-Na^+ exchange. It can be concluded that zeolite shows the highest affinity to Ag^+ and lowest affinity to Zn^{2+} among these cations.

The selectivity sequence of zeolite 4A is then $Ag^+ > Cu^{2+} > Zn^{2+}$.

This selectivity sequence can be explained in terms of hydration of cations.

Cations interact with water molecules in order to form hydration spheres. The characteristics of the hydration spheres depend on the size and the charge of the cation. Hydrated radius generally decreases with increasing cation radius. The hydrated radius of divalent cations is usually higher than that of monovalent cations [Top and Ülkü, 2004].

The ionic radius and the hydrated radius of the Ag^+, Cu^{2+} and Zn^{2+} are given in Table 5.2.

Table 5.2. Ionic and Hydrated Ionic Radius of Cations Used in This Study

Cation	Ionic Radius A^o	Hydrated Ionic Radius A^o
Ag^+ [Railsback's Some Fundamentals of Mineralogy and Geochemistry]	~1.26	~3.41
Cu^{2+} [Sand and Mumpton,1976]	0.82	4.19
Zn^{2+} [Sand and Mumpton,1976]	0.83	4.30

The effective pore size of zeolite NaA is 4A°. If the size of the hydrated ion is greater than the effective pore width of the zeolite, the species may be excluded or some of the waters of hydration must be stripped from the solvated ions to provide them to enter the pores of the zeolite [Hui et al., 2005].
According to the size of hydrated radii of ions in Table 5.2 the selectivity series is as $Ag^+ > Cu^{2+} > Zn^{2+}$ which is the same result obtained from thermodynamic analysis.

Highest selectivity of zeolite 4A towards silver can also be explained by polarizability of silver. Silver is very highly polarizable because of its electronic structure. It is highly polarized by the strong electric field within the zeolites and very tightly bound to the anionic framework [Auerbach, 2003].

Thermodynamic quantities reported in literature on the Ag^+-Na^+ and Zn^{2+}-Na^+ exchange are summarized in Table 5.3. The difference in the obtained Gibbs free energy can be due to the conditions employed, analytical methods used for the determination of the exchanging cations and different approaches used for the thermodynamic analysis.
In principle non-ideal behavior in the aqueous solution, can be calculated from different well-established electrolyte solution theories such as Bronsted, Guggenheim, Scatchard and Pitzer [Pabalan, 1994]. Using different theories will give different activity coefficient values.

Extrapolation of the Kielland plot can also cause to get different thermodynamic values.

Table 5.3. Comparison of Thermodynamic Data for Ag^{+}-Na^{+} and Zn^{2+}-Na^{+} Exchange at 25°C and 0.1N Solution Concentration

Reference	Study	ΔG kJ/mol
Sherry and Walton, 1967	Ag^{+}-Na^{+} exchange	-16.44 ± 0.17
present study	Ag^{+}-Na^{+} exchange	-14.46
Gal et al., 1970	Zn^{2+}-Na^{+} exchange	-3.64
Present study	Zn^{2+}-Na^{+} exchange	-4.59

5.5 Adsorption Isotherms for Binary Systems

Langmuir and Freundlich equations were used to describe the experimental data. Figures from 5.19 to 5.24 show the linearized forms of Langmuir and Freundlich isotherms for Ag^{+}-Na^{+}, Zn^{2+}-Na^{+} and Cu^{2+}-Na^{+} binary systems.

Comparison of linearized Langmuir and Freundlich isotherms shows that while Langmuir model represents a better fit to the experimental data of Cu^{2+}-Na^{+} exchange, Freundlich model gives a better fit to the experimental data of Ag^{+}-Na^{+} and Zn^{2+}-Na^{+} exchange.

Maximum theoretical exchange capacity of the commercial zeolite 4A for Cu was calculated as 182.3 mg/g (5.74 meq/g). When this is compared with the maximum exchange capacity obtained from Langmuir model (161.3 mg/g and/or 5.1 meq/g) it is seen that they are close to each other which proves the applicability of the model.

Table 5.4. The Parameters for Langmuir and Freundlich Isotherms

Isotherm parameters	Ag^{+}-Na^{+}	Zn^{2+}- Na^{+}	Cu^{2+}- Na^{+}
Langmuir			
R^2	0.923	0.835	0.965
qmax (mg/g)	555.6	140.9	161.3
Kd (L/mg)	0.062	0.382	0.365
Freundlich			
R^2	0.932	0.993	0.891
n	6.901	7.692	7.628
Kf (L/g)	181.835	62.589	72.06

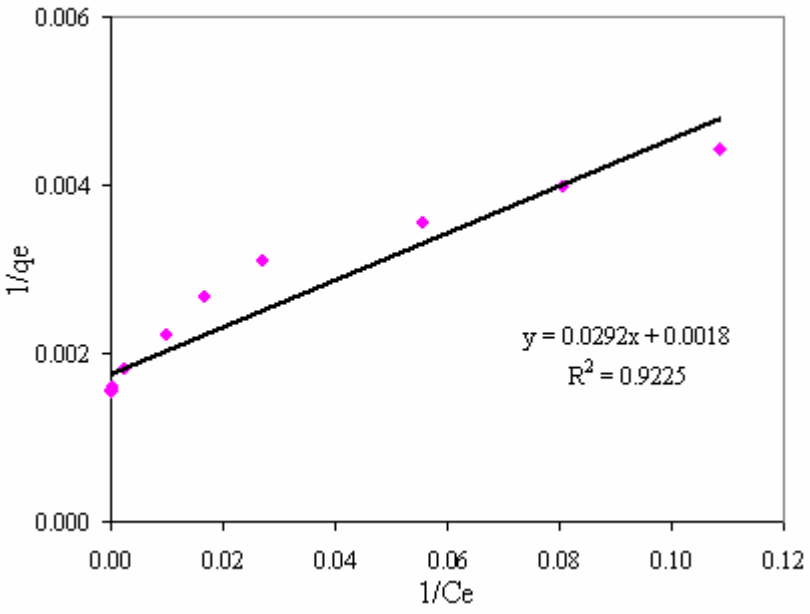


Figure 5.19. Linearized Langmuir Isotherm for Ag^{+}- Na^{+} System

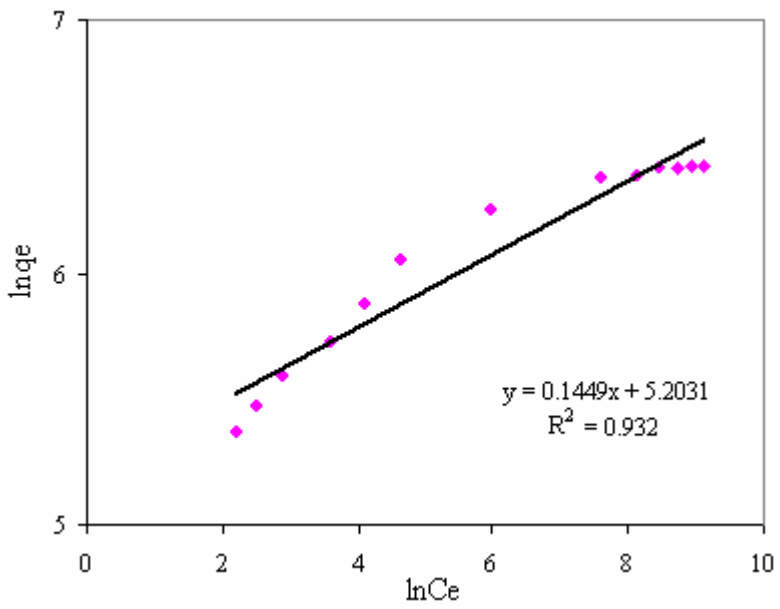


Figure 5.20. Linearized Freundlich Isotherm for Ag^{+}- Na^{+} System

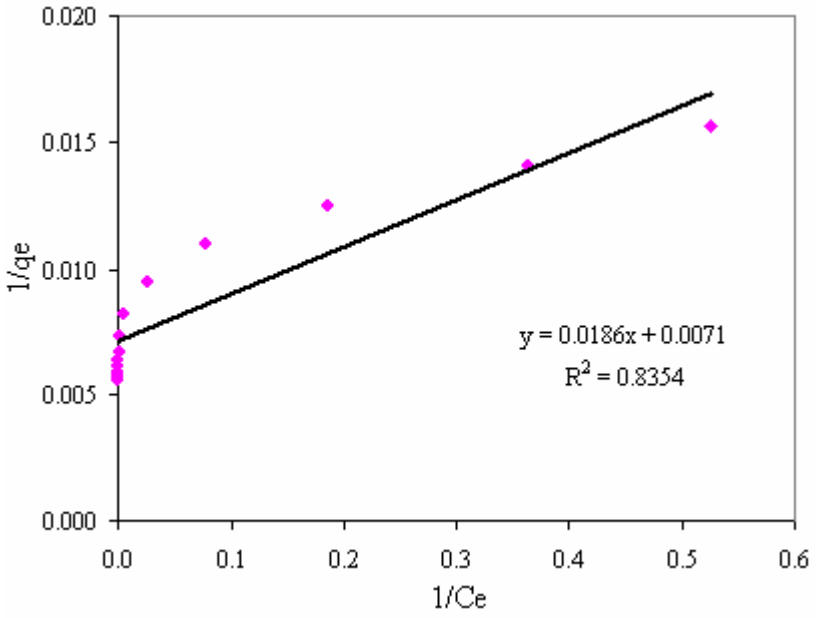


Figure 5.21. Linearized Langmuir Isotherm for Zn^{2+}- Na^{+} System

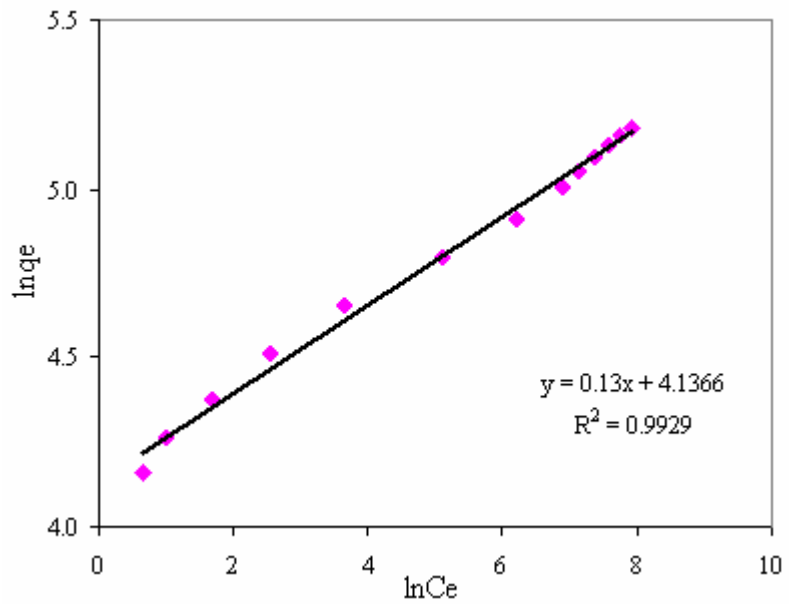


Figure 5.22. Linearized Freundlich Isotherm for Zn^{2+}- Na^{+} System

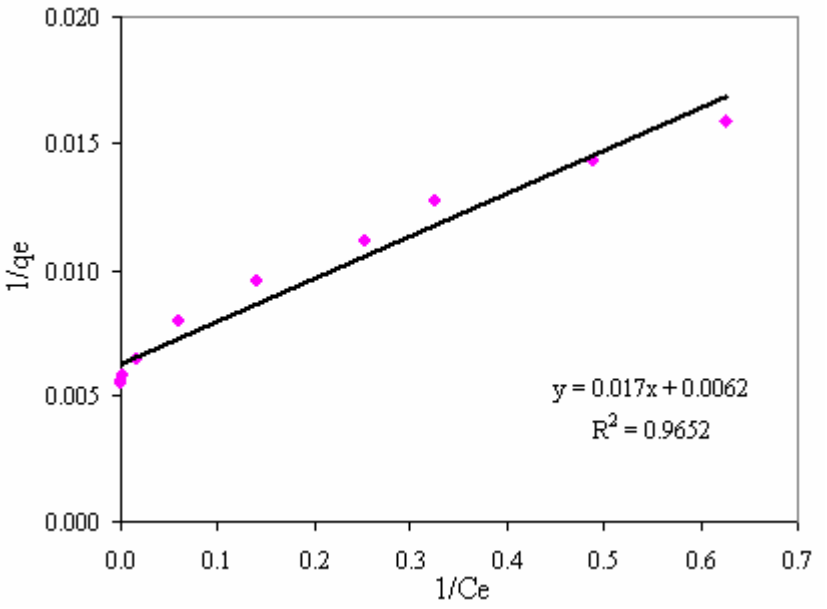


Figure 5.23. Linearized Langmuir Isotherm for Cu^{2+}- Na^{+} System

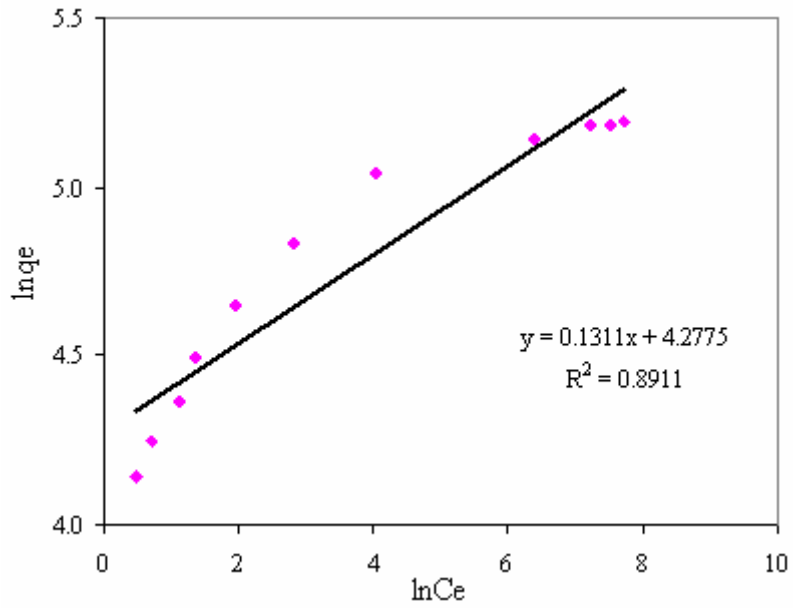


Figure 5.24. Linearized Freundlich Isotherm for Cu^{2+}- Na^{+} System

5.6 Ternary Systems Ion Exchange Isotherms

In order to determine the multicomponent ion exchange behavior of zeolite 4A, experimental isotherms of Ag^{+}-Zn^{2+}-Na^{+}, Ag^{+}-Cu^{2+}-Na^{+} and Cu^{2+}-Zn^{2+}-Na^{+} ternary systems were plotted in equilateral triangle graphs. Isotherms were drawn as equivalent fraction of exchanging cation in solution and equivalent fraction of exchanging cation in zeolite similar to the binary experiments. Ternary ion exchange isotherms for 0.25 g zeolite/20 mL solution are shown in Figure 5.25, 5.26, 5.27 and ternary ion exchange isotherms for 0.5 g zeolite/20 mL solution are shown in Figure 5.28, 5.29, 5.30. Since zeolites containing a combination of silver and zinc have attracted great interest in antibacterial applications, ion exchange of Ag^{+}-Zn^{2+}-Na^{+} for 1.0 g zeolite/20 mL solution was also studied and its isotherm is shown in Figure 5.31. The experimental data are given in Appendix E.

In ternary isotherms while the total concentration was kept constant at 0.1 N, initial concentration of the exchanging cations were varied from 0.01N to 0.09 N. In the figures, circles designate the equivalent fractions of exchanging cations in solution and squares designate the equivalent fractions of exchanging cations in zeolite. Each symbol shows three equivalent fractions. For Ag^{+}- Zn^{2+}- Na^{+} system while each circle shows the equivalent fraction of Ag^{+}, Zn^{2+} and Na^{+} ions in solution, each square shows the equivalent fraction of Ag^{+}, Zn^{2+} and Na^{+} ions in zeolite.

In order to determine the selectivity sequence from ternary diagrams, the point where initial concentration of each exchanging cation is equal to each other should be examined in detail. For the same initial concentration the cation which is taken up more than the other is favored more by the zeolite. As an example when the fifth point (where initial concentration of each cation is the same= 0.05N) in Figure 5.25 is examined the equivalent fractions of cations in the zeolite phase after equilibrium is 0.611 for Ag^{+}, 0.324 for Zn^{2+} and 0.065 for Na^{+} respectively. From these numerical values it may be concluded that silver is preferentially selected by zeolite 4A in the presence of zinc. When Figure 5.26 and Figure 5.27 are investigated in the same manner, it is concluded that zeolite 4A shows a higher affinity to silver than copper and its selectivity to copper is higher than that of zinc. When these three binary sequence is combined the selectivity sequence of zeolite 4A for the examined cations is determined as $Ag^{+}>Cu^{2+}>Zn^{2+}$ which is the same result obtained from the binary thermodynamic analysis.

When the amount of zeolite is increased, the total amount of exchange increases due to the higher exchange capacity per unit volume of solution. When Figure 5.26 is compared with Figure 5.29 it is clearly seen that, zeolite 4A with a mass of 0.5 g /20 mL solution has exchanged most of the cations in solution.

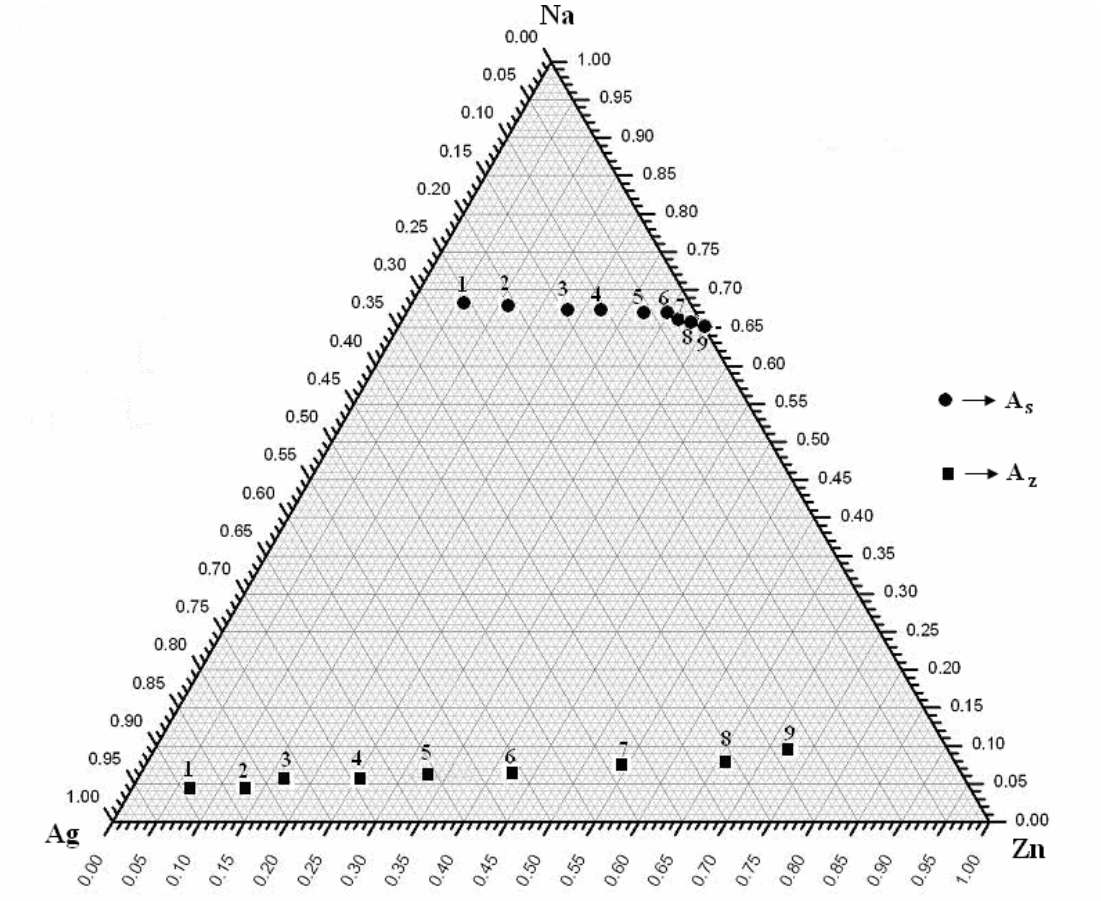


Figure 5.25. Ion Exchange Isotherm of Ag^{+}-Zn^{2+}-Na^{+} System for 0.25 g zeolite/20 mL solution at 25°C and 0.1 N

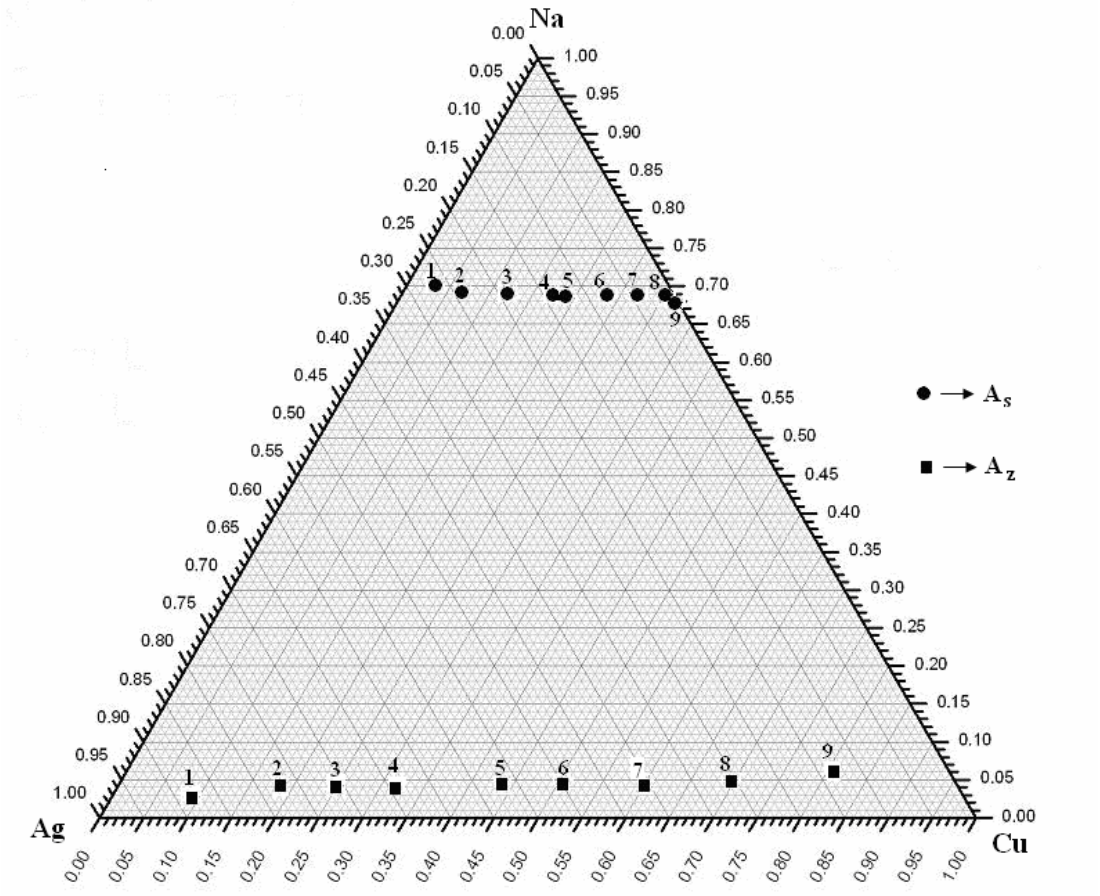


Figure 5.26. Ion Exchange Isotherm of Ag^{+}-Cu^{2+}-Na^{+} System for 0.25 g zeolite/20 mL solution at 25°C and 0.1 N

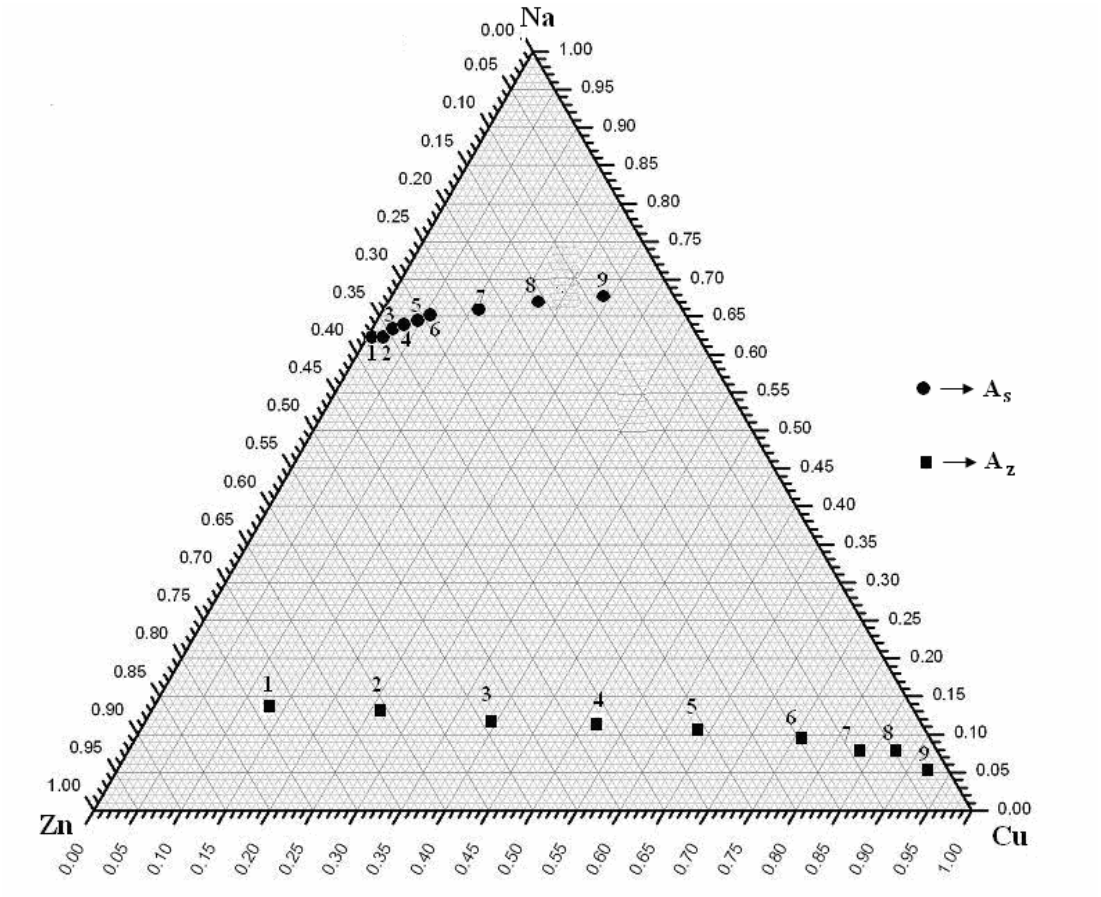


Figure 5.27. Ion Exchange Isotherm of Cu^{2+}-Zn^{2+}-Na^{+} System for 0.25 g zeolite/20 mL solution at 25°C and 0.1 N

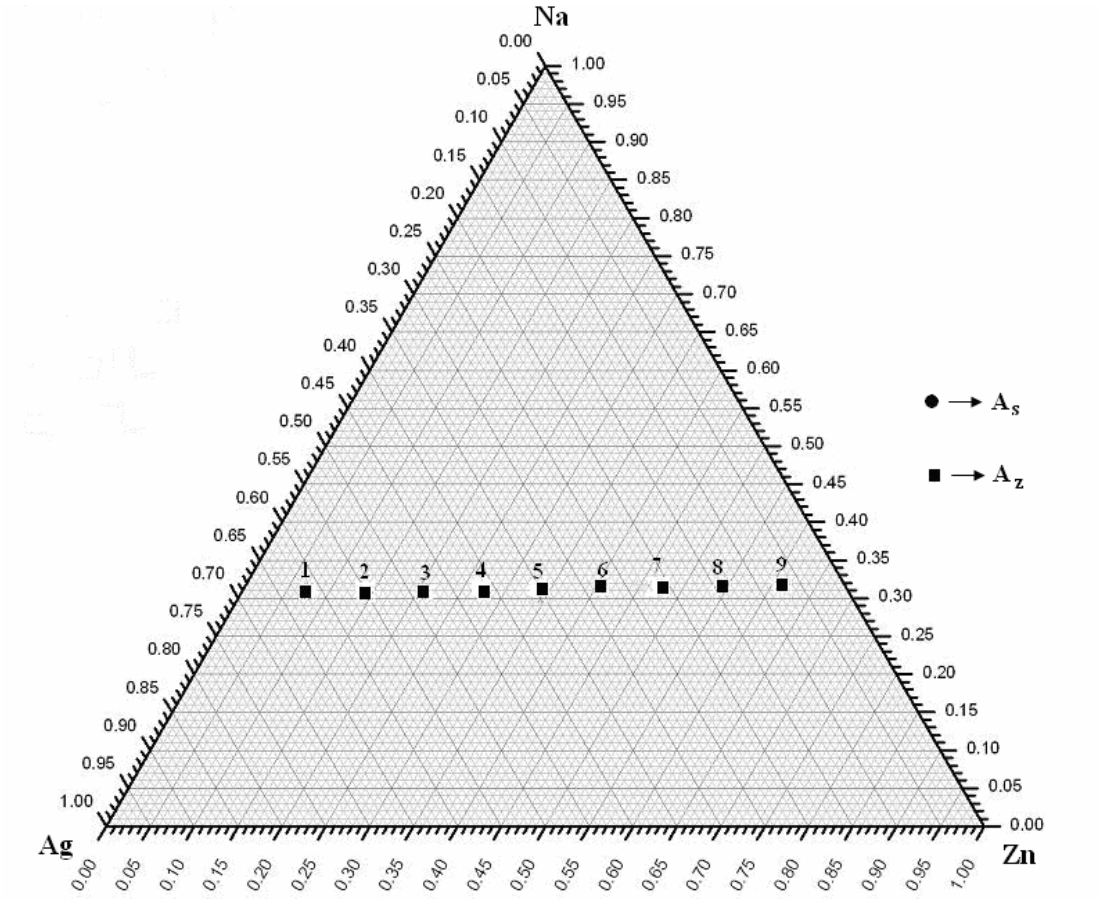


Figure 5.28. Ion Exchange Isotherm of Ag^{+}-Zn^{2+}-Na^{+} System for 0.5 g zeolite/20 mL solution at 25°C and 0.1 N

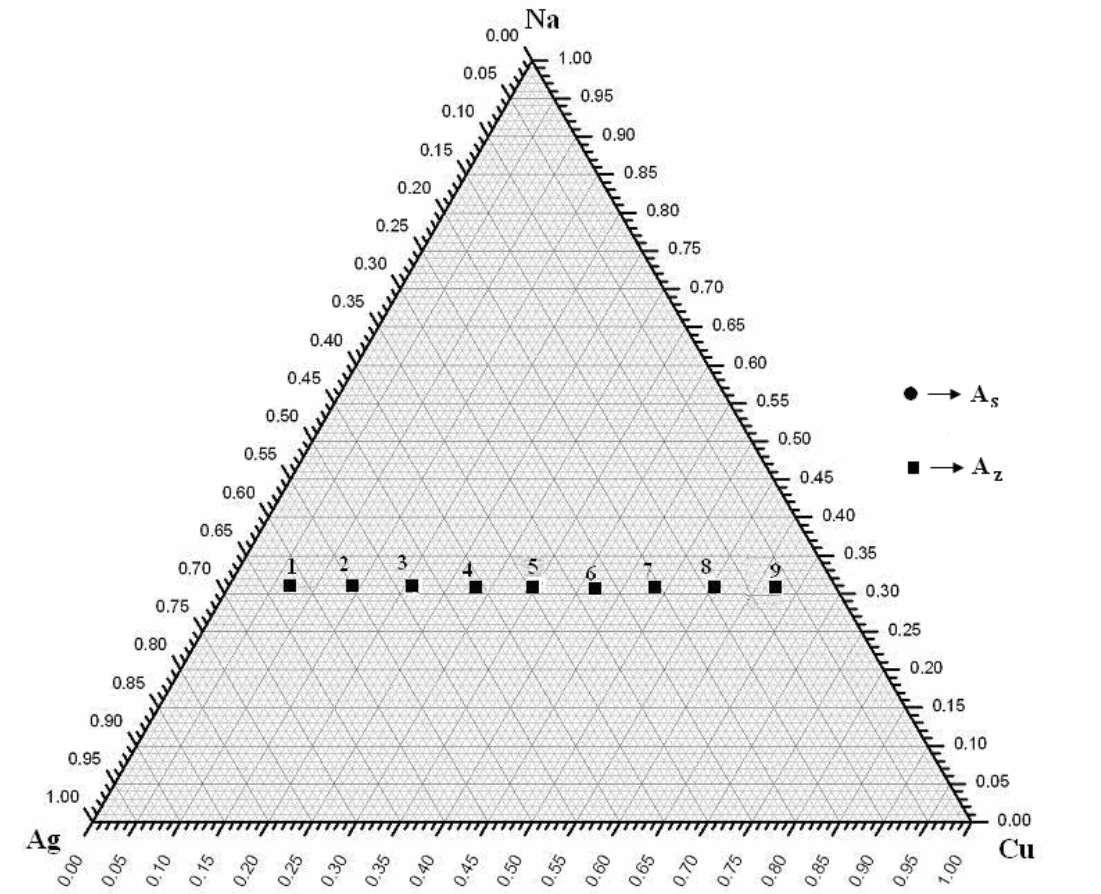


Figure 5.29. Ion Exchange Isotherm of Ag^{+}-Cu^{2+}-Na^{+} System for 0.5 g zeolite/20 mL solution at 25°C and 0.1 N

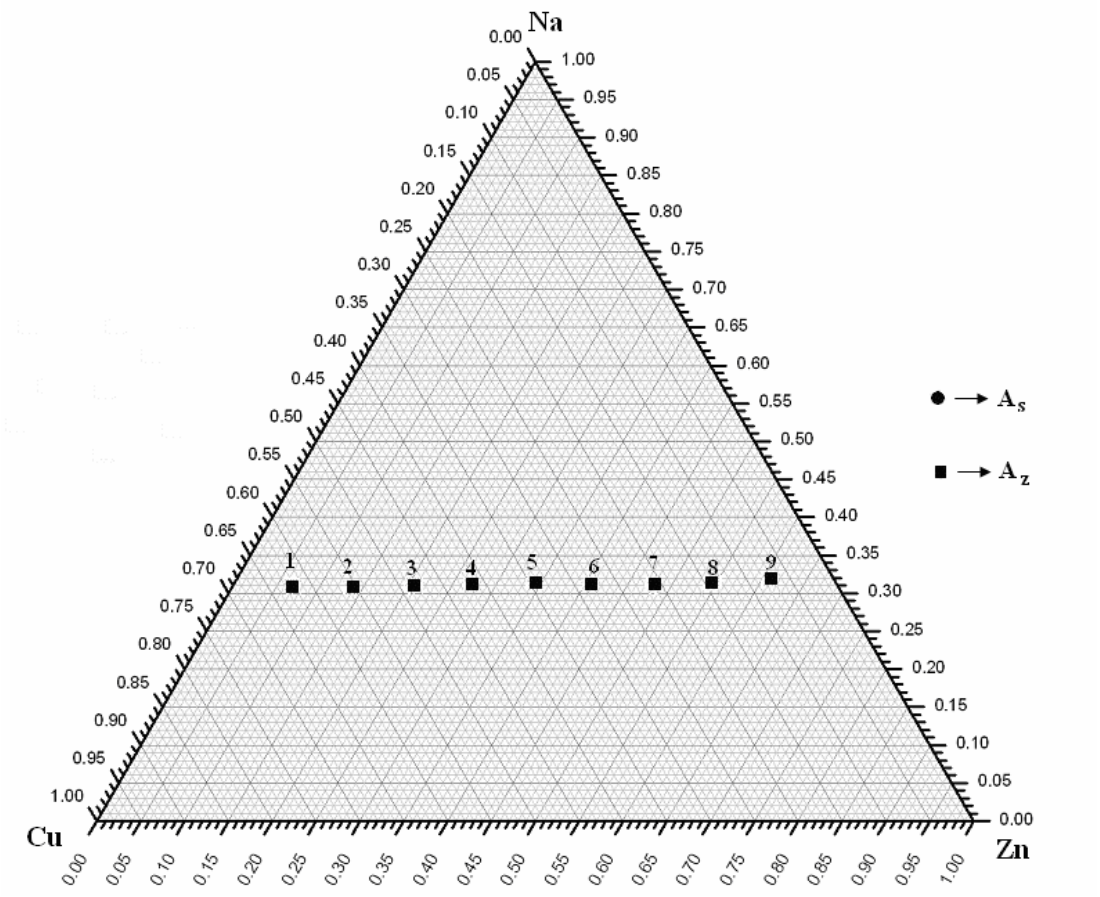


Figure 5.30. Ion Exchange Isotherm of Cu^{2+}-Zn^{2+}-Na^{+} System for 0.5 g zeolite/20 mL solution at 25°C and 0.1 N

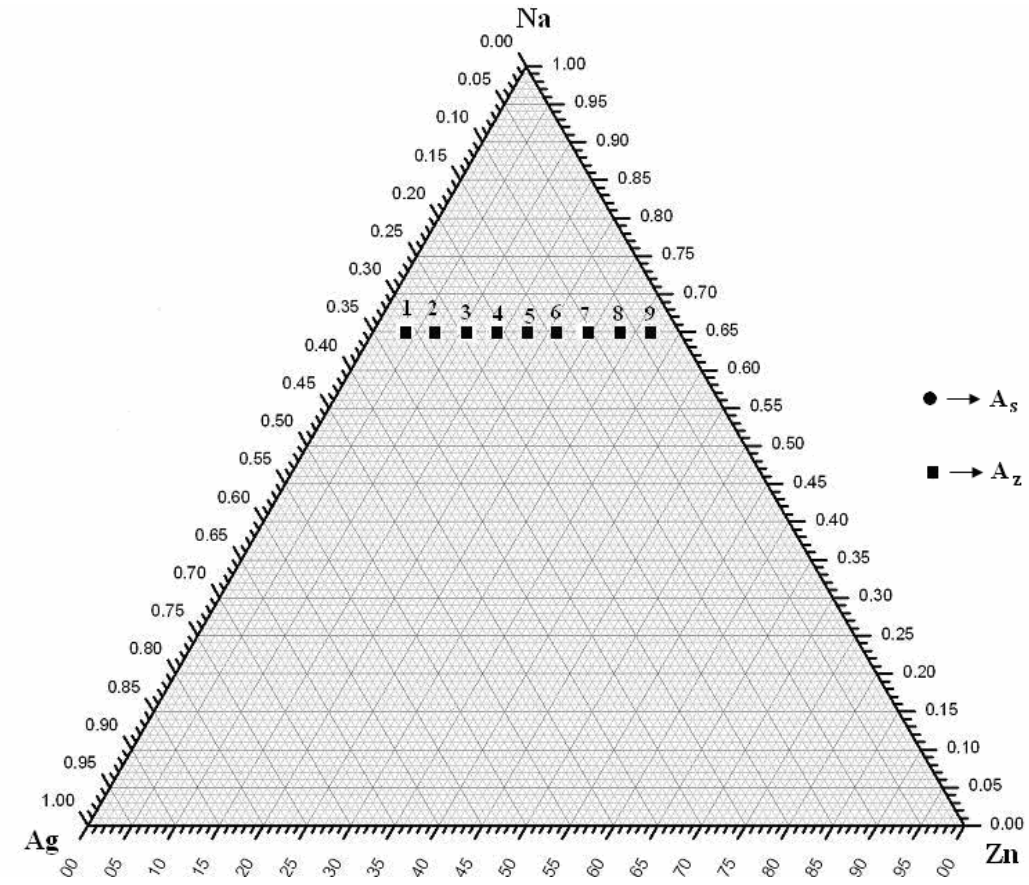


Figure 5.31. Ion Exchange Isotherm of Ag^{+}-Zn^{2+}-Na^{+} System for 1 g zeolite/20 mL solution at 25°C and 0.1 N

It is known that Zeolite 4A becomes more hydrated when exchanged with metal ions. The weight percent of the exchanged zeolites were calculated by neglecting this change and given in Table 5.5, 5.6 and 5.7.

Table 5.5. Weight Percent of Ag-Zn Zeolite

	I.N.	I.N.	0.25 g zeolite 4A		0.50 g zeolite 4A		1.00 g zeolite 4A	
#	Ag	Zn	Wt % Ag	Wt % Zn	Wt % Ag	Wt % Zn	Wt % Ag	Wt % Zn
1	0.09	0.01	38.37	0.84	29.47	0.99	16.81	0.57
2	0.08	0.02	36.24	1.69	26.80	2.03	15.14	1.15
3	0.07	0.03	34.67	2.23	24.00	3.10	13.42	1.74
4	0.06	0.04	31.69	3.45	21.07	4.20	11.66	2.36
5	0.05	0.05	28.73	4.62	18.02	5.35	9.85	2.99
6	0.04	0.06	24.83	6.24	14.78	6.58	7.99	3.63
7	0.03	0.07	19.52	8.30	11.38	7.90	6.08	4.30
8	0.02	0.08	13.74	10.68	7.82	9.30	4.11	4.98
9	0.01	0.09	7.51	13.03	4.02	10.75	2.08	5.69

There are different commercialized antibacterial zeolites around the world whose application areas are increasing day by day. For example AgION antimicrobial contains 2.5% (wt/wt) silver and 14 % (wt/wt) zinc [Galeano et al., 2003]. Bactekiller Ag-Zn-zeolite contains 3.5 % silver and 6.5 % zinc [Manohar and Stanley, 1994]. Both of these commercialized zeolite powders contain different amount of silver and zinc and show effective antibacterial activity. As it is seen from Table 5.5 zeolites containing various ratios of silver and zinc were prepared and they can be used in antibacterial applications.

Table 5.6. Weight Percent of Ag-Cu Zeolite

	Initial normality	Initial normality	0.25 g zeolite 4A		0.50 g zeolite 4A	
#	Ag	Cu	wt % Ag	wt % Cu	wt % Ag	wt % Cu
1	0.09	0.01	38.02	1.20	29.48	0.96
2	0.08	0.02	34.63	2.42	26.82	1.98
3	0.07	0.03	32.53	3.34	24.04	3.04
4	0.06	0.04	29.87	4.37	21.13	4.15
5	0.05	0.05	25.17	6.29	18.08	5.32
6	0.04	0.06	22.50	7.41	14.85	6.55
7	0.03	0.07	18.24	9.14	11.45	7.85
8	0.02	0.08	13.80	10.89	7.85	9.22
9	0.01	0.09	7.65	13.25	4.04	10.67

Table 5.7. Weight Percent of Zn-Cu Zeolite

	Initial normality	Initial normality	0.25 g zeolite 4A		0.50 g zeolite 4A	
No	Zn	Cu	wt % Zn	wt % Cu	wt % Zn	wt % Cu
1	0.09	0.01	13.11	2.33	11.02	1.21
2	0.08	0.02	11.00	4.52	9.84	2.44
3	0.07	0.03	8.79	6.78	8.61	3.66
4	0.06	0.04	6.68	8.97	7.38	4.88
5	0.05	0.05	4.66	11.06	6.15	6.11
6	0.04	0.06	2.59	13.27	4.93	7.33
7	0.03	0.07	1.62	14.41	3.72	8.55
8	0.02	0.08	0.89	15.21	2.49	9.76
9	0.01	0.09	0.43	15.96	1.24	10.99

CHAPTER 6

CONCLUSIONS

In this study, binary and ternary ion exchanges of silver, zinc and copper on zeolite 4A was investigated. Ion exchange isotherms revealed that zeolite 4A had a high selectivity to silver, zinc and copper with respect to sodium.

According to the results of thermodynamic analyses of Ag^{+}-Na^{+}, Zn^{2+}-Na^{+} and Cu^{2+}-Na^{+} binary ion exchange, selectivity sequence of zeolite 4A was determined as $Ag^{+} > Cu^{2+} > Zn^{2+}$.

Investigation of Ag^{+}-Zn^{2+}-Na^{+} and Ag^{+}-Cu^{2+}-Na^{+} ternary systems showed that silver was preferred by zeolite 4A in the presence of zinc and copper respectively. Examination of and Cu^{2+}-Zn^{2+}-Na^{+} ternary system revealed that zeolite 4A showed a higher affinity to copper in the presence of zinc. When these results were combined the selectivity series of zeolite 4A was concluded as $Ag^{+} > Cu^{2+} > Zn^{2+}$, same with binary systems.

Metal exchanged zeolites containing various ratios of heavy metals were prepared. Mixing 20 mL solution containing 0.02 N Ag^{+} and 0.08 N Zn^{2+} with 1 g zeolite 4A in a magnetic stirrer for 8 hours at room temperature forms an antibacterial zeolite having an approximate composition which is similar to the commercial one.

Since zeolite 4A has proven to have a high selectivity to silver, zinc and copper it can be used effectively in removing single and mixed heavy metals from aqueous solutions. This high selectivity can be made use of both in wastewater treatment and antibacterial applications.

CHAPTER 7

RECOMMENDATIONS

Binary and ternary ion exchanges of silver, zinc and copper on zeolite 4A was studied. It was seen that zeolite 4A was an effective ion exchanger ion removing single and mixed heavy metals from aqueous solutions. Antibacterial zeolites containing various ratios of these heavy metals have been prepared. In addition to what has been done in this study, suggestions on further work to be done are as follows

- The influence of temperature on ion exchange process can be studied.

- Ion exchange reactions can be performed at different initial metal ion concentrations.

- Antibacterial activities of the metal exchanged zeolites can be investigated. Since each of them contains different amounts of heavy metals, antibacterial effect will be different for each composition.

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APPENDIX A

CALCULATION OF EXCHANGE CAPACITY

The commercial zeolite NaA had the following chemical formula

$Na_{12}[(SiO_2)_{12}(AlO_2)_{12}]nH_2O$

Molecular weights of the atoms in the zeolite content

Na = 22.9898 g/mol

Si = 28.0855 g/mol

Al = 26.9815 g/mol

O = 15.9994 g/mol

H = 1.0079 g/mol

Molecular weight of the zeolite

$= 12xNa + 12xSi + 12xAl + 48xO + nx(2xH + O)$ (A.1)

$= 12x22.9898 + 12x28.0855 + 12x26.9815 + 48x15.9994 + nx(2x1.0079 + 15.9994)$

$= 1704.6528 + nx18.0512$

TGA analysis was done in order to find out the water content of the zeolite. Moisture content of the zeolite was found as 18.501 wt % from TGA analysis. So

$$\frac{n \times 18.0512}{1704.6528 + n \times 18.0512} \times 100 = 18.501 \quad \text{(A.2)}$$

n = 21.438

Having obtained the value of n, the molecular weight of the zeolite calculated as

MWzeolite = 1704.6528 + 21.4380x18.0512 = 2091.634 g/mol

By taking 12 mol Na per formula weight,

$$Exchange\ capacity = \frac{12x10^{3} meq/mol}{2091.634 g/mol} = 5.737 \text{ meq/g} \qquad \text{(A.3)}$$

APPENDIX B

BINARY SYSTEMS ION EXCHANGE CALCULATIONS

A_s (equivalent fraction of exchanging cation in solution) and A_z (equivalent fraction of exchanging cation in zeolite) values were calculated using the AAS results according to the following relations

$$A_s = \frac{\text{Normality of exchanging cation A}}{\text{Total Normality}} \quad \text{(B.1)}$$

$$A_z = \frac{\text{Number of exchanging cation A in zeolite}}{\text{Total equivalent of cations in zeolite}} \quad \text{(B.2)}$$

A sample calculation is given below for Ag^+- Na^+ binary ion exchange experiment at 25^0C.

Concentration of stock solution = 10750 ppm
Weight of zeolite = 0.4 g
Concentration of Ag at equilibrium = 385 ppm
Volume of solution = 20 mL

$$A_s = \frac{\frac{385mg}{L} \times \frac{1mol}{107868mg} \times \frac{1eq}{1mol}}{\frac{10750mg}{L} \times \frac{1mol}{107868mg} \times \frac{1eq}{1mol}} = 0.036$$

$$A_z = \frac{\frac{(10750-385)mg}{L} \times 0.02L \times \frac{1mol}{107868mg} \times \frac{1000meq}{1mol}}{0.4g \times \frac{5.737meq}{g}} = 0.837$$

The following tables summarize the above calculations for all binary experiments.

Table B.1. Equilibrium Data for Ag^{+}-Na^{+} Binary System at 25°C (Stock Solution = 10750 ppm)

Sample Weight	Ag concentration at equilibrium (mg/L)	Ag_s	Ag_z
0.05	9210.00	0.857	0.995
0.10	7670.00	0.713	0.995
0.15	6175.00	0.574	0.986
0.20	4650.00	0.433	0.986
0.25	3340.00	0.311	0.958
0.30	1950.00	0.181	0.948
0.40	385.00	0.036	0.837
0.50	102.00	0.009	0.688
0.60	59.50	0.006	0.576
0.70	37.00	0.003	0.495
0.80	18.00	0.002	0.434
0.90	12.40	0.001	0.386
1.00	9.20	0.001	0.347

Table B.2. Equilibrium Data for Zn^{2+}-Na^{+} Binary System at 25°C (Stock Solution = 3200 ppm)

Sample Weight (g)	Zn concentration at equilibrium (mg/L)	Zn_s	Zn_z
0.05	2755.00	0.861	0.949
0.10	2333.33	0.729	0.924
0.15	1935.00	0.605	0.899
0.20	1575.00	0.492	0.866
0.25	1250.00	0.391	0.832
0.30	962.50	0.301	0.795
0.40	493.75	0.154	0.722
0.50	166.00	0.052	0.647
0.60	38.25	0.012	0.562
0.70	12.80	0.004	0.486
0.80	5.40	0.002	0.426
0.90	2.75	0.001	0.379
1.00	1.90	0.001	0.341

Table B.3. Equilibrium Data for Cu^{2+}-Na^{+} Binary System at 25°C (Stock Solution = 3150 ppm)

Sample Weight (g)	Cu concentration at equilibrium (mg/L)	Cu_s	Cu_z
0.10	2248.00	0.714	0.990
0.15	1818.75	0.577	0.974
0.20	1373.00	0.436	0.975
0.30	587.50	0.187	0.937
0.40	57.00	0.018	0.848
0.50	16.80	0.005	0.688
0.60	7.10	0.002	0.575
0.70	3.97	0.001	0.493
0.80	3.08	0.001	0.432
0.90	2.05	0.001	0.384
1.00	1.60	0.001	0.345

APPENDIX C

THERMODYNAMIC CALCULATIONS FOR BINARY SYSTEMS

The mean molar stoichiometric activity coefficients of the single salt solution were first evaluated by modified Debye-Hückel equation.

$$\log \gamma_{\pm AX} = \frac{-A\, Iz_1z_2 I \sqrt{I}}{1 + Ba \sqrt{I}} + bI \qquad (C.1)$$

where A and B are the Debye Hückel parameters

a and b are the fitting parameters

I is the ionic strength

A = 0.5115 $(L/mol)^{0.5}$ and B = 0.3291×10^8 $(L/mol)^{0.5} cm^{-1}$ at 25°C [Stokes and Robinson, 1970]

To evaluate the constants in modified Debye Hückel relation, the given values of $\gamma_{\pm}$ by Stokes and Robinson (1970) are taken and solved simultaneously. Calculated values of constants are given in Table C.1.

Table C.1 Debye Hückel Constants

	$Na(NO_3)$	$Ag(NO_3)$	$Zn(NO_3)_2$	$Cu(NO_3)_2$
a (10^8 cm)	4.40251	3.49327	5.12333	4.75845
b	-0.07118	-0.15679	0.05192	0.03628

Ionic strength is defined by

$$I = 0.5\sum m_i z_i^{\,2} \qquad \text{(C.2)}$$

The summation is carried out over all the ions present, m being the concentration (mol/L).

Glueckauf's equations were used to calculate the mean molar stoichiometric activity coefficients of salts in mixed solutions. These are

$$\log \gamma_{(\pm AX)}^{(BX)} = \log \gamma_{(\pm AX)} - \left(\frac{m_B}{4I}\right)\left\{k_1 \log \gamma_{(\pm AX)} - k_2 \log \gamma_{(\pm BX)} - \frac{k_3}{(1+I^{-1/2})}\right\} \qquad \text{(C.3)}$$

and

$$\log \gamma_{(\pm BX)}^{(AX)} = \log \gamma_{(\pm BX)} - \left(\frac{m_A}{4I}\right)\left\{k_4 \log \gamma_{(\pm BX)} - k_5 \log \gamma_{(\pm AX)} - \frac{k_6}{(1+I^{-1/2})}\right\} \qquad \text{(C.4)}$$

$$k_1 = Z_B(2Z_B - Z_A + Z_X) \qquad \text{(C.5)}$$

$$k_2 = Z_A(Z_B + Z_X)^2(Z_A + Z_X)^{-1} \qquad \text{(C.6)}$$

$$k_3 = 0.5\left[Z_A Z_B Z_X (Z_A - Z_B)^2 (Z_A + Z_X)^{-1}\right] \qquad \text{(C.7)}$$

$$k_4 = Z_A(2Z_A - Z_B + Z_X) \qquad \text{(C.8)}$$

$$k_5 = Z_B(Z_A + Z_X)^2(Z_B + Z_X)^{-1} \qquad \text{(C.9)}$$

$$k_6 = 0.5\left[Z_A Z_B Z_X (Z_B - Z_A)^2 (Z_B + Z_X)^{-1}\right] \qquad \text{(C.10)}$$

The solution non-ideality correction factor was evaluated through the relation 2.12 which is given as

$$\Gamma = \frac{\gamma_B^{z_A}}{\gamma_A^{z_B}} = \frac{\left[\gamma_{\pm BX}^{(AX)}\right]^{z_A(z_B+z_x)/z_x}}{\left[\gamma_{\pm AX}^{(BX)}\right]^{z_B(z_A+z_x)/z_x}}$$

Mass action quotient was calculated by equation 2.8

$$K_m = \frac{A_z^{z_B} m_B^{z_A}}{B_z^{z_A} m_A^{z_B}}$$

Then Kielland quotient was determined through the relation 2.14

$$K_c = K_m \Gamma$$

Having obtained the value of Γ and Km, thermodynamic equilibrium constant was evaluated by equation 2.13.

$$\ln K_a = (z_B - z_A) + \int_0^1 \ln K_c dA_z$$

The second term was determined by the graphical integration of Kielland plot.

Finally Gibbs free energy of exchange was calculated via equation 2.15

$$\Delta G = -(RT \ln K_a) / z_A z_B$$

A sample calculation for Zn^{2+}-Na^{+} Binary ion exchange experiment at 25°C is given below.

Concentration of stock solution = 3200 ppm

Weight of zeolite = 0.4 g

Concentration of Zn^{2+} at equilibrium = 493.75 ppm

$$TN = \frac{3200\ \text{mg}}{\text{L}} x \frac{1mol}{65380mg} x \frac{2\text{eq}}{1\ mol\ \text{Zn}} = 0.09789eq/L$$

$$m_{Zn_i} = \frac{3200\ \text{mg}}{\text{L}} x \frac{1mol}{65380mg} = 0.04894mol/L$$

$$m_{Zn_f} = \frac{493.75mg}{L} x \frac{1mol}{65380mg} = 7.552x10^{-3} mol/L$$

$$\text{A}_\text{s} = \frac{\frac{493.75\text{mg}}{\text{L}} \times \frac{1mol}{65380mg} \times \frac{2eq}{1mol}}{\frac{3200\text{mg}}{\text{L}} \times \frac{1mol}{65380mg} \times \frac{2eq}{1mol}} = 0.1543$$

$$A_z = \frac{\frac{(3200-493.75)mg}{L} \times 0.02L \times \frac{1mol}{65380mg} \times \frac{2eq}{1mol} \times \frac{1000meq}{1eq}}{0.4\text{g} \times \frac{5.737\text{meq}}{\text{g}}} = 0.7215$$

Since the total normality of the solution is constant, the concentration of Na^{+} can be found as

$$m_{Na} = 0.09789 - \frac{7.552x10^{-3} mol}{L} x \frac{2eq}{1molZn} = 0.08279eq/L = 0.08279mol/L$$

Concentration of the anion does not change throughout the experiment. So

$$m_{NO_3} = 0.09789 mol/L$$

$$I = 0.5x(4xm_{Zn} + \mathrm{m_{Na}} + \mathrm{m_{NO_3}})$$

$$I = 0.5x(4x7.552x10^{-3} + 0.08279 + 0.09789) = 0.10544 \text{ mol/L}$$

a was calculated as 5.12333×10^{-8} and 4.40251×10^{-8} cm for $Zn(NO_3)_2$ and $Na(NO_3)$ respectively.

b was calculated as 0.05192 and -0.07118 for $Zn(NO_3)_2$ and $Na(NO_3)$ respectively.

$$\log \gamma_{\pm Zn(NO_3)_2} = \frac{-0.5115 \times (2 \times 1) \times \sqrt{0.10544}}{1 + 0.3291 \times 10^{8} \times 5.12333 \times 10^{-8} \times \sqrt{0.10544}} + 0.05192 \times 0.10544$$

$$\log \gamma_{\pm Zn(NO_3)_2} = -0.20919$$

$$\log \gamma_{\pm Na(NO_3)} = \frac{-0.5115 \times (1 \times 1) \times \sqrt{0.10544}}{1 + 0.3291 \times 10^{8} \times 4.402515 \times 10^{-8} \times \sqrt{0.10544}} - 0.071181 \times 0.10544$$

$$\log \gamma_{\pm Na(NO_3)} = -0.12046$$

The constants in the Glueckauf's equations were calculated as follows

$$k_1 = Z_B(2Z_B - Z_A + Z_X) = 1(2\times1-2+1) = 1$$

$$k_2 = Z_A(Z_B + Z_X)^2(Z_A + Z_X)^{-1} = 2(1+1)^2(2+1)^{-1} = 2.6667$$

$$k_3 = 0.5\left[Z_A Z_B Z_X (Z_A - Z_B)^2 (Z_A + Z_X)^{-1}\right] = 0.5\left[2\times1\times1(2\text{-}1)^2(2+1)^{-1}\right] = 0.3333$$

$$k_4 = Z_A(2Z_A - Z_B + Z_X) = 2(2\times2-1+1) = 8$$

$$k_5 = Z_B(Z_A + Z_X)^2(Z_B + Z_X)^{-1} = 1(2+1)^2(1+1)^{-1} = 4.5$$

$$k_6 = 0.5\left[Z_A Z_B Z_X (Z_B - Z_A)^2 (Z_B + Z_X)^{-1}\right] = 0.5\left[2\times1\times1\times(1-2)^2(1+1)^{-1}\right] = 0.5$$

$$\log\gamma_{(\pm AX)}^{(BX)} = -0.20919 - \left(\frac{0.08279}{4\times0.10544}\right)\left\{1\times(-0.20919) - 2.6667\times(-0.12046) - \frac{0.3333}{(1+0.10544^{-1/2})}\right\}$$

$$\log\gamma_{(\pm AX)}^{(BX)} = -0.21515$$

$$\gamma_{(\pm AX)}^{(BX)} = 0.60933$$

$$\log\gamma_{(\pm BX)}^{(AX)} = -0.12046 - \left(\frac{7.552\times10^{-3}}{4\times0.10544}\right)\left\{8\times(-0.12046) - 4.5\times(-0.20919) - \frac{0.5}{(1+0.10544^{-1/2})}\right\}$$

$$\log\gamma_{(\pm BX)}^{(AX)} = -0.11787$$

$$\gamma_{(\pm BX)}^{(AX)} = 0.76231$$

Then solution phase non-ideality correction factor was determined as follows

$$\Gamma = \frac{\gamma_B^{z_A}}{\gamma_A^{z_B}} = \frac{\left[\gamma_{\pm BX}^{(AX)}\right]^{z_A(z_B+z_x)/z_x}}{\left[\gamma_{\pm AX}^{(BX)}\right]^{z_B(z_A+z_x)/z_x}} = \frac{\left[0.76231\right]^{2(1+1)/1}}{\left[0.60933\right]^{1(2+1)/1}} = 1.49269$$

$$K_m = \frac{A_z^{z_B} m_B^{z_A}}{B_z^{z_A} m_A^{z_B}} = \frac{0.7217^1 \times 0.08279^2}{0.2786^2 \times (7.552 \times 10^{-3})^1} = 8.4354$$

$$K_c = K_m \Gamma = 8.4354 \times 1.49269 = 12.5914$$

K_c value was calculated for each data point. Then $\ln K_c$ versus A_z plot was drawn and the integral was taken as follows

$$\int_0^1 \ln K_c dA_z = \frac{(8.6086 + 0.7939) \times 1}{2} = 4.70125$$

$$\ln K_a = (z_B - z_A) + \int_0^1 \ln K_c dA_z = (1-2) + 4.70125$$

$$K_a = 40.49$$

Finally the standard free energy of exchange was calculated as follows.

$$\Delta G^o = -(\mathrm{RT ln K_a}) / z_A z_B = -\frac{8.314(J/molK) \times 298.15K \times 3.701}{2 \times 1} = -4.59 kJ/mol$$

The following tables summarize the thermodynamic calculations for all binary experiments.

Table C.2. Ionic Strengths, Solution Phase Activity Coefficients, Corrected Selectivity Coefficients for $Ag(NO_3)$ -$Na(NO_3)$ System at 25°C

Sample Weight	Ag Conc. at Eqb. (mg/L)	Ionic Strength (mol/L)	$\gamma_{Ag(NO_3)_2}$	$\gamma_{Na(NO_3)}$	$\gamma_{\pm Ag(NO_3)}^{Na(NO_3)}$	$\gamma_{\pm Na(NO_3)}^{Ag(NO_3)}$	Γ	K_c
0.05	9210.00	0.09966	0.73434	0.71090	0.73264	0.72085	0.96807	35.126
0.10	7670.00	0.09966	0.73434	0.71090	0.73094	0.71917	0.96807	84.357
0.15	6175.00	0.09966	0.73434	0.71090	0.72929	0.71755	0.96807	49.500
0.20	4650.00	0.09966	0.73434	0.71090	0.72761	0.71590	0.96807	87.645
0.25	3340.00	0.09966	0.73434	0.71090	0.72618	0.71449	0.96807	48.895
0.30	1950.00	0.09966	0.73434	0.71090	0.72465	0.71299	0.96807	79.665
0.40	385.00	0.09966	0.73434	0.71090	0.72294	0.71131	0.96807	134.278
0.50	102.00	0.09966	0.73434	0.71090	0.72263	0.71101	0.96807	223.115
0.60	59.50	0.09966	0.73434	0.71090	0.72259	0.71096	0.96807	236.132
0.70	37.00	0.09966	0.73434	0.71090	0.72256	0.71094	0.96807	274.321
0.80	18.00	0.09966	0.73434	0.71090	0.72254	0.71091	0.96807	441.774
0.90	12.4	0.09966	0.73434	0.71090	0.72254	0.71091	0.96807	526.074
1.00	9.2	0.09966	0.73434	0.71090	0.72253	0.71091	0.96807	600.921

Table C.3. Ionic Strengths, Solution Phase Activity Coefficients, Corrected Selectivity Coefficients for $Zn(NO_3)_2$ -$Na(NO_3)$ System at 25°C

Sample Weight	Zn Conc. at Eqb. (mg/L)	Ionic Strength (mol/L)	$\gamma_{Zn(NO_3)_2}$	$\gamma_{Na(NO_3)}$	$\gamma^{Na(NO_3)}_{\pm Zn(NO_3)_2}$	$\gamma^{Zn(NO_3)_2}_{\pm Na(NO_3)}$	Γ	K_c
0.05	2775.00	0.14004	0.59231	0.73437	0.59101	0.75832	1.60194	2.587
0.10	2333.33	0.13359	0.59648	0.73835	0.59392	0.75883	1.58273	5.023
0.15	1935.00	0.12750	0.60064	0.74226	0.59686	0.75940	1.56413	7.030
0.20	1575.00	0.12199	0.60459	0.74592	0.59969	0.76000	1.54693	7.714
0.25	1250.00	0.11702	0.60833	0.74934	0.60240	0.76061	1.53104	8.382
0.30	962.50	0.11262	0.61178	0.75247	0.60492	0.76120	1.51670	9.171
0.40	493.75	0.10545	0.61774	0.75777	0.60933	0.76231	1.49269	12.604
0.50	166.00	0.10044	0.62218	0.76165	0.61265	0.76319	1.47541	26.016
0.60	38.25	0.09849	0.62397	0.76321	0.61399	0.76356	1.46856	68.787
0.70	12.80	0.09810	0.62433	0.76352	0.61427	0.76364	1.46718	130.729
0.80	5.40	0.09798	0.62444	0.76361	0.61435	0.76366	1.46678	219.140
0.90	2.75	0.09794	0.62447	0.76364	0.61437	0.76367	1.46664	327.538
1.00	1.90	0.09793	0.62449	0.76365	0.61438	0.76367	1.46659	379.446

Table C.4. Ionic Strengths, Solution Phase Activity Coefficients, Corrected Selectivity Coefficients for $Cu(NO_3)_2$ -$Na(NO_3)$ System at 25°C

Sample Weight	Cu Conc. at Eqb. (mg/L)	Ionic Strength (mol/L)	$\gamma_{Cu(NO_3)_2}$	$\gamma_{Na(NO_3)}$	$\gamma^{Na(NO_3)}_{\pm Cu(NO_3)_2}$	$\gamma^{Cu(NO_3)_2}_{\pm Na(NO_3)}$	Γ	K_c
0.10	2248.00	0.13452	0.58420	0.73777	0.58212	0.75361	1.63513	345.935
0.15	1818.75	0.12776	0.58912	0.74209	0.58602	0.75502	1.61465	140.935
0.20	1373.00	0.12075	0.59453	0.74677	0.59036	0.75662	1.59279	355.795
0.30	587.50	0.10839	0.60494	0.75557	0.59881	0.75986	1.55262	259.524
0.40	57.00	0.10004	0.61270	0.76197	0.60519	0.76239	1.52416	594.508
0.50	16.80	0.09940	0.61331	0.76247	0.60570	0.76260	1.52195	394.258
0.60	7.10	0.09925	0.61346	0.76259	0.60583	0.76265	1.52142	423.409
0.70	3.97	0.09920	0.61351	0.76263	0.60587	0.76266	1.52125	458.184
0.80	3.08	0.09919	0.61352	0.76265	0.60588	0.76267	1.52120	411.290
0.90	2.05	0.09917	0.61354	0.76266	0.60589	0.76267	1.52114	467.762
1.00	1.60	0.09917	0.61354	0.76266	0.60590	0.76268	1.52112	478.267

APPENDIX D

EQUILIBRIUM ADSORPTION DATA FOR BINARY SYSTEMS

Table D.1. Equilibrium Adsorption Data for Ag^{+}-Na^{+} Binary System at 25°C

Sample weight (g)	Ce mg/L	Qe mg/g	1/Ce	1/qe	lnCe	lnqe
0.05	9210.00	616.000	0.0001	0.0016	9.1280	6.4232
0.10	7670.00	616.000	0.0001	0.0016	8.9451	6.4232
0.15	6175.00	610.000	0.0002	0.0016	8.7283	6.4135
0.20	4650.00	610.000	0.0002	0.0016	8.4446	6.4135
0.25	3340.00	592.800	0.0003	0.0017	8.1137	6.3849
0.30	1950.00	586.667	0.0005	0.0017	7.5756	6.3745
0.40	385.00	518.250	0.0026	0.0019	5.9532	6.2505
0.50	102.00	425.920	0.0098	0.0023	4.6250	6.0543
0.60	59.50	356.350	0.0168	0.0028	4.0860	5.8759
0.70	37.00	306.086	0.0270	0.0033	3.6109	5.7239
0.80	18.00	268.300	0.0556	0.0037	2.8904	5.5921
0.90	12.40	238.610	0.0806	0.0042	2.5177	5.4748
1.00	9.20	214.82	0.1087	0.0047	2.2192	5.3698

Table D.2. Equilibrium Adsorption Data for Zn^{2+}-Na^{+} Binary System at 25°C

Sample weight (g)	Ce mg/L	Qe mg/g	1/Ce	1/qe	lnCe	lnqe
0.05	2755.00	178.000	0.0004	0.0056	7.9212	5.1818
0.10	2333.33	173.334	0.0004	0.0058	7.7551	5.1552
0.15	1935.00	168.667	0.0005	0.0059	7.5679	5.1279
0.20	1575.00	162.500	0.0006	0.0062	7.3620	5.0907
0.25	1250.00	156.000	0.0008	0.0064	7.1309	5.0499
0.30	962.50	149.167	0.0010	0.0067	6.8695	5.0051
0.40	493.75	135.313	0.0020	0.0074	6.2020	4.9076
0.50	166.00	121.360	0.0060	0.0082	5.1120	4.7988
0.60	38.25	105.392	0.0261	0.0095	3.6441	4.6577
0.70	12.80	91.063	0.0781	0.0110	2.5494	4.5116
0.80	5.40	79.865	0.1852	0.0125	1.6864	4.3803
0.90	2.75	71.050	0.3636	0.0141	1.0116	4.2634
1.00	1.90	63.962	0.5263	0.0156	0.6419	4.1583

Table D.3. Equilibrium Adsorption Data for Cu^{2+}-Na^{+} Binary System at 25°C

Sample Weight	Ce mg/L	Qe mg/g	1/Ce	1/qe	lnCe	lnqe
0.10	2248.00	180.400	0.0004	0.0055	7.7178	5.1952
0.15	1818.75	177.500	0.0005	0.0056	7.5059	5.1790
0.20	1373.00	177.700	0.0007	0.0056	7.2248	5.1801
0.30	587.50	170.833	0.0017	0.0059	6.3759	5.1407
0.40	57.00	154.650	0.0175	0.0065	4.0431	5.0412
0.50	16.80	125.328	0.0595	0.0080	2.8214	4.8309
0.60	7.10	104.763	0.1408	0.0095	1.9601	4.6517
0.70	3.97	89.887	0.2519	0.0111	1.3788	4.4985
0.80	3.08	78.673	0.3247	0.0127	1.1249	4.3653
0.90	2.05	69.954	0.4878	0.0143	0.7178	4.2478
1.00	1.60	62.968	0.6250	0.0159	0.4700	4.1426

APPENDIX E

EQUILIBRIUM DATA FOR TERNARY ION EXCHANGE ISOTHERMS

Ternary system ion exchange calculations were carried by using the relations which were given for binary systems. The equilibrium data for the ternary systems are given in the following tables.

Table E.1. Equilibrium Data for Ag^{+}-Zn^{2+}-Na^{+} Ternary System at 25°C and 0.1 N by using 0.25 g Zeolite/ 20 mL Solution

#	Initial normality of Ag	Initial normality of Zn	Ag Conc. at Eqb. (mg/L)	Zn Conc. at Eqb. (mg/L)	Ag_s	Zn_s	Na_s	Ag_z	Zn_z	Na_z
1	0.09	0.01	2812.50	176.00	0.261	0.054	0.685	0.891	0.064	0.044
2	0.08	0.02	2247.63	356.25	0.208	0.109	0.683	0.825	0.127	0.048
3	0.07	0.03	1537.5	593.75	0.143	0.182	0.676	0.777	0.165	0.058
4	0.06	0.04	1121.38	725.00	0.104	0.222	0.674	0.692	0.249	0.060
5	0.05	0.05	670.34	875.00	0.062	0.268	0.670	0.611	0.324	0.065
6	0.04	0.06	366.08	968.75	0.034	0.296	0.670	0.510	0.423	0.066
7	0.03	0.07	266.25	1025.00	0.025	0.314	0.662	0.384	0.539	0.077
8	0.02	0.08	160.00	1062.50	0.015	0.325	0.660	0.258	0.662	0.079
9	0.01	0.09	38.56	1137.50	0.004	0.348	0.648	0.134	0.770	0.096

Table E.2. Equilibrium Data for Ag^{+}-Cu^{2+}-Na^{+} Ternary System at 25°C and 0.1 N by using 0.25 g Zeolite/ 20 mL Solution

#	Initial normality of Ag	Initial normality of Cu	Ag Conc. at Eqb. (mg/L)	Cu Conc. at Eqb. (mg/L)	Ag_s	Cu_s	Na_s	Ag_z	Cu_z	Na_z
1	0.09	0.01	2894.00	102.36	0.268	0.032	0.699	0.881	0.095	0.025
2	0.08	0.02	2625.00	216.00	0.243	0.068	0.689	0.776	0.184	0.040
3	0.07	0.03	2017.13	385.00	0.187	0.121	0.692	0.715	0.249	0.035
4	0.06	0.04	1512.00	545.50	0.140	0.172	0.688	0.641	0.318	0.040
5	0.05	0.05	1383.63	587.00	0.128	0.185	0.687	0.518	0.440	0.042
6	0.04	0.06	810.00	752.85	0.075	0.237	0.688	0.453	0.506	0.041
7	0.03	0.07	493.25	850.00	0.046	0.268	0.687	0.355	0.603	0.042
8	0.02	0.08	154.00	961.00	0.014	0.302	0.683	0.259	0.694	0.047
9	0.01	0.09	19.40	1025.00	0.002	0.323	0.676	0.137	0.805	0.058

Table E.3. Equilibrium Data for Cu^{2+}-Zn^{2+}-Na^{+} Ternary System at 25°C and 0.1 N by using 0.25 g Zeolite/ 20 mL Solution

#	Initial normality of Zn	Initial normality of Cu	Zn Conc. at Eqb. (mg/L)	Cu Conc. at Eqb. (mg/L)	Zn_S	Cu_S	Na_S	Zn_Z	Cu_Z	Na_Z
1	0.09	0.01	1225.00	12.54	0.375	0.004	0.621	0.732	0.134	0.134
2	0.08	0.02	1175.00	43.55	0.359	0.014	0.627	0.614	0.260	0.126
3	0.07	0.03	1137.50	66.25	0.348	0.021	0.631	0.491	0.389	0.120
4	0.06	0.04	1087.50	97.00	0.333	0.031	0.637	0.373	0.515	0.112
5	0.05	0.05	1025.00	141.68	0.314	0.045	0.642	0.260	0.635	0.105
6	0.04	0.06	968.75	170.80	0.296	0.054	0.650	0.145	0.762	0.094
7	0.03	0.07	768.75	338.80	0.235	0.107	0.658	0.090	0.827	0.082
8	0.02	0.08	537.50	551.60	0.164	0.174	0.662	0.050	0.873	0.077
9	0.01	0.09	270.00	770.00	0.083	0.242	0.675	0.024	0.917	0.059

Table E.4. Equilibrium Data for Ag^{+}-Zn^{2+}-Na^{+} Ternary System at 25°C and 0.1 N by using 0.5 g Zeolite/ 20 mL Solution

#	Initial normality of Ag	Initial normality of Zn	Ag Conc. at Eqb. (mg/L)	Zn Conc. at Eqb. (mg/L)	Ag_S	Zn_S	Na_S	Ag_Z	Zn_Z	Na_Z
1	0.09	0.01	79.50	3.20	0.007	0.001	0.992	0.622	0.069	0.309
2	0.08	0.02	74.50	5.40	0.007	0.002	0.991	0.553	0.138	0.309
3	0.07	0.03	69.00	13.00	0.006	0.004	0.990	0.484	0.206	0.310
4	0.06	0.04	60.20	28.75	0.006	0.009	0.986	0.414	0.273	0.313
5	0.05	0.05	45.50	46.00	0.004	0.014	0.982	0.346	0.339	0.316
6	0.04	0.06	37.75	58.00	0.003	0.018	0.979	0.276	0.406	0.318
7	0.03	0.07	27.50	60.50	0.003	0.019	0.979	0.207	0.475	0.317
8	0.02	0.08	11.00	62.00	0.001	0.019	0.980	0.139	0.545	0.317
9	0.01	0.09	4.80	73.00	0.000	0.022	0.977	0.069	0.612	0.319

Table E.5. Equilibrium Data for Ag^{+}-Zn^{2+}-Na^{+} Ternary System at 25°C and 0.1 N by using 1.0 g Zeolite/ 20 mL Solution

#	Initial normality of Ag	Initial normality of Zn	Ag Conc. at Eqb. (mg/L)	Zn Conc. at Eqb. (mg/L)	Ag_S	Zn_S	Na_S	Ag_Z	Zn_Z	Na_Z
1	0.09	0.01	3.60	0.70	0.000	0.000	0.999	0.314	0.035	0.652
2	0.08	0.02	3.55	0.55	0.000	0.000	1.000	0.279	0.070	0.652
3	0.07	0.03	3.26	0.40	0.000	0.000	1.000	0.244	0.105	0.652
4	0.06	0.04	2.86	0.36	0.000	0.000	1.000	0.209	0.139	0.652
5	0.05	0.05	1.92	0.25	0.000	0.000	1.000	0.174	0.174	0.651
6	0.04	0.06	1.39	0.22	0.000	0.000	1.000	0.139	0.209	0.651
7	0.03	0.07	0.98	0.15	0.000	0.000	1.000	0.105	0.244	0.651
8	0.02	0.08	0.52	0.11	0.000	0.000	1.000	0.070	0.279	0.651
9	0.01	0.09	0.29	0.07	0.000	0.000	1.000	0.035	0.314	0.651

Table E.6. Equilibrium Data for Ag^{+}-Cu^{2+}-Na^{+} Ternary System at 25°C and 0.1 N by using 0.5 g Zeolite/ 20 mL Solution

#	Initial normality of Ag	Initial normality of Cu	Ag Conc. at Eqb. (mg/L)	Cu Conc. at Eqb. (mg/L)	Ag_S	Cu_S	Na_S	Ag_Z	Cu_Z	Na_Z
1	0.09	0.01	77.50	2.76	0.007	0.001	0.992	0.622	0.069	0.308
2	0.08	0.02	71.00	3.97	0.007	0.001	0.992	0.553	0.139	0.308
3	0.07	0.03	59.25	5.15	0.005	0.002	0.993	0.484	0.208	0.308
4	0.06	0.04	46.00	8.23	0.004	0.003	0.993	0.415	0.277	0.308
5	0.05	0.05	33.00	11.72	0.003	0.004	0.993	0.346	0.346	0.307
6	0.04	0.06	22.25	13.05	0.002	0.004	0.994	0.277	0.415	0.307
7	0.03	0.07	12.77	14.42	0.001	0.005	0.994	0.208	0.485	0.307
8	0.02	0.08	6.18	16.54	0.001	0.005	0.994	0.139	0.554	0.307
9	0.01	0.09	2.14	18.00	0.000	0.006	0.994	0.070	0.624	0.307

Table E.7. Equilibrium Data for Cu^{2+}-Zn^{2+}-Na^{+} Ternary System at 25°C and 0.1 N by using 0.5 g Zeolite/ 20 mL Solution

#	Initial normality of Cu	Initial normality of Zn	Cu Conc. at Eqb. (mg/L)	Zn Conc. at Eqb. (mg/L)	Cu_S	Zn_S	Na_S	Cu_Z	Zn_Z	Na_Z
1	0.09	0.01	16.05	5.20	0.005	0.002	0.993	0.624	0.069	0.307
2	0.08	0.02	14.80	8.60	0.005	0.003	0.993	0.555	0.138	0.308
3	0.07	0.03	10.15	17.30	0.003	0.005	0.992	0.486	0.205	0.309
4	0.06	0.04	8.05	29.50	0.003	0.009	0.988	0.417	0.273	0.311
5	0.05	0.05	6.55	42.00	0.002	0.013	0.985	0.347	0.340	0.313
6	0.04	0.06	4.87	48.50	0.002	0.015	0.984	0.278	0.408	0.314
7	0.03	0.07	4.10	57.00	0.001	0.017	0.981	0.208	0.476	0.316
8	0.02	0.08	3.75	63.05	0.001	0.019	0.980	0.139	0.544	0.317
9	0.01	0.09	2.82	83.64	0.001	0.026	0.974	0.069	0.610	0.321